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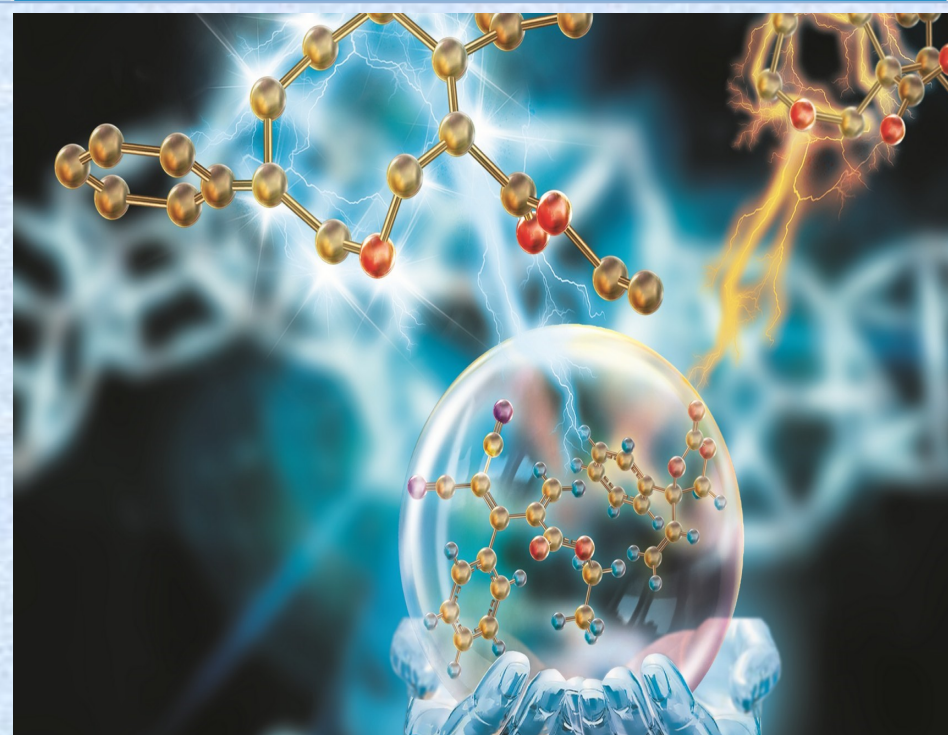
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Recent Trends in Chemistry and Futuristic Catalysts

First Edition

Editors

Dr. Azad Kumar
Dr. Hari Singh



**Thanuj International Publishers,
Tamil Nadu, India**

Recent Trends in Chemistry and Futuristic Catalysts

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About the book

This book includes a wide variety of topics that represent the diversity of current chemistry and catalysis developments. It features cutting-edge research from some of the world's smartest and most well-known experts. Contributions vary from creative uses of current approaches to new methods to help readers comprehend.

Catalysis is a not often used expression in everyday life, but it plays a major role in our existence. Only the catalytic activity of enzymes allows the human body to function. In addition, the synthesis of ammonia fertiliser is a significant achievement in the realm of catalysis with significant societal implications. Catalysts have gotten a lot of interest because they can be used to make sustainable energy, fuels, and value-added compounds. This book examines some of the underlying challenges surrounding various developments in new catalytic systems and designs, as well as their applications. The book provides an overview about the greatness that lies in the recent progress in chemistry.

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Chapter: 1

Comparative analysis of various physiochemical characteristics of different samples of water using coconut shell as an adsorbent

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Abstract Wastewater treatment using low-cost by-products from agricultural wastes has been acknowledged as a viable option. The various methods are used to remove contaminants from different samples of wastewater while also contributing to waste minimization, recovery, and reuse. Despite the fact that several evaluations have been published in recent years, direct comparison of data acquired using various sorbents is still challenging due to discrepancies in data presentation. In this context, the activated carbon prepared from agriculture waste was used as an adsorbent for a contact period of 2 hours to remove various impurities from the different samples of water and compared the same with normal drinking water. The findings observed that the Electrical conductivity of wastewater and drinking water was found as 586 and 806.4 $\mu\text{mho/cm}$, however the same was reduced to neutral value after using an adsorbent. Later the findings were compared with IS-10500-2012.

Keywords wastewater, dying water Coconut shell, adsorption

1. Introduction

Adsorption is the densification of a fluid at an interface. The interface might be solid-liquid, gas-liquid, liquid-liquid, or solid-gas in nature. The separation technique of adsorption is widely used in the manufacturing industry and in everyday life. Adsorption performance is greatly controlled by the mass transfer of the species between the solution and the adsorbent surfaces and the adsorption reaction rate.

Adsorption is strictly an interfacial phenomenon, unlike “absorption” wherein the absorptive species penetrates the absorbent. Each molecule in the adsorbed phase has less entropy than in the bulk gas phase, but due to attractive interactions at the interface, it also has a lower enthalpy. Activated carbon is a form of carbonaceous material that has been activated. It possesses a crystalline structure and a well-developed internal pore structure Tan and Hameed (2017) For the production of AC, a variety of materials are employed, including silica gel, zeolites, molecular sieves, activated alumina, and synthetic resins (Zhou et al., 2010) Low-cost materials such as cotton silk and coconut shell, sawdust, palm shell, olive stone, walnut shell, grape stem, bamboo, olive mill, pistachio shell, tropical wood, and almond shell have recently been used by researchers Jankowska et al., (2010). Environmental pollution and global warming are increasing as a result of greenhouse and harmful gases produced by the dumping and burning of fossils, implying the effective and environmentally friendly processes to purify contaminated water and air are required. Activated carbon prepared from agricultural wastes is one of the best solutions for removing impurities as the removal of gas by AC depends on the attraction force between the gas chemicals and carbon surface groups with the pressure Reza et al.,(2020). Agriculture, industries, and other sources have a negative impact on the environment. It was discovered that these waste materials may be utilized as a low-cost adsorbent for the treatment of wastewater to make it appropriate Gupta et al.,(2009). Successful research on these materials might benefit poor nations and be easily integrated into the creation of relevant technology. Because of its great adsorption capability, the successful use of agricultural waste in wastewater treatment would be very cost-effective (Drake et al., 1996, Shukhla and Sakhardane, 1992, Weber 1996, Chand et al., 1994, Laszlo 1996, Siddiqui et al., 1994, Ayub, et al., 1998, 1999, 2001, 2002, 2003, 2006, 2012, 2013)The extensive use of chromium has resulted in huge amounts of chromium waste being dumped into the environment, and unlike metals like cadmium and lead, the differing toxicity of trivalent and hexavalent chromium makes determining possible health concerns difficult. In comparison to trivalent chromium compounds, hexavalent chromium compounds are more mobile and hazardous Calder, 1988.It was observed from the literature that prepared adsorbent was mainly employed for the removal of methylene blue where otheothersiochemical characteristics need equal attention. To this end, activated carbon was prepared from coconut shell aiming to

remove the various impurities present in wastewater and dying water and compared the same with drinking water as per Indian standard

2. Material Methodology

2.1 Sample collection and preparation

The coconut shell was collected from the local shop of Khanna, Punjab, the wastewater was collected from one of the village from Khanna while as the dying water was collected local shop of the same area. After the collection of the material, the coconut shell was washed w-4 times with distilled water and left for drying in an oven for 24 hours. After drying the material was grinded and the sieve analysis was done. Finally, the sample was prepared for use.

2.2 Chemicals Reagents

The common reagents are used to make the sample like Sodium chloride, Silver nitrate, Buffer tablets, Ammonia Buffer, etc

2.3 Activated Carbon

The cleaned coconut shell was used as an adsorbent in different samples of water for a contact period of 2 hours. A certain amount of prepared adsorbent was poured into different samples of water and with the help of a stirrer it ,was mixed into the sample and left into it for the desired time. After that, activated carbon prepared from the coconut shell was applied for both dying and wastewater samples and the findings were compared with the normal drinking water.

2.4 Determination of pH, Turbidity and Electrical Conductivity

The pH values of the various water samples were determined using an electrometric pH meter. In separate beakers, two distinct samples of effluent and drinking water were collected. At first, the device was calibrated at room temperature with known buffer tablets of pH 7 and 9. Following calibration, the electrode was placed into an unknown quantity of wastewater and the pH value of the wastewater was recorded. The same method was followed to get the pH value of dying water. The identical technique was used with and without the adsorbent, with a 4 hour contact time. For the measurement of turbidity value, a turbidity meter was employed. The instrument was calibrated using a known solution of silica at a room temperature of 27°. Later, a sample of wastewater and dying water was obtained separately in a glass tube, and the turbidity of water samples was measured using the same calibration. The process was carried out both with and without an adsorbent for a contact period of 2 hours. Electric Conductivity was used to measure the conductivity of unknown samples of wastewater and dying water. A sample of drinking water was collected; the cell immersed in it, and the instrument was set to mohs. The conductivity is also affected by

temperature; as the temperature rises, the activity of ions rises, and the conductivity rises with it. Following that, 50 mL samples of wastewater and dying water were placed in a 100 mL beaker and the conductivity test was performed with and without adsorbent for a 4 hour contact time.

2.5 Determination of alum Dose Coagulation

The optimum amount of coagulant is the minimum dose or strength of coagulant that will result in maximum turbidity removal. This test was done by using a jar test apparatus having 4 paddles. These paddles can independently move up and down. An electric motor operates the stirrer; a speed controller is there to regulate the speed between 0-130 rpm and a timer to prefix the time of coagulation. 4 glass jars each of capacity 1 liter, a pipette of capacity 10 ml were taken. The more frequent coagulant employed is Alum $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. An alum solution of concentration 1% was prepared by dissolving 1gm of Alum in 1ltr of distilled water. A 5ml of alum solution was added to the first beaker, then 10ml of alum solution was added in the second beaker, 15ml in the 3rd beaker, and 20ml in the fourth beaker. In order for a more precise evaluation of color, turbidity was measured. After that, the beakers were placed on the platform and the paddle was lowered and locked in the position. The sample was stirred for 1-2 minutes at a speed of 100-120rpm, and then the speed was reduced to 20rpm and ran for 30 minutes. After completing the stirring the apparatus was turned off and the floc was allowed to settle down for some time then the extent of turbidity removal was observed in beaker no.2 in which 2ml of alum solution was added i.e, 10ml per liter of water. A 5ml of alum solution was added to the first beaker, then 10ml of alum solution was added in the second beaker, 15ml in the 3rd beaker, and 20ml in the fourth beaker. In order for a more precise evaluation of color, turbidity was measured. After that, the beakers were placed on the platform and the paddle was lowered and locked in the position. The sample was stirred for 1-2 minutes at a speed of 100-120rpm, then the speed was reduced to 20rpm and ran for 30 minutes. After completing the stirring the apparatus was turned off and the floc was allowed to settle down for some time then the extent of turbidity removal was observed in beaker no.2 in which 2ml of alum solution was added i.e, 10ml per liter of water. with 5ml of was measured as 6.2, the pH value of the sample with alum dose of 10ml was measured as 5.5 and for the sample with 15ml alum, the dose was measured as 4.7. It was determined the floc formation at a 5ml dose of alum was found good, and for 10ml, & 15ml it was found excellent.

2.6 Coagulation of Wastewater

Four beakers were filled with wastewater of 1 liter in each, were carried for coagulation test and 5ml, 10ml, 20ml and 30ml of alum solution was added into the beaker 1, 2, 3, & 4 respectively after testing, the extent of removal of turbidity was observed in beaker no. 3. The pH value of the samples with alum dose 0, 5, 10, 15ml was found as 9.3, 9.0, 7.5, 6.5 respectively, and the floc formation was good at 15ml alum dose sample, whereas at 5ml, 10ml floc formation was found as Bad and Excellent respectively. The same was found reduced after using an adsorbent for a contact period of 2 hours. The pH value was reduced for the samples with alum doses 5, 10, 15ml were 7.3, 6.9 and 6.5 respectively and the floc formation for these samples was found as Excellent, Good, and Good respectively.

2.7 Coagulation of Dying water

Four beakers were filled with dying water of 1 liter in each, were carried for the test, and 0ml, 5ml, 10ml, and 20ml of alum solution were added into the beaker 1, 2, 3 & 4 respectively. After testing the removal of turbidity was observed in beaker no. 3, and the pH value of the samples was found as 7.5, 7.3, 6.9, and 6.5 respectively, whereas after using an adsorbent for a contact period of 2 hours the extent of removal was observed in the beaker no. 2 and the pH value of the samples was reduced to 7.5, 7.2, 6.5 and 6.0 respectively and the floc formation for the sample with 5, 10 and 15ml were found as excellent, good and good respectively.

3. Result and Discussion

3.1 Effect of prepared adsorbent on pH value, Turbidity value, and Conductivity value

It was observed that the prepared adsorbent deeply affected the different samples of water and turned the samples neutral. Initially, the pH value of wastewater was found as 9.3 after using an adsorbent for a contact period of 2 hours the same was reduced to 7.8. Initially, the pH value of dying water was observed as 9.69 however after using an adsorbent for a contact period of 2 hours the same was reduced to 7.79. The observed values of different samples of water were compared with the pH value normal drinking water it was observed that the pH value of normal drinking water was 6.96 but as per IS code 10500-2012 the permissible limit for the normal drinking water 6.5 to 8 and within this range water is considered to be safe for living consumption. Fig 1 shows the pH value of different samples with and without adsorbent. It was observed that adsorbents prepared from agriculture waste affected the turbidity,

the turbidity of normal drinking water was observed as 2.6 NTU. Initially, the turbidity of wastewater was observed as 7.98 NTU which is very high as per IS 10500-2012 and when compared the same with the normal drinking found not suitable. However after using an adsorbent for a contact period of 2 hours the same was reduced to 3.68 NTU and for dying water, the turbidity was found as 6.79 NTU it was reduced to 2.79 NTU. The observed values of different samples of water were then compared with normal drinking water and found acceptable as per Indian Standard. Fig 2 shows the turbidity of various samples with and without adsorbent. The conductivity of normal drinking water was found as 478.5 $\mu\text{mho}/\text{cm}$. The test was performed for the wastewater and dying water it was found as 586 and 806.4 $\mu\text{mho}/\text{cm}$ which is very high as per Indian Standard and when compared with the conductivity of normal drinking water found not suitable any use. After using as an adsorbent for a contact period of 2 hours the conductivity of wastewater was reduced to 468 $\mu\text{mho}/\text{cm}$ while as for dying water it was reduced to 476.2 $\mu\text{mho}/\text{cm}$. which when compared with the normal drinking water as per Indian Standard found suitable for consumption. Fig 3 shows the electrical conductivity of various samples.

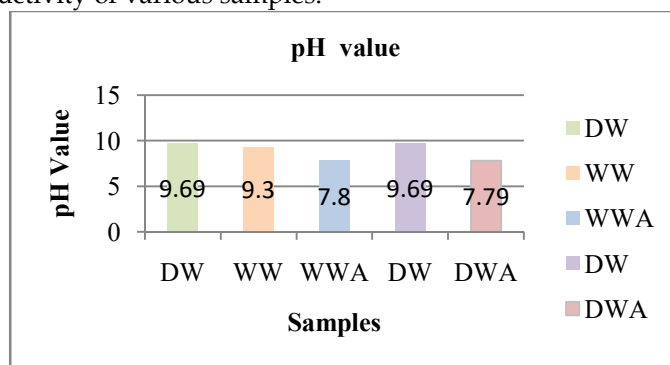


Fig 1 pH value of various samples

3.2 Effect of Prepared adsorbent on Alum dose for Coagulation

The test was formed for drinking water, wastewater, dying water, wastewater with adsorbent, and without adsorbent. It was observed that at different doses of alum the pH value also varies. After using an adsorbent the results were better at a lower dose of alum therefore it is worth using coconut shell as an adsorbent. Fig 4 shows the graphical presentation of the analysis of drinking water, fig 5 shows the graphical analysis of wastewater, fig 6 shows the graphical analysis of dying water, after using an adsorbent for a

contact period of 2 hours it was observed that there variation in alum dose fig 7 shows the graphical analysis of wastewater after using and adsorbent, figure 8 shows the graphical analysis of dying water after using and adsorbent for a contact

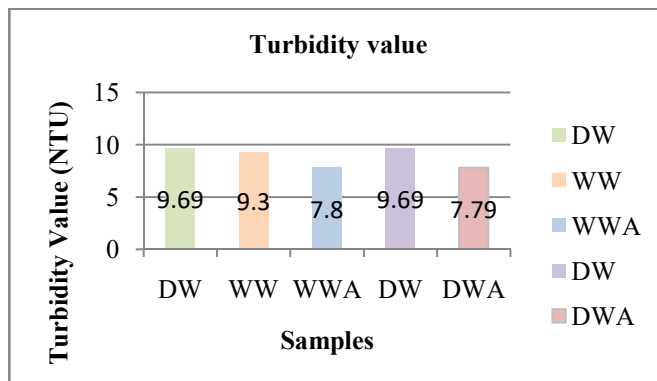


Fig 2 shows the turbidity value of various samples

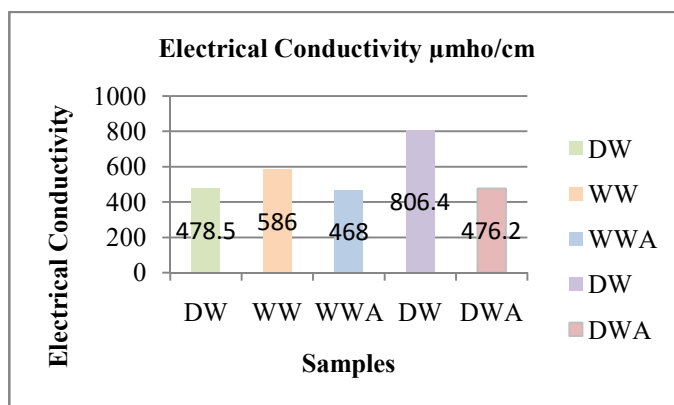


Fig 3 shows the electrical conductivity

3.3 Formation of alum in wastewater and dying water

It was observed that at different doses of alum the quality of floc formation was different also the pH value was varying, at a dosage of 10ml of alum the quality of floc formation was found excellent with a pH value of 7.5. Therefore it was found that the prepared adsorbent has a good effect on wastewater. The dying water contains many chemicals it because of the presence of various chemicals the pH value of dying water remains high. It was found that with a

dosage of 15 ml of alum the sample turned out to be neutral with excellent quality of floc formation whereas, at other doses quality of floc was not satisfactory.

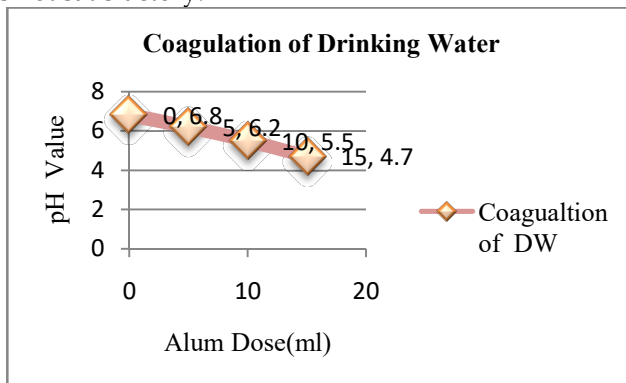


Fig 3 shows the coagulation of drinking water

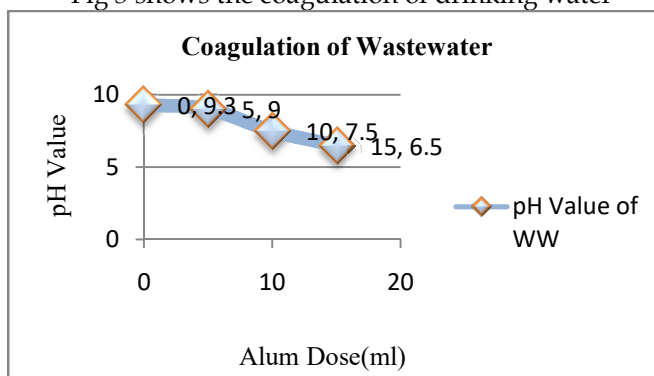


Fig 4 Coagulation of wastewater

3.4 Effect of prepared adsorbent on the formation of floc in wastewater and dying water:

At initial, the floc formation was excellent at an alum dosage of 10 ml but after using an adsorbent for a contact period of 2 hours the floc formation showed an excellent quality of floc formation within a dosage of 5ml of alum. For dying water, within alum dosage of 15ml, the quality of floc formation was found excellent with pH value being neutral, after using an adsorbent for a contact period of 2 hours the floc formation was excellent at 5ml dosage of alum with pH 7.2. Therefore it is worth using coconut shell as an adsorbent in dying water.

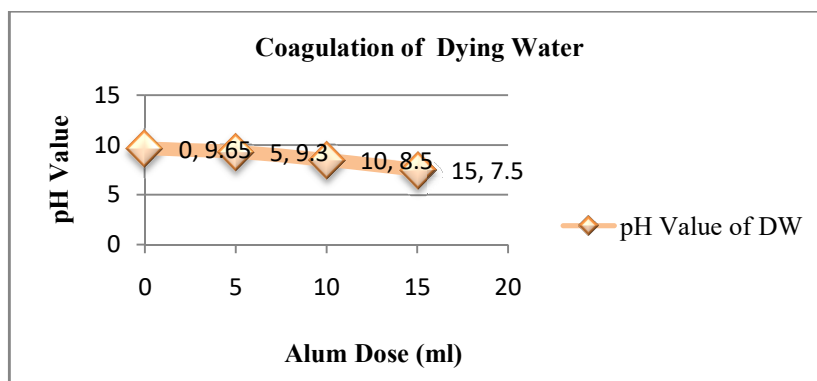


Fig 6 Coagulation of wastewater

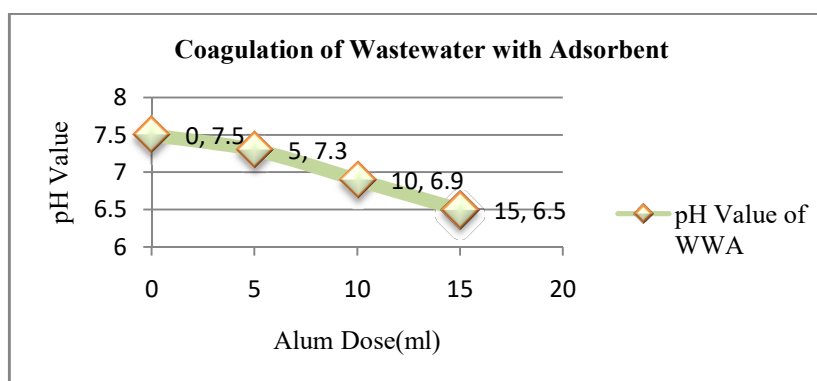


Fig 7 Coagulation of wastewater with adsorbent

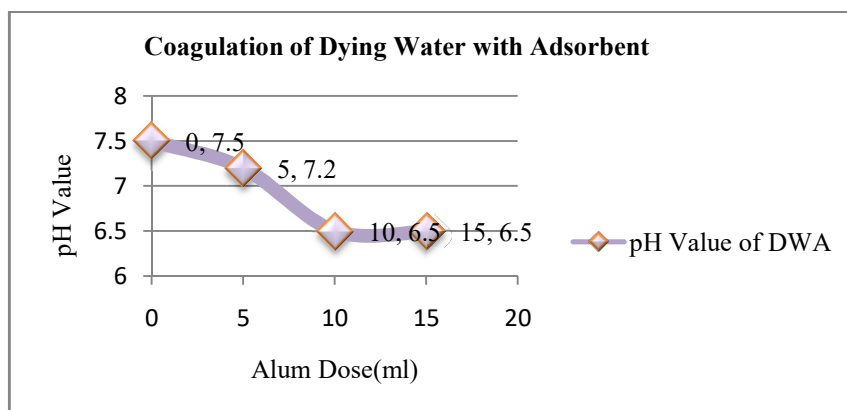


Fig 8 Coagulation of dying water with adsorbent

Conclusion

1. From the study it was concluded that a low-cost adsorbent from coconut shell could be successfully applied for the removal of impurities present in wastewater and dying water.
2. It was also observed that the agriculture waste can cause various environmental problems hence may lead to global warming
3. The prepared adsorbent was applied for the removal extra impurities present in different samples of water.
4. The pH value of wastewater and dying water was 9.3 and 9.69 after using an adsorbent the same was reduced to 7.8 and 7.79 respectively and the turbidity of wastewater was observed 7.98 and 6.79 NTU and the same was reduced to 3.68 and 2.79 NTU respectively.
5. It was discovered that the pH value varied depending on the amount of alum used. Because the outcomes were better with a lower amount of alum after using an adsorbent, it is worthwhile to use coconut shell as an adsorbent.

Reference

1. Ayub SS, Ali SI, Khan NA, Danish HS. Treatment of waste water by agricultural waste—a review. Environmental Pollution Control Report. 1998.
2. Ayub S, Ali SI, Khan NA, RAO R. Extraction of Chromium from the wastewater by Adsorption. Environmental Pollution Cont. Journal. 1999;2(5):27-31.
3. Ayub S, Ali SI, Khan NA. Adsorption studies on the low cost adsorbent for the removal of Cr (VI) from electroplating wastewater. Environmental pollution control journal. 2002;5(6):10-20.
4. Ayub S, Ali SI, Khan NA. A Study of the Removal of CR (VI) By Sugar Cane Bagasse From Wastewater. Pollution Research. 2001;20(2):233-7.
5. Ayub S, Ali SI, Khan NA. Comparative study of different agro based adsorbents for the treatment of wastewater. Current World Environment. 2006;1(2):109.
6. Ayub S, Agarwal AK. Water quality status in India and some of the leading cities of world: a review. Global Journal of Modern Biology & Technology. 2012; 2(2):2.
7. Ayub S, Aggarwal AK. Water quality status near Kalindi vihar colony, Tedi Bagiya Agra UP India". EInternational Journal of engineering and technology. 2013; 2 (2).
8. Ayub S, Ali S I, Khan, N. A.. Chromium removal by adsorption on coconut shell. Journal of Indian association for Environmental Management, NEERI. 2003; 30(23).
9. Chand SH, Agarwal VK, Kumar P. Removal of hexavalent chromium from wastewater by adsorption. Indian Journal of Environmental Health. 1994;36(3):151-8.
10. Calder L, Ed JO, Nriagu d E N, Chromium contamination of groundwater. In: chromium in the natural and human environment, Wiley series in advances in environmental science and tech. 1988;20(5)215-229,
11. Drake LR, Lin S, Rayson GD, Jackson PJ. Chemical modification and metal binding studies of Datura innoxia. Environmental Science & Technology. 1995 Dec 27;30(1):110-4.

12. Gupta VK, Carrott PJ, Ribeiro Carrott MM, Suhas. Low-cost adsorbents: growing approach to wastewater treatment—a review. *Critical reviews in environmental science and technology*. 2009 Oct 9;39(10):783-842.
13. Idouraine A, Khan MJ, Weber CW. In vitro binding capacity of wheat bran, rice bran, and oat fiber for Ca, Mg, Cu, and Zn alone and in different combinations. *Journal of Agricultural and Food Chemistry*. 1996 Aug 15;44(8):2067-72.
14. Jankowska EA, Rozentryt P, Witkowska A, Nowak J, Hartmann O, Ponikowska B, Borodulin-Nadzieja L, Banasiak W, Polonski L, Filippatos G, McMurray JJ. Iron deficiency: an ominous sign in patients with systolic chronic heart failure. *European heart journal*. 2010 Aug 1;31(15):1872-80.
15. Laszlo JA. Preparing an ion exchange resin from sugarcane bagasse to remove reactive dye from wastewater. *Textile Chemist & Colorist*. 1996 May 1;28(5).
16. Reza MS, Yun CS, Afroze S, Radenahmad N, Bakar MS, Saidur R, Taweeekun J, Azad AK. Preparation of activated carbon from biomass and its' applications in water and gas purification, a review. *Arab Journal of Basic and Applied Sciences*. 2020 Jan 1;27(1):208-38.
17. Shukhla SR, Sakhardane VD, Column studies on metal iron removal by dyed cellulosic materials. 1991 11 (4); pp284-289,
18. Siddiqui ZM, Paroor S. Removal of chromium (VI) by different Adsorbents—A comparative Study. *Indian Journal of Environmental Protection*. 1994;14(4):273-8.
19. Tan KL, Hameed BH. Insight into the adsorption kinetics models for the removal of contaminants from aqueous solutions. *Journal of the Taiwan Institute of Chemical Engineers*. 2017 May 1;74:25-48.
20. Weber, C.W, In Vitro binding capacity of wheat bran, rice bran and oat fiber for Ca, Mg, Cu and Zn alone and in different combinations, *Journal of agric. Food Chem*, 44, pp 2067-2072, 1996
21. Zhou Y, Wu W, Qiu K. Recovery of materials from waste printed circuit boards by vacuum pyrolysis and vacuum centrifugal separation. *Waste management*. 2010 Nov 1;30(11):2299-304

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Chapter: 2

Recent Advances in Catalytic Conversion of Toluene to Benzonitrile

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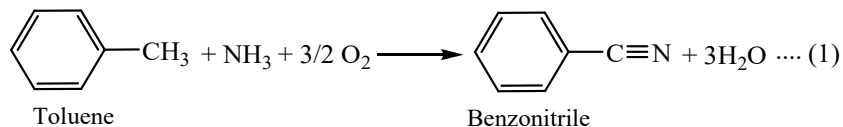
Abstract

Ammonoxidation of alkyl aromatics is a simple gas-phase reaction that yields aromatic nitriles. These nitriles, especially benzonitrile have versatile applications. This chapter project focuses on the ammonoxidation of toluene: catalysts employed in industrial and lab-scale, significance and challenges and mechanistic approaches; we have also tried to provide comparative studies of the mechanisms involved with the variable-valence transition metals (Mars-Van Krevelen mechanism) and confined single alkali metal ions within Y-zeolite pores involving acid-base catalysis.

Keywords: catalytic Csp³-H activation, ammonoxidation of toluene, selective benzonitrile synthesis, heterogeneous catalysis

1. Introduction

Direct functionalization of C_{sp}³-H hybridized inactive hydrocarbons to form oxygenated products under mild conditions is a major challenge in chemical and pharmaceutical industrial aspects [1-10]. Toluene to benzonitrile production via ammonoxidation (as shown in Equation 1) serves as a potential instance:



2. Niche uses of Benzonitrile

Benzonitrile has been commercially used as a common building block for high-performance rubbers, polymers and, molecular electronics, and is an integral part of producing pharmaceuticals, agrochemicals

and fine chemicals, such as vitamins, heterocycles and various carboxylic acid derivatives [11]. Benzonitrile is a powerful solvent. At room temperature it dissolves poly(vinyl chloride), poly(vinyl acetate) resins, polystyrene, polymethacrylate, and nitrocellulose [12]. Halogen substituted benzonitriles are used for the synthesis of different dyestuffs, herbicides, pharmaceuticals, and pesticides, particularly, 2-chlorobenzonitrile is an important chemical intermediate used for the production of 2-chlorobenzylamine, which can be used as an analgesic, antihypertensive, antitumor active, bloodstream disorder disease remedy, anticoagulant, antifolate and anticholesteremic agent [13].

3. Significance and Challenges in Ammoxidation Process

Generally, organic nitriles were synthesized by cyanation of aldehydes using hydrogen cyanide or metal cyanides (e.g. KCN, NaCN, $\text{Zn}(\text{CN})_2$ and CuCN), [14,15] which are hypertoxic and caused a few environmental disasters around the world like the cyanide spill in Bhopal (India, 1984) and in Baia Mare (Romania, 2000). Therefore, developing a green route to avoid the toxic cyanides for production of nitriles is important. Metal-catalyzed direct ammoxidation has been regarded as a sustainable strategy for producing nitriles due to the significant advantage in avoidance of toxic cyanides [11,16-24]. In these cases, much success has been achieved by employing primary alcohols, aldehydes, and aldoximes as precursors for the formation of C-N bonds [11,21-23]. In contrast, the ammoxidation of more easily available hydrocarbon is challenging, because of the high stability of sp^3 -hybridized C-H bonds.

In the past few years, homogeneous copper and palladium catalysts have been regarded to be active for C-N formation from C-H bonds, however, these homogeneous catalysts are difficult to separate and regenerate from the reaction system [11]. Based on the atom utilization concept described by Sheldon and Dakka [25], in general, gas-phase oxidations using heterogeneous catalytic systems are preferred over liquid-phase oxidation processes. Moreover, the use of gas-phase oxygen as an oxidant is highly desirable since besides the oxidation product only water is produced. The Environmental Quotient (EQ), which is defined by the amount of waste per kilogram of the product multiplied by an unfriendliness quotient (Q) is as low as possible for oxidation reactions. In this respect, aromatic nitriles can be used as intermediates in selective oxidations. According to Equation 1, the aromatic nitrile (benzonitrile) is manufactured with

high atom utilization; only water (having a low Q value) is formed as a side product.

However, in a gas-phase ammoxidation reaction, another important point to be considered is the oxidation of NH_3 . There is always a competition between NH_3 oxidation and ammoxidation on the catalyst surface. Moreover, the contact of ammonia with the catalyst surface, particularly at high temperatures, causes a partial reduction of the oxide surface due to the occurrence of NH_3 oxidation. Therefore, control of the rate of unselective oxidation of ammonia to N_2 (NO_x) is an important factor in determining the selectivity of the nitrile product in the ammoxidation reaction, because this side reaction limits the availability of surface ammonia (N-insertion) species that are necessary for nitrile formation [13]. It is known that the oxidation of ammonia is faster than the ammoxidation reaction; excess ammonia modifies the surface oxidation characteristics of a catalyst and decreases the ammoxidation activity. Nevertheless, it is also very difficult to completely avoid ammonia oxidation but it can only be minimized to the maximum possible extent. Besides, coordinatively unsaturated sites act as Lewis acidic sites for the chemisorption of methyl aromatics and NH_3 . On the other hand, the acidity of the catalyst plays a critical role in the ammoxidation reaction. It is obvious that enhanced acidity is favorable for the better performance of catalysts as it is known that NH_3 can adsorb on the catalyst surface in the form of either NH_4^+ on Bronsted acid sites or coordinatively adsorbed NH_3 on Lewis acid sites. Moreover, the strong acidity of the catalyst always leads to the formation of undesired products such as de-methylated products and carbon oxides due to the strong adsorption of methyl aromatic compounds. Hence, it is indispensable to maintain a good balance between the redox and acidic properties to attain high ammoxidation activity and selectivity.

4. Industrial Process of Benzonitrile Production

It is prepared by ammoxidation of toluene that is its reaction with ammonia and oxygen (or air) at 400 to 450 °C [12]. Benzonitrile is produced by the high-temperature vapor-phase oxidation of toluene in the presence of ammonia. The traditional catalysts are vanadium and molybdenum, but they suffer from low selectivity and serious decomposition of ammonia [12]. A tungsten-manganese complex catalyst showed better performance [12]. With the latter catalyst, the reaction is carried out in a fixed-bed reactor at 450 °C. The reaction converts 97% of the toluene and 30% of the ammonia. The selectivity

is 87.4 %. The crude product, which contains ammonia, hydrogen cyanide, toluene, and high-boilers, is purified by distillation. Benzonitrile has also been produced from benzoic acid and ammonia in the vapor phase at 400-410 °C over alumina [12] or in the liquid phase at 225-245 °C [12]. Other methods include liquid-phase ammoxidation of toluene in the presence of a cobalt or manganese bromide catalyst [12], dehydrogenative condensation of benzyl alcohol or benzaldehyde with ammonia, the high-temperature reaction of toluene with nitrous oxide, and cyanation of benzene with cyanogen chloride or dicyanogen. However, the use of the high reaction temperature (>350 °C) and use of excess toxic chemicals compelled to welcome the researchers to make the development of catalysis in the ammoxidation of toluene in the light of environmental benignity.

5. Catalysts for Ammoxidation of Toluene to Benzonitrile

Generally, the catalysts that are active in ammoxidation reactions consist mainly of mixed oxides containing variable-valence transition metals which possess moderate redox potentials and sufficient M-O bond strengths to provide active lattice oxygen and oxygen atoms at the catalyst surfaces for the redox catalysis, e.g. V_2O_5 [26-39], Cr_2O_3 [40-42], MoO_3 [43-50], Fe_2O_3 -based catalysts [51-54]. Major research groups applied vanadium oxides as active components in ammoxidation reactions of aromatics. In the reaction course, it is believed that vanadium undergoes redox cycles where V^{5+} species with $V=O$ bonds are severely reduced to V^{4+} via insertion of lattice oxygen into an oxygen-containing intermediate through a Mars-van Krevelen mechanism [55], and then such reduced vanadium species are reoxidized by surface-adsorbed oxygen, recovering to the original catalyst structure. In the past few decades, a large number of mechanistic studies on the aforementioned reactions have suggested bifunctional catalysis: namely, acid sites given by cocatalysts and redox sites originating from vanadium and other transition metal oxides. However, recently, Iwasawa and his group reported the preparation of single-site Cs^+ cation confined within the pores of Y-zeolite and its catalytic activity in the ammoxidation of toluene via direct oxidative cyanation of C_{sp^3} -H bond [56]. The catalysts showed high efficiency of NH_3 utilization in ammoxidation as well as a high yield of benzonitrile (>92.0%). The chemical confinement of the Cs^+ single-ion sites in the Y zeolite pores, making $Cs-O$ (lattice) bonds that provided a new trimolecular assembly platform to enable the

coordination promoted concerted pathway which is different from the traditional redox catalysis mechanisms.

6. Toluene Ammoxidation Mechanism

The mechanism of the ammoxidation of toluene is reviewed. Ammoxidation of toluene is mainly studied over vanadia-based catalysts. During ammoxidation, the catalyst is reduced by ammonia the hydrocarbon. It is generally accepted that lattice oxygen reoxidizes the catalyst during ammoxidation. Although the literature is not consistent with respect to the exact mechanism some general trends can be observed. The rate-determining step is hydrocarbon activation. Most authors agree on the formation of an oxygenated adsorbed organic intermediate. Toluene is adsorbed on the catalyst surface as a benzyl fragment. This benzyl species is oxygenated to form an adsorbed benzaldehyde surface structure. This structure is sometimes also referred to as benzoate species. Additionally, a reaction pathway via sequential dehydrogenation of adsorbed benzyl species to an adsorbed amine and imine is plausible. Oxygen is supplied as surface oxygen, according to a Mars-Van Krevelen like mechanism [55]. The exact nature of the nitrogen insertion site is studied less extensively. The amount of ammonia plays a decisive role in the catalyst oxidation state. Strong ammonia adsorption leads to an inactive catalyst, whereas weak ammonia adsorption leads to combustion reactions.

On the other hand, Iwasawa and his group [56] proposed (in the light of DFT) that at the initial stage of the reaction, NH_3 plays an important role in the coadsorption of toluene and O_2 on Cs^+ single sites, where the donation from NH_3 to Cs^+ is essential for the interaction between the toluene methyl group and the O_2 molecule to form a C-O bond on a Cs^+ single site. Then, the neighboring NH_3 molecule joins the ammoxidation reaction, which proceeds successively via several reaction intermediates and transition states with C-N bond, C=N bond, and finally $\text{C}\equiv\text{N}$ bond on a large-sized Cs^+ single site confined in the Y zeolite pore.

Conclusions and Outlook

Vapor-phase ammoxidation reactions have been extensively studied over mixed transition metal oxide catalysts with moderate redox potentials and sufficient M-O bond strengths that bring about active lattice oxygen and oxygen atoms at the catalyst surfaces to promote redox catalysis. However, alkali and alkaline earth metal ions with noble gas electronic structures have been thought to be inactive for

selective oxidation processes; however, it was indicated in the light of DFT that the reduction of the HOMO-LUMO gap and the variation of the HOMO component by the chemical confinement of the Cs⁺ single-ion sites in the Y zeolite pores, making Cs-O(lattice) bonds that provided a new trimolecular assembly platform to enable the coordination promoted concerted pathway, which is different from the traditional redox catalysis mechanisms. However, in regard to benzonitrile synthesis from hydrocarbon feedstocks to meet the need of potentially practical and sustainable prodproductst rely on activating C-H bonds at mild temperatures, minimizing side reactions is still challenging. Satisfying the demand of benzonitrile production via the development of suitable catalytic systems may open up a wide field of potential applications in near future.

7. References

1. R. A. Sheldon, H. van Bekkum, *Fine chemicals through heterogeneous catalysis*, Wiley-VCH, Weinheim, 2001, vol. 1.
2. L. Kesavan, R. Tiruvalam, M. H. A. Rahim, M. I. B. Saiman, D. I. Enache, R. L. Jenkins, N. Dimitratos, J. A. Lopez-Sanchez, S. H. Taylor, D. W. Knight, C. J. Kiely, G. J. Hutchings, Solvent-free oxidation of primary carbon-hydrogen bonds in toluene using Au-Pd alloy nanoparticles, *Science* 331 (2011), 195-199.
3. X. Chen, K. M. Eagle, D. H. Wang, J. Q. Yu, Palladium (II)-catalyzed C-H activation/C-C cross-coupling reactions: versatility and practicality, *Angew. Chem.* 48 (2009), 5094-5115.
4. Y. Wang, K. Yamaguchi, N. Mizuno, Manganese oxide promoted liquid-phase aerobic oxidative amidation of methylarenes to monoamides using ammonia surrogates, *Angew. Chem.* 124 (2012), 7362-7365.
5. M. Yang, B. Su, Y. Wang, K. Chen, X. Jiang, Y. F. Zhang, X. S. Zhang, G. Chen, Y. Cheng, Z. Cao, Q. Y. Guo, L. Wang, Z. J. Shi, Silver-catalysed direct amination of unactivated C-H bonds of functionalized molecules, *Nat. Comm.* 5 (2014), 4707.
6. S. S. Acharyya, S. Ghosh, R. Tiwari, B. Sarkar, R. K. Singha, T. Sasaki, C. Pendem, R. Bal, Preparation of the CuCr₂O₄ spinel nanoparticles catalyst for selective oxidation of toluene to benzaldehyde, *Green Chem.* 16 (2014), 2500-2508.
7. S. Ghosh, S. S. Acharyya, D. Tripathi, R. Bal, Preparation of silver-tungsten nanostructure materials for selective oxidation of toluene to benzaldehyde with hydrogen peroxide, *J. Mater. Chem. A* 2 (2014), 15726-15733.
8. S. S. Acharyya, S. Ghosh, R. Bal, Fabrication of three dimensional (3D) hierarchical Ag/WO₃ flower-like catalyst materials for the selective oxidation of m-xylene to isophthalic acid, *Chem. Commun.* 51 (2015), 5998-6001.
9. L. Wang, Y. Zhu, J. Q. Wang, F. Liu, J. Huang, X. Meng, J. M. Basset, Y. Han, F. S. Xiao, Two-dimensional gold nanostructures with high activity for selective oxidation of carbon-hydrogen bonds, *Nat. Comm.* 6 (2015), 6957.
10. S. Ghosh, S. S. Acharyya, S. K. Sharma, R. Bal, Fabrication of Ag/Mn₃O₄ nano-architectures for the one-step selective oxidation of 3-picoline to niacin: a key to vitamin B₃ production, *Catal. Sci. Technol.* 6 (2016), 4644-4654.
11. L. Wang, G. Wang, J. Zhang, C. Bian, X. Meng, F. S. Xiao, Controllable cyanation of carbon-hydrogen bonds by zeolite crystals over manganese oxide

- catalyst, *Nat. Commun.* 8 (2017), 15240.
12. T. Maki, K. Takeda, *Benzoic Acid and Derivatives*, Ullmann's Encyclopedia of Industrial Chemistry 2012, Vol. 5 pp329-342; Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim DOI: 10.1002/14356007.a03_555.
 13. H. B. Bathula, K. T. V. Rao, Y.-W. Suh, P. S. S. Prasad, N. Lingaiah, One-step selective synthesis of 2-chlorobenzonitrile from 2-chlorotoluene via ammoxidation, *New J. Chem.*, 42 (2018), 1892-1901.
 14. Y. Wang, K. Yamaguchi, N. Mizuno, Manganese oxide promoted liquid-phase aerobic oxidative amidation of methylarenes to monoamides using ammonia surrogates. *Angew. Chem.* 51 (2012), 7250-7253.
 15. L. Wang, Y. Zhu, J.-Q. Wang, F. Liu, J. Huang, X. Meng, J.-M. Basset, Y. Han, F.-S. Xiao, Two-dimensional gold nanostructures with high activity for selective oxidation of carbon-hydrogen bonds. *Nat. Commun.* 6 (2015), 6957.
 16. R. V. Jagadeesh, H. Junge, M. Beller, Green synthesis of nitriles using non-noble metal oxides-based nanocatalysts. *Nat. Commun.* 5 (2014), 4123.
 17. J. Yang, M. R. Karver, W. Li, S. Sahu, N. K. Devaraj, Metal-catalyzed one-pot synthesis of tetrazines directly from aliphatic nitriles and hydrazine. *Angew. Chem.* 51 (2012), 5222-5225.
 18. P. Anbarasan, T. Schareina, M. Beller, Recent developments and perspectives in palladium-catalyzed cyanation of aryl halides: synthesis of benzonitriles. *Chem. Soc. Rev.* 40 (2011), 5049-5067.
 19. S. I. Murahashi, N. Komiya, H. Terai, Ruthenium-catalyzed oxidative cyanation of tertiary amines with hydrogen peroxide and sodium cyanide. *Angew. Chem.* 44 (2005), 6931-6933.
 20. S. I. Murahashi, N. Komiya, H. Terai, T. Nakae, Aerobic ruthenium catalyzed oxidative cyanation of tertiary amines with sodium cyanide, *J. Am. Chem. Soc.* 125 (2003), 15312-15313.
 21. T. Oishi, K. Yamaguchi, N. Mizuno, Catalytic oxidative synthesis of nitriles directly from primary alcohols and ammonia, *Angew. Chem.* 48 (2009), 6286-6288.
 22. W. Yin, C. Wang, Y. Huang, Highly practical synthesis of nitriles and heterocycles from alcohols under mild conditions by aerobic double dehydrogenative catalysis, *Org. Lett.* 15 (2013), 1850-1853.
 23. J. Kim, S. S. Stahl, Cu/nitroxyl-catalyzed aerobic oxidation of primary amines into nitriles at room temperature, *ACS Catal.* 3 (2013), 1652-1656
 24. Y. Li, J. N. Armor, Ammoxidation of ethane to acetonitrile over metal-zeolite catalysts, *J. Catal.* 173 (1998), 511-518.
 25. R.A. Sheldon, J. Dakka, Heterogeneous catalytic oxidations in the manufacture of fine chemicals, *Catal. Today* 19 (1994), 215-246.
 26. P. Cavalli, F. Cavani, I. Manenti, F. Trifiro, Ammoxidation of toluene to benzonitrile on vanadium-titanium oxides catalysts prepared by precipitation. The role of catalyst composition, *Ind. Eng. Chem. Res.* 26 (1987), 639-647.
 27. J. C. Otamiri, A. Andersson, A. Kinetics and mechanisms in the ammoxidation of toluene over a V₂O₅ catalyst. Part 2: Non-selective reactions, *Catal. Today* 3 (1988), 211-222.
 28. R. Rapolu, K. R. Panja, Highly Selective V-P-O/ γ -Al₂O₃ Catalysts in the ammoxidation of toluene to benzonitrile, *J. Chem. Soc., Chem. Commun.* (1993), 1175-1176.
 29. M. Sanati, A. Andersson, L. R. Wallenberg, B. Rebenstorf, Zirconia-supported vanadium oxide catalysts for ammoxidation and oxidation of toluene: A characterization and activity study, *Appl. Catal. A* 106 (1993), 51-72.
 30. A. Martin, H. Berndt, B. Lücke, M. Meisel, Reaction pathway of benzonitrile formation during toluene ammoxidation on vanadium phosphate catalysts,

- Top. Catal. 3 (1996), 377–386.
31. Y. Zhang, A. Martin, H. Berndt, B. Lücke, M. Meisel, FTIR investigation of surface intermediates formed during the ammoxidation of toluene over vanadyl pyrophosphate, *J. Mol. Catal. A* 118 (1997), 205–214.
 32. G. Centi, F. Marchi, S. Perathoner, Effect of ammonia chemisorption on the surface reactivity of V-Sb-oxide catalysts for propane ammoxidation, *Appl. Catal. A* 149 (1997), 225–244.
 33. A. Martin, F. Hannour, A. Brückner, B. Lücke, Ammoxidation of toluene on vanadyl polyphosphates-VO (PO₃)₂, 2. Catalytic properties, *React. Kinet. Catal. Lett.* 63 (1998), 245–251.
 34. K. V. R. Chary, C. P. Kumar, P. V. R. Rao, V. V. Rao, Dispersion and reactivity of V₂O₅ catalysts supported on Al₂O₃-ZrO₂, *Catal. Commun.* 2004, 5, 479–484.
 35. A. Martin and B. Lucke, Ammoxidation and oxidation of substituted methyl aromatics on vanadium-containing catalysts, *Catal. Today*, 57 (2000), 61–70.
 36. A. Martin, Ur. Bentrup and G. U. Wolf, The effect of alkali metal promotion on vanadium-containing catalysts in the vapour phase oxidation of methyl aromatics to the corresponding aldehydes, *Appl. Catal. A* 2002, 227, 131–142.
 37. Y. Jeon, S. W. Row, A. Dorjgotov, S. D. Lee, K. Oh and Y. G. Shul, Catalytic activity and characterization of V₂O₅/γ-Al₂O₃ for ammoxidation of *m*-xylene system, *Korean J. Chem. Eng.* 30 (2013), 1–5.
 38. Y. Goto, K. Shimizu, K. Kon, T. Toyao, T. Murayama, W. Ueda, NH₃-efficient ammoxidation of toluene by hydrothermally synthesized layered tungsten-vanadium complex metal oxides, *J. Catal.* 344 (2016), 346–353.
 39. X. Li, L. Sun, M. Hu, R. Huang, C. Huang, Hydrothermal Synthesis of Urchin-like W-V-O Nanostructures with Excellent Catalytic Performance *Inorg. Chem.* 57 (2018), 14758–14763.
 40. M. K. Younes, A. Ghorbel, Catalytic nitrooxidation of toluene into benzonitrile on chromia-alumina aerogel catalyst, *Appl. Catal. A* 197 (2000), 269–277.
 41. R. G. K. O. Risajev, S. D. Mechtjev, S. J. K. Magerramova, V. J. Scheinin, M. M. Miratajev, I. A. O. Guseinov, Benzonitrile prodn. by ammoxidation of toluene-over a mixed oxide catalyst contg. vanadium, chromium, antimony and bismuth, 1976, DE2632628A1.
 42. S. S. Acharyya, S. Ghosh, R. Khatun, R. Bal, Unravelling the role of Ag-Cr interfacial synergistic effect in Ag/Cr₂O₃ nanostructured catalyst for the ammoxidation of toluene via low temperature activation of C_{sp}³-H bond, *Catal. Commun.* 152 (2021), 106290.
 43. A. Andersson, S. Hansen, Ammoxidation of toluene over molybdenum oxides, *Catal. Lett.* 1 (1988), 377–383.
 44. K. V. R. Chary, K. R. Reddy, T. Bhaskar, G. V. Sagar, Dispersion and reactivity of Mo/Nb₂O₅ catalysts in the ammoxidation of toluene to benzonitrile, *Green Chem.* 4 (2002), 206–209.
 45. J. Haber, M. Wojciechowska, Ammoxidation of toluene on MgF₂-supported monolayer vanadium oxide catalysts, *Catal. Lett.* 10 (1991), 271–278.
 46. T. Bhaskar, K. R. Reddy, C. P. Kumar, M. R. V. S. Murthy, K. V. R. Chary, Characterization and reactivity of molybdenum oxide catalysts supported on zirconia, *Appl. Catal. A* 211 (2001), 189–201.
 47. K. V. R. Chary, K. R. Reddy, G. Kishan, J. W. Niemantsverdriet, G. Mestl, Structure and catalytic properties of molybdenum oxide catalysts supported on zirconia, *J. Catal.*, 226 (2004), 283–291.
 48. B. Hari Babu, G. Parameswaram, A. Sri Hari Kumar, P. S. Sai Prasad, N. Lingaiah, Vanadium containing heteropoly molybdates as precursors for the preparation of Mo-V-P oxides supported on alumina catalysts for ammoxidation of *m*-xylene *Appl. Catal. A* 445– 446 (2012) 339–345.

49. M. A. de Boer, A. J. A. Van Dillen, D. C. A. Koningsberger, J. W. A. Geus, M. A. A. Vuurman, I. E. A. Wachs, Remarkable spreading behavior of molybdena on silica catalysts. An in situ EXAFS-Raman study, *Catal. Lett.* 11 (1990), 227–240.
50. A. Teimouri, B. Najari, A. N. Chermahini, H. Salavatia, M. F. Najafabadi, Characterization and catalytic properties of molybdenum oxide catalysts supported on $\text{ZrO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$ for ammoxidation of toluene, *RSC Adv.* 4 (2014), 37679–37686.
51. E. Rombi, I. Ferino, R. Monaci, C. Picciau, V. Solinas, R. Buzzoni, Toluene ammoxidation on $\alpha\text{-Fe}_2\text{O}_3$ -based catalysts, *Appl. Catal. A*, 266 (2004), 73–79.
52. P. Nagaraju, N. Lingaiah, M. Balaraju, P. S. Sai Prasad, Studies on vanadium-doped iron phosphate catalysts for the ammoxidation of methylpyrazine, *Appl. Catal. A* 339 (2008), 99–107.
53. P. Nagaraju, C. Srilakshmi, N. Pasha, N. Lingaiah, I. Suryanarayana, P. S. Sai Prasad, Effect of method of preparation on the activity and selectivity of iron phosphate catalyst in the ammoxidation of 2-methyl pyrazine, *Catal. Today* 131 (2008), 393–401.
54. M. D. Allen, G. J. Hutchings, M. Bowker, Iron antimony oxide catalysts for the ammoxidation of propene to acrylonitrile: comments on the method of preparation of tellurium promoted catalysts, *Appl. Catal. A* 217 (2001), 33–39.
55. P. Mars, D. W. van Krevelen, Oxidations carried out by means of vanadium oxide catalysts, *Chem. Eng. Sci.* 3 (1954), 41–59.
56. S. S. Acharyya, S. Ghosh, Y. Yoshida, T. Kaneko, T. Sasaki, Y. Iwasawa, Unprecedented catalysis of Cs^+ single sites confined in Y zeolite pores for selective $\text{C}_{\text{sp}^3}\text{-H}$ bond ammoxidation: transformation of inactive Cs^+ ions with a noble gas electronic structure to active Cs^+ single sites, *ACS Catal.* 11 (2021), 6698–6708.

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Chapter: 3

Investigation of Air Quality and Assessment in Srinagar City

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Abstract

Air pollution in the aerospace is increasing at a rapid rate from numerous sources, depending upon their location, pollution rates may alter from area to area. Many factors contribute to increasing pollution levels, such as mass production, which is necessary for the development, over usage of natural reserves, and expanding populace. High pollution rates are not only responsible for deteriorating environmental health, but also for the health of people. Many cardiac, as well as pulmonary diseases, are growing at a much faster rate because of increasing levels of pollution. The research was conducted in Srinagar city to investigate the air quality of this place. The samples were collected at two different places in Srinagar city. For PM_{2.5}, samples were collected from Rajbagh and Jahangir Chowk, and for SO₂ and NO_x; samples were collected from the Rajbagh area of Srinagar. During the research, the samples were taken monthly and investigated for NO_x, SO_x, and particulate matter. This was the first time that analysis for NO_x and SO_x was conducted in Kashmir. The concentration of PM_{2.5} as per yearly average is mostly seen up. Also, it has been seen that the concentration of PM_{2.5} in the Rajbagh area of Srinagar is less in contrary to the Jahangir Chowk area. Jahangir Chowk is a commercial area, the main reason for high pollution levels can be transportation i.e. the vehicular movement is more than Rajbagh, which is a residential area. Also, the road condition at Jahangir Chowk is no good, resulting in the rise of dust in the atmosphere thus, leading to the rise of PM_{2.5}. The concentration of NO_x is seen to be lower as compared to the permissible limit and that of SO_x is also fairly low. The overall air quality of Rajbagh was seen as fairly moderate than that of Jahangir Chowk.

Keywords: Air Quality, Air Quality monitoring, Srinagar

1. Introduction

Air quality problems and concern over it is not a new thing. Atmospheric pollution is a cause of worry and concern for centuries now. The Ancient Romans were the first to write a report on pollution in the air as they were well aware of the consequences that air pollution could cause [1]. At that time it was thought that air pollution was a local phenomenon that was believed to affect the health of local communities only. When coal was first used in London, many complaints were recorded from various places [1]. Now, it is apparent that pollutions can travel long distances and are not confined to a particular place or area. According to the reports of WHO, there are about 2 million premature deaths due to pollution [1]. Bad air quality hurts the health of living beings. Respiratory diseases are the result of pollution and bad air quality.

The quality of air depends upon:

- It depends upon the pollutant type that is discharged [2].
- It depends upon the ratio at which they are discharged [2].
- The time for which they are trapped in the atmosphere [2].

Deteriorating air quality can be caused by two sources:-

- Natural sources: Such as volcanic eruptions and forest fires.
- Man-made sources: Such as waste disposals and chemical manufacture.

As the air quality is deteriorating day by day, it becomes necessary to keep a check on the quality of air so that various measures could be taken to reduce the pollution into the atmosphere. Due to the bad air quality, the health of the people is badly affected which in turn is putting the life of the people at risk.

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TABLE 1: Health Effects of Some of the Particulate Matters

S. no	POLLUTANTS	HEALTH EFFECTS
1.	Suspended particulate matter	Respiratory Diseases and Reduced visibility
2.	Respirable Suspended Particulate Matter	Respiratory Diseases
3.	SO ₂	Irritation of eyes, Respiratory distress with excess mucus formation along with cough
4.	NO ₂	Impairing the function of the lungs.
5.	CO	Impairing the functioning of blood to carry oxygen i.e. reduction in oxygen-carrying capacity and cardiac diseases.
6.	Hydrocarbons	Excess mucus production and Lung cancer.
7.	Pb	Readily absorbed into the organs, less rate of excretion, impairing the functioning of the central nervous system, Impairs the process of Erythropoiesis, Plumbism i.e. anaemia, and amenorrhea.
8.	Benzene	Leukaemia, a Genetic abnormality, Affects the immune system thus increasing the chances of infection in the body.

2. Air Quality Index And Standards

It gives us the measurement of the levels of air pollution present in the atmosphere. It gives us the levels of pollutants into the atmosphere that affect the quality of air. In India, National Air Quality Index (NAQI) is used while in other countries AQI is represented by different names. The Air Quality Index gives us the levels of eight different pollutants present in the atmosphere and they are [3]:

- PM₁₀
- PM_{2.5}
- SO₂
- NO₂
- CO

- O₃
- NH₃
- Pb

These pollutants are represented in a different color to make them more prominent to people as to how dangerous these pollutants are and how rapidly they are spreading into the atmosphere

TABLE 2: CPCB Air Quality Standards

0-50	Good
51-100	Satisfactory
101-200	Moderate
201-300	Poor
301-400	Very poor
401-500	Severe

Air Quality Index helps in ranking locations based on different pollutant levels present in the air. The Air Quality Index is a must to check the increasing level of pollution in various places which in turn will help in giving preference as to where the pollution needs to be reduced with immediate effect.

The air quality index (AQI) is generally used by Government agencies to communicate to people about the current quality of air and to keep records with themselves in case needed now or someday. By AQI it becomes easier for these agencies to spread information among people about the levels of pollutants that may be harmful to a particular community. AQI is obtained by air quality monitoring, if the levels of pollutants increase then AQI increases. If AQI increases, then problems related to health increase, and in the long run weather also get affected. An increase in these problems means that this will have a direct effect on a particular community in a negative way. AQI is generally increased by an increase in emission from different sources like industrial sectors and transportation sectors [4]. These sectors release pollutants at an alarming rate into the atmosphere thus increasing the AQI of that place. When AQI is increasing at

the alarming rate then health advisories are issued for the people, especially people with health issues such as pulmonary and cardiac problems as these groups are sensitive to such air conditions and are affected the most. During the worst AQI people are advised of wearing masks, masks somehow prevent the pollutants from entering one's body. AQI of a particular place defines that place and is decided how the place is safe for the local people and people coming from outside. AQI for various zones is also represented by using colors. What representation of colors does is that it helps people recognize easily the situation of the atmosphere [4]. People can differentiate the risks related to the increase in pollutant levels as each color is associated with a specific situation. The color representation is kept standard for the whole world and represents the same situation throughout.

The various colors used to represent AQI are green, yellow, orange, red, purple, and maroon respectively. The color representation associated with AQI standards is shown in the table below [5];

TABLE 3: Colour Presentation Associated With AQI Standards

COLOUR	AIR QUALITY STANDARDS	LEVELS OF CONCERN
Green	0-50	Good
Yellow	51-100	Moderate
Orange	101-200	Unhealthy for sensitive groups
Red	201-300	Unhealthy
Purple	301-400	Very unhealthy
Maroon	401-500	Hazardous

- GREEN – Air level is satisfactory, acceptable and safe for all groups.
- YELLOW – Some contamination is seen in the air, but is fairly acceptable.
- ORANGE – Air is polluted and the sensitive groups are likely to get health issues but safe for healthy people.
- RED – Some people from the general population may face health concerns, but the people of sensitive groups may face serious health problems.
- PURPLE – Serious health concerns can be faced by both groups.

- MAROON - Health alert. A Health emergency can be declared by the Government of that particular place.

3. Central Pollution Control Board

The Central Pollution Control Board (CPCB) is an organization that comes under the Ministry of Environment, Forest and Climate and was established in 1947. The CPCB performs the function of an agency that provides services such as technical services for the Ministry of Environment and provides records at the time of need. The CPCB holds accounts of all the records that come under the provision of the Environment Protection Act (EPA)[6]. The CPCB coordinates activities between various states and works, a link between these states. The CPCB is the main body and other agencies are the branching that functions under the CPCB. The rule formation is done and the CPCB and the states are advised to follow them and organizations in different states are expected to work under the guidelines of CPCB. The CPCB makes sure that all the records collected by the organizations reach here so that results can be assessed by the members. In India, the head office of CPCB is in New Delhi [6]. CPCB is responsible for the assessment of environmental pollution be it water pollution or air pollution. It makes sure that the air quality survey is done regularly and the data is recorded and the assessment is done under the standard guidelines. The board has employees from various streams like engineers, scientists, and environmental protection specialists. Functions of CPCB come under both National level as well as state level. Its main aim is to provide clean streams be it air or water and promote cleanliness and control pollution in the country [6].

The CPCB is led by the chairperson who is appointed by the Appointment Committee of the Cabinet of the Government of India. In states, State Pollution Control Boards are established so that the work can be distributed and work can be done in a specialized way [6]. Many NGOs also work in alliance with the Government and carry works related to Environment protection.

3.1 Organisational Structure Of CPCB[7]

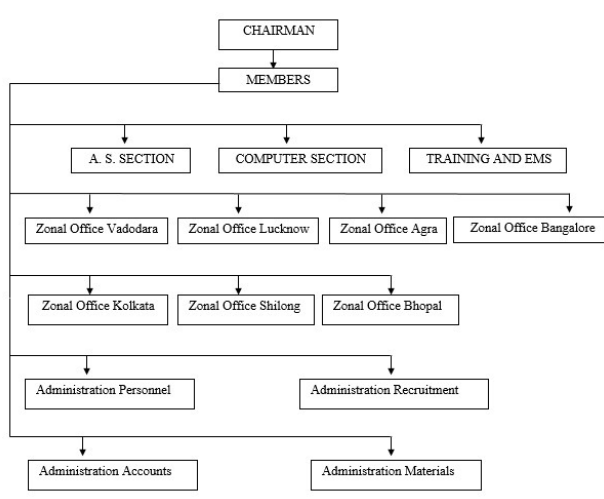


Figure 1: Organisational structure of CPCB

3.2 Working and Planning Structure of CPCB[7]

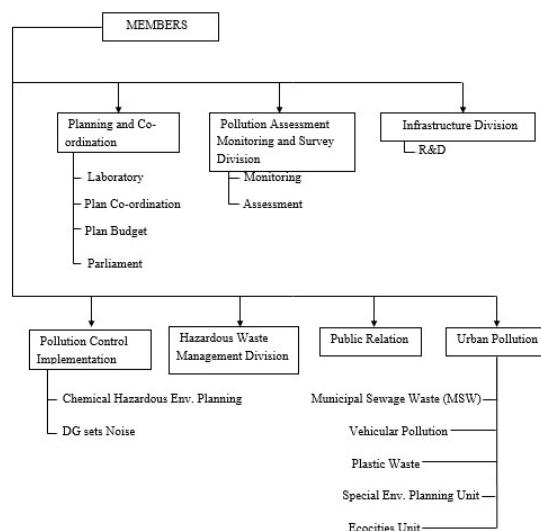


Figure 2: Working and planning structure of CPCB

4. Air Quality Monitoring

“Environmental Monitoring is a general term that is used for observing what is going on in the atmosphere systematically.”

“Environmental/Air Quality Monitoring is defined as a system of measurements, evaluations, and forecasts of environmental states and the collecting, processing and spreading of information on the environment.”[8]

Since air quality and control is a major issue and is in consideration at the international stage as well, Air Quality Monitoring is of prime importance. During Air Quality Monitoring, the study of an area is done where the problem has arisen and every minor and major detail is taken into consideration. Various stations are set and machinery units are installed and monitoring is started. The monitoring from one station is carried up for 24 hours.

In Air Quality Monitoring, levels of pollution are accessed. Those levels are used to determine how degraded the environment in that area is. Air Quality Monitoring is also used to see the impact of the policies that are made to control the pollution levels; accordingly, changes in these policies can be made.

4.1 Ambient/Industrial Air Quality Monitoring

Both Ambient/Industrial Air Quality Monitoring is a must to check the levels of pollution in the atmosphere. Ambient/Industrial Air Quality Monitoring helps us to generate data systematically so that the present levels of pollutants can be obtained and can be compared with previous data, and make changes in the previous policies accordingly and can formulate and implement new rules to decrease the levels of pollution [9]. On the other hand, it can also be seen that if the levels of pollutants have decreased as compared to previous data, then how good are the policies, and if we could further make changes in them to get better results than before. The Ambient/Industrial Air Quality Monitoring aids in determining the existing condition of the air quality. Air quality has a direct impact on the health of humans living in a particular area and hence is essential to keep an eye on the present scenario to work accordingly and to ensure that levels could be maintained according to the set value system.

During monitoring of air quality, it has to be keenly decided as to when and where the monitoring is going to take place. It is usually done near the industries, places with more traffic flow. Ambient/Industrial Air Quality Monitoring also helps in the determination of types of pollution. It helps in regulating 12 types of pollutants which include SO₂, NO₂, PM₁₀, PM_{2.5}, O₃, Pb, As, Ni, CO, NH₃, C₆H₆, and BaP [10].

Many of these pollutants prove to be toxic in the long run. If a person is exposed to these pollutants for a small period, then they may not cause harm at all, but if a person is exposed for a long period then they can turn to be fatal.

4.2 Air Quality Monitoring Process

The first process involves the selection of the location for the installation of the instrument. The second process involves the collection of air samples and the air sample is taken into the laboratory for assessment and the data obtained is collected.

5. SITE SELECTION

Site selection plays a very important role while monitoring air quality. The sites where the monitoring stations are located can directly or indirectly influence the results. Improperly selected sites can cause unwanted variations in results which can directly affect the changes that are to be made in the present policies. Not necessarily we can get a proper site that meets all the standards made by the EPA (Environment protection act) but it must be made sure to select the site which would meet nearly all the standards to get almost accurate results that are beneficial in making new policies or make changes in old policies.

5.1 NUMBER OF SITES

The number of sites needed for monitoring air quality depends upon a variety of attributes such as population density, sources of pollution, etc. which are known to be crucial. During monitoring, not necessarily one can get a perfect site that can fulfill all the requirements that are set by the guidelines, but it should be made sure that we can achieve get that site will fulfill almost all the conditions. The same is the case with getting the number of sites so that a sufficient amount of data can be collected to get the right levels of pollutants in the environment.

The various factors that are taken into consideration in selecting the number of sites are as follows [11];

- Type of data required
- Population distribution
- Population density
- Topography of that place
- Climatology
- Industrial area
- Vehicular movement in that place

6. Determination of RSPM, NRSPM, and TSPM

Air Quality Monitoring helps in the determination of the concentration of pollutants in the atmosphere. Monitoring can be done both by satellite reading as well as manually, but it has been seen that manual monitoring gives more preference because of the accuracy of the results. By Air Quality Monitoring, the concentration of the following pollutants can be detected [12]:

- Respirable Suspended Particulate Matter (RSPM)
- Non-Respirable Suspended Particulate Matter (NRPM)
- Total Suspended Particulate Matter (TSPM)

These pollutants have been proved to be fatal to both humans as well as the environment.

- Respirable Suspended Particulate Matter: The detection for the concentration of RSPM is done by using Whatman glass filter paper of approximately 20.3" × 25.4" in size [13]. Before using the filter paper, it is desiccated i.e. dried in a desiccator for about 24 hours. The filter paper is left in the desiccator for 24 hours so that it is completely dry and no moisture is left in the filter paper. In case this step is not followed then there might be chances of variations in the result because the moisture content of the filter paper will also add to the results. After the filter paper is taken out of the desiccators when it is completely dried, the dried filter paper is weighed and the reading is noted. Then the filter paper is fixed in the filter paper holder of the Air Monitoring Device i.e. Respirable Dust Sampler (RDS).

The sample collection is done for nearly 6-8 hours. The initial flow rate in the device is noted and after the sample collection, the final flow rate is noted. It can be seen that the flow rate will be decreased because of the dust collection on the filter paper. Then the filter paper is removed from the device and again desiccated for 24 hours and the filter paper is again weighed. The concentration of RSPM is taken as the difference between the initial weight and final weight in micrograms per meter cube [13].

- Non-Respirable Suspended Particulate Matter: Coarse particles are collected in a cup-like structure which is weighed before sampling and then after sampling. The cup in which coarse particles are collected is thoroughly cleaned so that each dust particle can be collected and weighed [13]. The concentration is taken out by the difference in weight divided by the volume of air sampled in micrograms per meter cube.

- Total Suspended Particulate Matter: Total concentration of Respirable Suspended Particulate Matter and Non-respirable Suspended Particulate Matter gives the concentration of Total Suspended Particulate Matter in micrograms per meter cube [13].

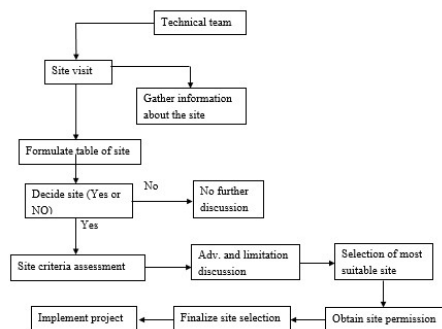


Figure 3: Procedure for site selection [14]

7. Results

7.1 Air Quality Monitoring Data for PM_{2.5} for Comparison

Table 4: Air Quality Monitoring data for PM_{2.5} for the year 2017-2018

Month	Rajbagh	Jahangir Chowk near Civil Sectt.
August-2017	69.70 $\mu\text{g}/\text{m}^3$	100.98 $\mu\text{g}/\text{m}^3$
September-2017	66.95 $\mu\text{g}/\text{m}^3$	100.41 $\mu\text{g}/\text{m}^3$
October-2017	64.63 $\mu\text{g}/\text{m}^3$	74.37 $\mu\text{g}/\text{m}^3$
November-2017	54.66 $\mu\text{g}/\text{m}^3$	67.50 $\mu\text{g}/\text{m}^3$
December-2017	49.93 $\mu\text{g}/\text{m}^3$	65.35 $\mu\text{g}/\text{m}^3$
January-2018	57.91 $\mu\text{g}/\text{m}^3$	69.43 $\mu\text{g}/\text{m}^3$
February-2018	49.41 $\mu\text{g}/\text{m}^3$	63.00 $\mu\text{g}/\text{m}^3$
March-2018	45.55 $\mu\text{g}/\text{m}^3$	69.66 $\mu\text{g}/\text{m}^3$
Yearly Average	57.34 $\mu\text{g}/\text{m}^3$	76.33 $\mu\text{g}/\text{m}^3$

NOTE:-

- 1) All mentioned data is taken for the financial year 2017-2018
- 2) The monitoring data is restricted to the samples collected only.
- 3) The permissible limit of RSPM (PM_{2.5}) for 24 hours=60 $\mu\text{g}/\text{m}^3$ and the year=40 $\mu\text{g}/\text{m}^3$

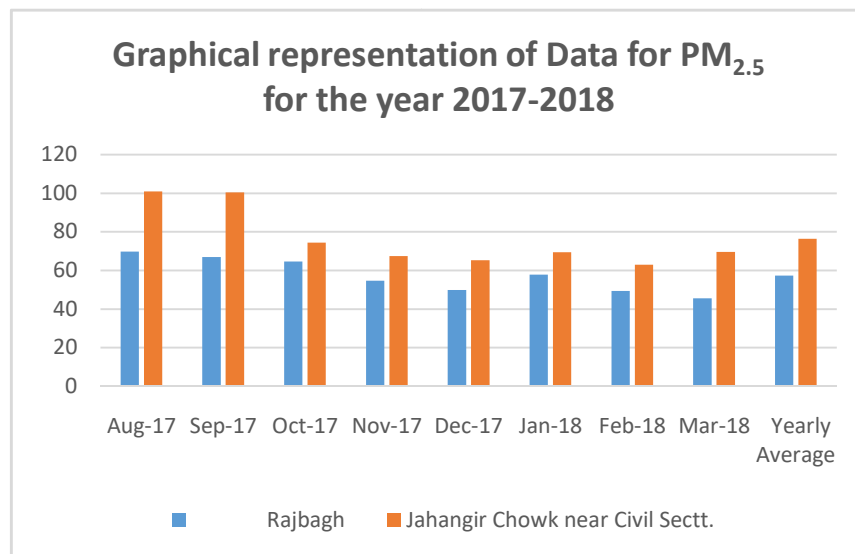


Figure 4: Graphical representation of data for PM_{2.5} for the year 2017-2018

Table 5: Air Quality Monitoring data for PM_{2.5} for the year 2018-2019

Month	Rajbagh	Jahangir Chowk near Civil Sectt.
April-2018	39.65 µg/m³	60.45 µg/m³
May-2018	42.12 µg/m³	49.76 µg/m³
June-2018	41.71 µg/m³	56.64 µg/m³
July-2018	32.48 µg/m³	43.52 µg/m³
August-2018	29.09 µg/m³	44.78 µg/m³
September-2018	40.94 µg/m³	48.87 µg/m³
October-2018	43.63 µg/m³	67.38 µg/m³
November-2018	94.51 µg/m³	129.66 µg/m³
December-2019	111.49 µg/m³	141.60 µg/m³
January-2019	92.98 µg/m³	131.47 µg/m³
February-2019	38.37 µg/m³	56.00 µg/m³
March-2019	36.21 µg/m³	45.58 µg/m³
Yearly Average	53.59 µg/m³	72.97 µg/m³

NOTE:-

- 1) All mentioned data is taken for the financial year 2018-2019
- 2) The monitoring data is restricted to the samples collected only.
- 3) The permitted limit of RSPM (PM_{2.5}) for 24 hours=60 µg/m³ and the year=40 µg/m³

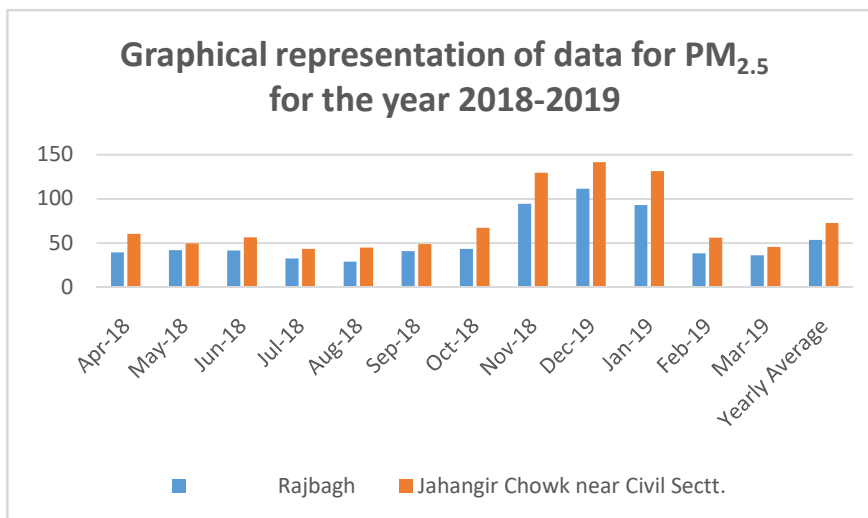


FIGURE 5: Graphical representation of data for PM_{2.5} for the year 2018-2019

TABLE 6: Air Quality Monitoring data for PM_{2.5} for the year 2019-2020

Month	Rajbagh	Jahangir Chowk
April-2019	36.58 µg/m ³	45.47 µg/m ³
May-2019	35.08 µg/m ³	45.58 µg/m ³
June-2019	40.70 µg/m ³	50.19 µg/m ³
July-2019	39.91 µg/m ³	47.01 µg/m ³
August-2019	-	-
September-2019	38.86 µg/m ³	41.94 µg/m ³
October-2019	38.08 µg/m ³	39.91 µg/m ³
November-2019	38.21 µg/m ³	44.84 µg/m ³
December-2019	120.31 µg/m ³	95.02 µg/m ³
January-2020	48.51 µg/m ³	49.50 µg/m ³
February-2020	43.21 µg/m ³	51.09 µg/m ³
March-2020	38.80 µg/m ³	48.30 µg/m ³
Average	47.11 µg/m ³	50.80 µg/m ³

NOTE:-

- 1) All mentioned data is taken for the financial year 2019-2020.
- 2) The monitoring data is restricted to the samples collected only.
- 3) The permitted limit of RSPM (PM_{2.5}) for 24 hours=60 µg/m³ and the year=40 µg/m³

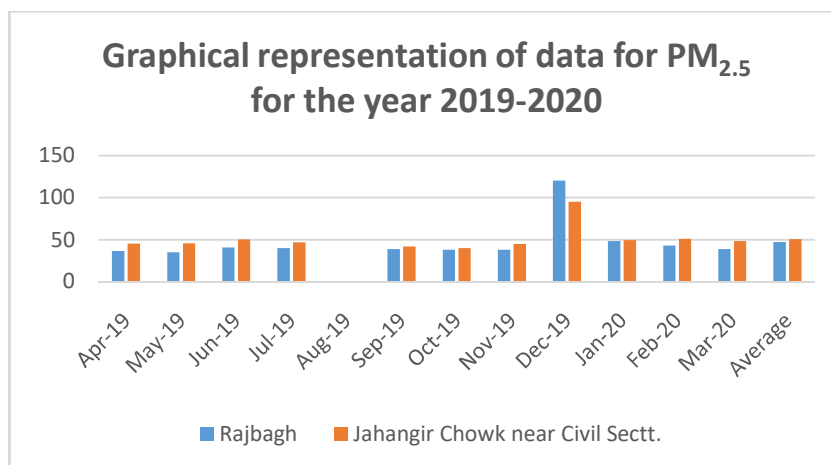


FIGURE 6: Graphical representation of data for PM_{2.5} for the year 2019-2020

TABLE 7: Air Quality Monitoring data for PM_{2.5} for the year 2020-2021

Month	Rajbagh	Jahangir Chowk near Civil Sectt.
April-2020	Sampling could not be carried out due to lockdown and strict restrictions in the Kashmir valley.	Sampling could not be carried out due to lockdown and strict restrictions in the Kashmir valley.
May-2020	26.58 µg/m ³	Sampling could not be carried out due to lockdown and strict restrictions in the Kashmir valley.
June-2020	26.14 µg/m ³	38.38 µg/m ³
July-2020	27.53 µg/m ³	34.03 µg/m ³
August-2020	24.25 µg/m ³	30.36 µg/m ³
September-2020	37.92 µg/m ³	41.08 µg/m ³

October-2020	47.24 $\mu\text{g}/\text{m}^3$	56.28 $\mu\text{g}/\text{m}^3$
November-2020	43.98 $\mu\text{g}/\text{m}^3$	43.17 $\mu\text{g}/\text{m}^3$
December-2020	38.88 $\mu\text{g}/\text{m}^3$	41.60 $\mu\text{g}/\text{m}^3$
January-2021	46.45 $\mu\text{g}/\text{m}^3$	42.67 $\mu\text{g}/\text{m}^3$
February-2021	54.35 $\mu\text{g}/\text{m}^3$	55.84 $\mu\text{g}/\text{m}^3$
March-2021	52.51 $\mu\text{g}/\text{m}^3$	54.54 $\mu\text{g}/\text{m}^3$
Average	38.71 $\mu\text{g}/\text{m}^3$	43.79 $\mu\text{g}/\text{m}^3$

NOTE:-

- 1) All mentioned data is taken for the financial year 2020-2021.
- 2) The monitoring data is restricted to the samples collected only.
- 3) The permitted limit of RSPM ($\text{PM}_{2.5}$) for 24 hours= $60 \mu\text{g}/\text{m}^3$ and the year= $40 \mu\text{g}/\text{m}^3$

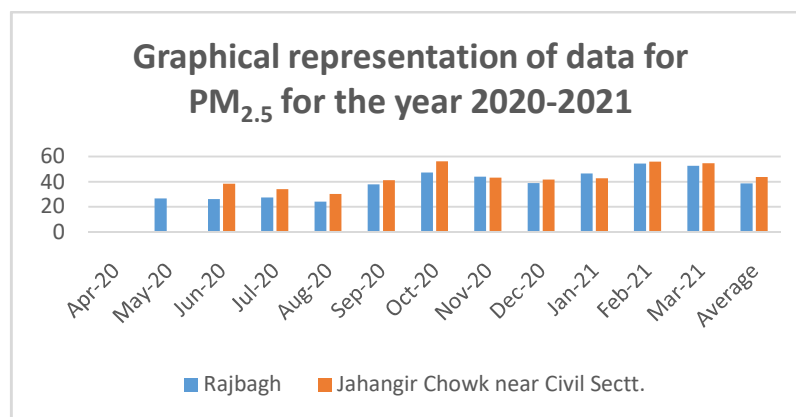


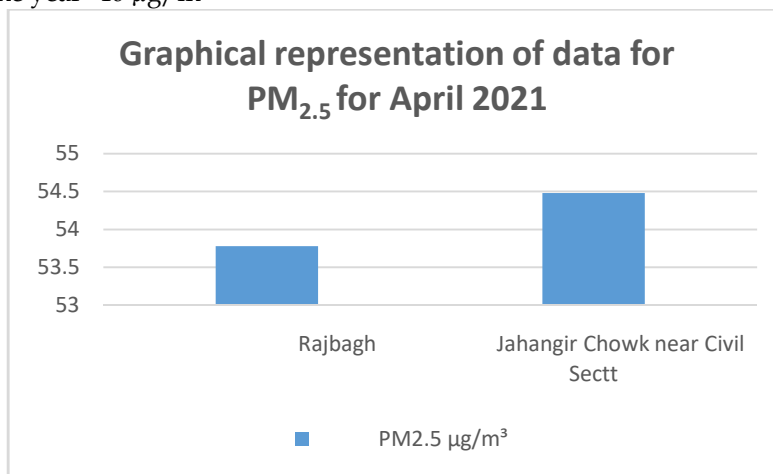
FIGURE 7: Graphical representation of data for $\text{PM}_{2.5}$ for the year 2020-2021

TABLE 8: Air Quality Monitoring data for PM_{2.5} for April 2021

S.NO	Name of sampling Station	PM _{2.5} µg/m ³
1.	Rajbagh	53.78
2.	Jahangir Chowk near Civil Sectt	54.48

NOTE:-

- 1) The mentioned data is taken for April 2021.
- 2) The monitoring data is restricted to the samples collected only.
- 3) The permitted limit of RSPM (PM_{2.5}) for 24 hours=60 µg/m³ and the year=40 µg/m³

**FIGURE 8:** Graphical representation of data for PM_{2.5} for April 2021**TABLE 9:** Air Quality Monitoring data for PM_{2.5} for May 2021

S.NO	Name of sampling Station	PM _{2.5} µg/m ³
1.	Rajbagh	24.80
2.	Jahangir Chowk near Civil Sectt	27.55

- NOTE:-**
- 1) The mentioned data is taken for May 2021.
 - 2) The monitoring data is restricted to the samples collected only.
 - 3) The permitted limit of RSPM (PM_{2.5}) for 24 hours=60 µg/m³ and the year=40 µg/m³

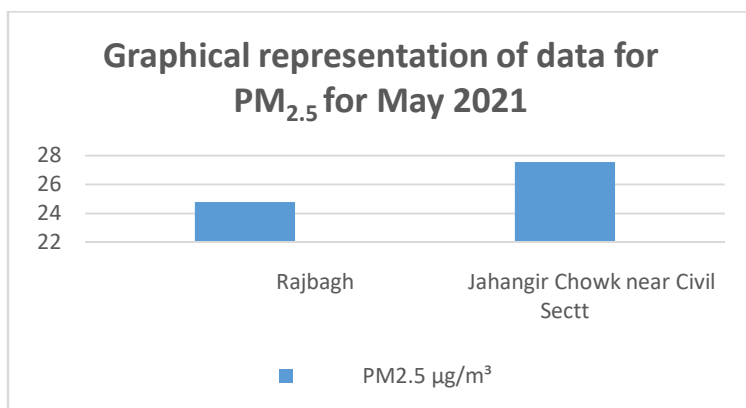


FIGURE 9: Graphical representation of data for PM_{2.5} for May 2021

7.2 Air Quality Monitoring Data for NO_x for Comparison

TABLE 10: Air Quality Monitoring data for NO_x for January 2021

S.No.	Place	Date of sampling received/analyzed	Result (NO _x)
1.	Srinagar	12-01-2021	41.68
2.	Srinagar	15-01-2021	21.73
3.	Srinagar	22-01-2021	40.09
Average			34.5

NOTE: - 1) All mentioned values are in µg/m³
 2) The monitoring data is restricted to the samples collected only.
 3) The permissible limit of NO_x for 24 hours=80 µg/m³ and the year=60 µg/m³

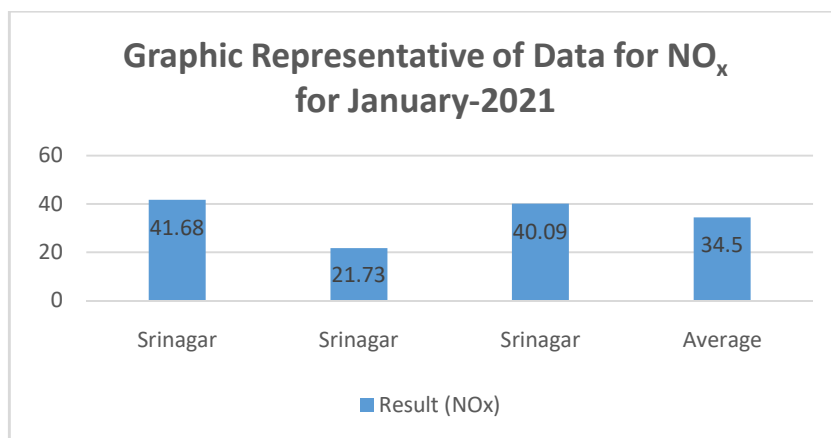


Figure 10: Graphical representation of data for NO_x for January 2021

7.3 Air Quality Monitoring Data for SO_x for Comparison

TABLE 11: Air Quality Monitoring data for SO_x for April 2021

S.No.	Place	Date of sampling received/analysed	Result (SO _x)
1.	Srinagar	01-04-2021	1.04

NOTE: -

- 1) All mentioned values are in $\mu\text{g}/\text{m}^3$
- 2) The monitoring data is restricted to the samples collected only.
- 3) The permissible limit of SO_x for 24 hours=80 $\mu\text{g}/\text{m}^3$ and the year=60 $\mu\text{g}/\text{m}^3$

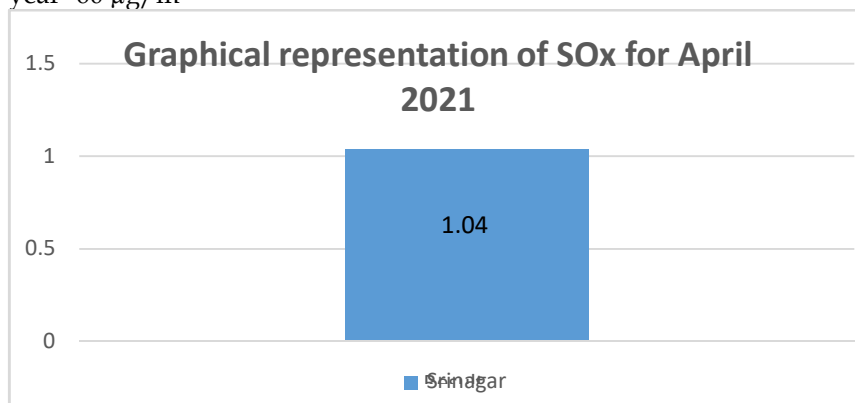


FIGURE 11: Graphical representation of SO_x for April 2021

8. Conclusion

The Air Quality Monitoring device for measurement of the concentration of $PM_{2.5}$ was installed at two places i.e. Rajbagh and Jahangir Chowk. At Rajbagh, the device was installed in the premises of the Pollution Control Board Department and at Jahangir Chowk; the device was installed on the rooftop of the fire control room.

The concentration of $PM_{2.5}$ as per yearly average is mostly seen raised. As per the yearly average, the concentration of $PM_{2.5}$ in the atmosphere should be mostly around $40\mu g/m^3$ which is considered as the permissible limit of $PM_{2.5}$.

During the prelockdown phase i.e. 2017-2019, the yearly average concentration of $PM_{2.5}$ is seen higher as compared to the post lockdown phase i.e. 2019-2021 which is seen to be less. The vehicular movement and other day-to-day activities before lockdown were going on in a normal routine, but during the lockdown, the vehicular movement was completely shut which can be seen as one of the reasons for the decline in the concentration of $PM_{2.5}$.

Also, it has been seen that the concentration of $PM_{2.5}$ in the Rajbagh area of Srinagar is less as compared to the Jahangir Chowk area. The main reason is transportation i.e. the vehicular movement at Jahangir Chowk is more than Rajbagh. Also, the road condition at Jahangir Chowk is not up to the mark, resulting in the rise of dust in the atmosphere thus, leading to the rise of $PM_{2.5}$.

The influence of dust producers such as roads, construction, dirt, etc. plays a critical role in the increased concentration of $PM_{2.5}$. The bad conditions of roads and heavy vehicle movements lead to a rise in dust production, which leads to an increase in the concentration of $PM_{2.5}$. In the autumn season, when leaves fall, people burn the leaves to produce coal. This also leads to an increase in the concentration of $PM_{2.5}$. The concentration of NO_x is seen to be lower as compared to the permissible limit and that of SO_x is also fairly low.

Overall, it can be seen that the poor condition of the air quality is because of the vehicular movement and the poor condition of the roads. The movement of the vehicles on the poorly maintained roads leads to dust, thus deteriorating the air quality. Therefore, necessary maintenance work on the roads needs to be done in these areas to improve the quality of air and to maintain the air quality within the permissible limits.

Declaration of competing interest

The authors announce that they have no known economic interests or peculiar relationships that could have appeared to influence the work reported in this paper.

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References

1. Wardencki, W. (2020). Air Pollution: Monitoring. In B. D. Fath, & S. E. Jorgensen, *Managing Air Quality and Energy System* (pp. 361-364). CRC Press.
2. Kulkarni, V., & Ramachandra, T. V. (2006). *Environmental Management*. TERI Press, New Delhi.
3. Aastha, A. (2019, December). *Air Pollution: What Is Air Quality Index, How Is It Measured And Its Health Impact*. Retrieved July 2021, from NDTV: <https://swachhindia.ndtv.com>
4. *Using Air Quality Information to Protect Yourself from Outdoor Air Pollution*. (2020, September). Retrieved July 2021, from American Lung Association: <https://www.lung.org>
5. *AQI Fundamentals*. (n.d.). Retrieved July 2021, from AirNow: <https://www.airnow.gov>
6. (2021, October). Retrieved from Central Pollution Control Board: <https://cpcb.nic.in>
7. *Central Pollution Control Board*. (2021, September). Retrieved September 2021, from Wikipedia: <https://en.wikipedia.org>
8. *Managing Air Quality - Ambient Air Monitoring*. (2021, August 2). Retrieved 2021, from EPA: <https://www.epa.gov/air-quality-management-process/managing-air-quality-ambient-air-monitoring>
9. *Managing Air Quality - Ambient Air Monitoring*. (2021, August). Retrieved 2021, from EPA: <https://www.epa.gov>
10. *Monitoring, effects, prevention and Control of Air Pollution*. (2016). Retrieved August 2021, from Slideshare: <https://www.slideshare.net>
11. Kimbrough, & Sue. (2009). *Air pollution monitoring site selection*. Retrieved July 2021, from Access Science: <https://www.accessscience.com>
12. *Ambient Air Quality Monitoring System*. (n.d.). Retrieved August 2021, from OIZOM: <https://oizom.com>
13. Reddy, Y. B., Reddy, S. M., & Reddy, C. B. (2015). Determination of Respirable Suspended Particulate Matter, non-Respirable Suspended Particulate Matter and Total Suspended Particulate Matter in Piduguralla Industrial Area India. *International Research Journal of Environment Sciences*, 3-4.
14. Haq, G., & Schwefa, D. (2008). *Air Quality Monitoring*. Sweden: Stockholm Environment Institute.

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Chapter: 4

Green chemistry and Microwave synthesis

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Abstract

Green chemistry is a method of designing, manufacturing, and using chemical compounds that actively reduces or eliminates chemical risks. It focuses on reducing, reusing, and eliminating the use of harmful and hazardous chemicals in manufacturing processes by identifying creative, alternate ways for producing the required products that have the least impact on the environment. Sustainable economic growth necessitates the use of safe, long-term resources for industrial output. This article provides an overview of the fundamental tenets upon which the Green Chemistry idea is founded. In traditional heating methods, an oil bath or hot plate is used to provide heat to a chemical process. In chemical synthesis, microwave irradiation is commonly utilised as a source of heating. Dipolar polarisation and conduction are the fundamental processes seen in microwave mediated synthesis. Microwave-assisted synthesis provides clean synthesis with the benefits of increased reaction rates, higher yields, greater selectivity, and lower costs for the synthesis of a large number of organic molecules, which has prompted many chemists to switch from conventional heating methods to microwave assisted chemistry.

Keywords: Green Chemistry, Microwave, Polarization, green solvent,

What exactly Green Chemistry is?

Green chemistry is a proactive pollution-prevention strategy. Pollution is targeted before it even begins at the design stage. If chemists are educated to design goods and materials without employing hazardous compounds, many wastes, dangers, and expenses can be avoided. Green science is the advancement of synthetic items and cycles that decrease or dispose of the use or potentially formation of risky compounds. The improvement, plan, and utilization of compound items and cycles to lessen or kill the utilization and engendering of unsafe substances.¹

Green Chemistry concept

1. Prevention
2. Atom Economy
3. Less hazardous Chemical Synthesis
4. Designing safer chemicals
5. Safer solvents and auxiliaries
6. Design for energy efficiency
7. Use of renewable feedstock
8. Reduce Derivatives
9. Catalysis
10. Design for degradation
11. Real time analysis for pollution Prevention
12. Inherently safer chemistry for accident prevention

The Principles of Green Chemistry

The numerous important objectives, The twelve principles of green chemistry were defined. For many chemical processes, these principles are plainly impossible to implement right away. It's great to witness so many creative discoveries at diverse scientific and commercial processes after twenty years of Green Chemistry projects and industrial applications. Chemists, engineers, material scientists, bioscientists, and technologists collaborated to produce intriguing discoveries. The associative approach has broadened the scope of green chemistry and resulted in some magnificent non-toxic products and cost savings for chemical companies.²

Scientific Approaches for Practical Applications

The following regions were proposed for particular attention under the green concepts. Green Chemistry and Green Engineering are attempting to develop new feasible development approaches.

1. Utilization of alternative feedstock.
2. Utilization of less hazardous reagents
3. Use of biocatalytic techniques
4. Utilization of alternative solvents
5. Design of safer chemicals, intermediates, and products
6. Developing alternative conditions of reactions
7. Reducing energy consumption

Green Chemistry aspires to transition to renewable feedstock. The lower toxicity and environmental impact of basic starting materials is

the second most desired property. The protection of workers' health and safety, as well as the environment, is a top priority. Green Chemistry proposes a shift in focus to biological primal matter (plant and animal atrophy, products from the fermentation of plant atrophy, biogas, etc). There are many challenges in using these matters, but there have been inspiring new prospects for big-scale manufacturing and the use of substitute, reusable matters in recent years.²

Green Chemistry is deal with the amount of hazardous organic solvents used in synthetic methods and chemical reactions as a whole. First, green chemistry principle is to use as little solvent as possible, or to replace it with a less toxic different, or to use different that do not require solvents. Solvents in chemical company are one of the most serious issues in terms of worker health and safety, as well as environmental pollution due to waste. Solvents are used in a variety of processes, including synthesis, separation, cleaning, drying, analysis, and recycling. It is not an easy task to change solvents and technological processes. There are numerous differences, but they may be more expensive, time-consuming, or difficult to implement in the established order of chemical strategy. Although surrounding contamination from solvents can be a serious issue for many chemical industries, replacement solutions are not ever obtainable.

Research on various industrial applications has been very successful, yielding significant benefits in terms of energy consumption, less toxic products, and reduced waste. These advancements have primarily benefited the safety and health of workers in chemical industries, basic matters workshops, and other professionals involved in the transport and distribution of these products. Second, green chemistry discovered other ways to reduce energy use, such as by modifying processes or developing novel stimulant approaches. Industry's energy use is not only a source of economic growth but also a significant environmental issue. Third, green chemistry lowered environmental problems significantly by using alternative solvents (e.g., "toluene instead of benzene, cyclohexane instead of carbon tetrachloride, dichloromethane instead of chloroform"). Finally, green chemistry provided breakthroughs for industrial items during their use or as trash at the end of their useful life cycle. These are critical adjustments for achieving long-term growth goals.

Green Chemistry focuses on cleaner production practices and less harmful consumer products through design and improved synthetic approaches. "Pesticides, fertilizers, elastomers, plastics, pharmaceuticals, analytical reagents, and other commercial products are all being phased out in favor of safer, healthier, and more

environmentally friendly alternatives.” At the same time, the industry contributes to the aims of sustainability and environmental protection, not only because technology improvements give alternative techniques, but also because it makes economic sense and avoids future feedstock and energy shortages.

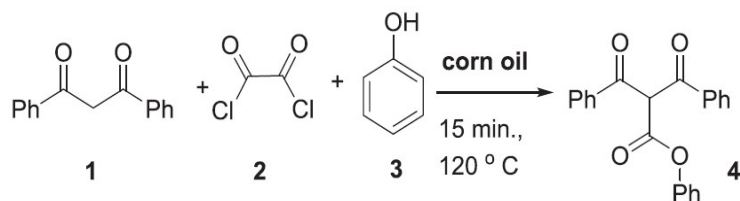
Green solvent-based synthetic strategies

Solvents are required in large quantities in every product development process and in various industrial applications, concluding in massive aggregate of waste. Novel technologies and various methods have discussed solvent-free methods, which is not widely used in all regions of research due to market scrutinization. Following the solventless ideas, chemists and medicinal scientists have looked for solvents that are suitable for green chemistry. Some of the green solvents are illustrated here.

1. Green solvents: vegetable oils

“Vegetable oils are oleochemicals extracted from the seeds of many plants. They are renewable resources with a triglyceride structure in which three hydroxyl groups of glycerol are substituted with various fatty acids, resulting in liquids or solid products”.

For example, Dibenzoyl methane (1), oxalyl chloride (2), and phenol (3) were refluxed in maize oil for 15 minutes at 120°C. Compound (1) CH₂ was easily acylated. [Scheme 1]³

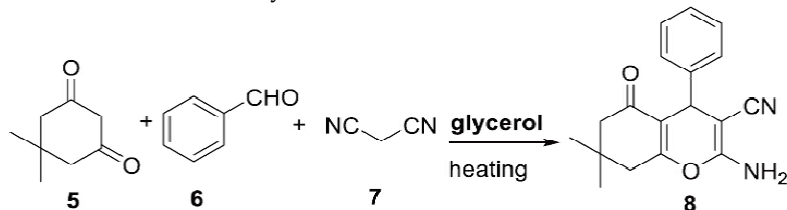


Acylation reaction in Maize oil (Scheme 1)

2. Green solvents: Glycerol

Glycerol (glycerin) is a polyalcohol that is generated from natural oils and is the second part of the oleochemicals family. Glycerol is used in a variety of industries, including the pharmaceutical and food industries, tobacco, and cellulose films. Glycerol is a good green solvent because of its long life and inexpensive cost. In this regard, pharmaceutical companies and scientists have given glycerol more consideration as different from other organic solvents that are dangerous, volatile, poisonous, and damaging.

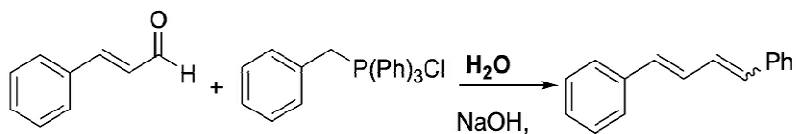
Using glycerol as a green solvent, Safaei et al. amalgamate 4H-pyran using a catalyst-less, one-pot, three-component method (Scheme 2).⁴ The reactions yielded a significant percentage of pyran derivatives, up to 93%, and the reactions produced several types of pyran compounds. In addition, the scientists examined the reaction in water and discovered that the yield of the reactions was reduced to 70%.



One Pot and three component strategy in glycerol (Scheme 2)

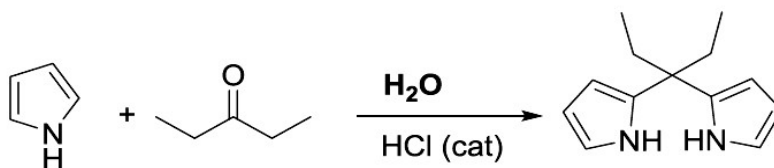
3. Green solvents: Water

Water is a green solvent since it is inexpensive, abundantly available, nontoxic, nonpolluting, and nonflammable. Organic chemistry basic reactions are used in pharmaceutical science to create drugs. Wittig reaction is one of these reactions. The Wittig reaction is extremely important because it results in the formation of a new C-C bond. Morsch et al. have thus reported a green treaty for the Wittig reaction, which is carried out in the water at 25°C.⁵



Wittig reaction by using water as green solvent (Scheme 3)

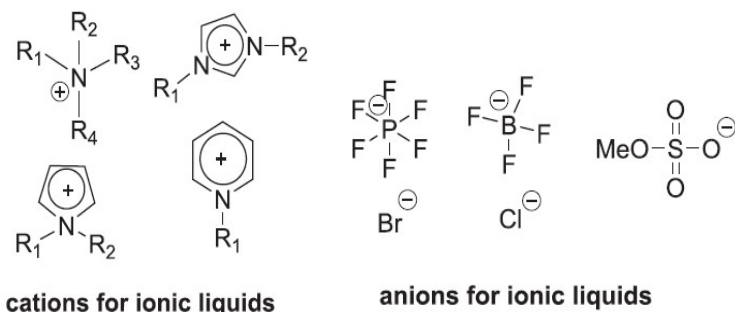
Pyrrole is a condemnatory starting material for medicine design, and its reactions are equally salient. Sobral reported a green master plan in which pyrrole and diethyl ketone were reacted in water to produce 2,2'-dipyrromethane (Scheme 4). Sobral reported that the reaction yielded 80% and that the reaction was progressed as gram scale.



Synthesis of dipyrromethane using water (Scheme 4)

4. Other solvents

Organic salts that are liquid at room temperature are referred to as ionic liquids. They are nonvolatile, incendiary, tepid, and chemically stable, making them a better green chemistry alternative than conventional organic solvents. Because of their high duality, they can be used in a variety of chemical and biochemical reactions. Aside from their unique physical composition, they are less soluble in water and are generally immiscible with a wide range of organic solvents, including hexane(s). They have a substantially higher viscosity than other organic solvents, possibly because of the presence of more hydrogen bonds and Van der Waals forces. The most essential aspect of ionic liquids is that they can be modified by changing the cation, anion, and alkyl parts, resulting in a variety of green organic solvents that may be managed.⁶ Figure 1 depicts some of the most common cation and anion components.



Ionic liquids (Figure 1)

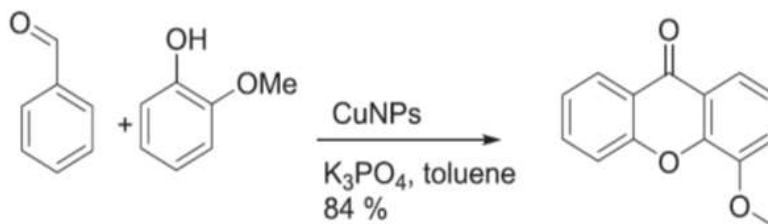
Green catalysts-based\synthetic strategies

1. Nanocatalysts as a sustainable solution

Catalyst is one of the major rules of green sciences that chemists and medical scientists should consider. Catalysts are classified into two types: heterogeneous and homogeneous. Homogeneous catalysts outperform heterogeneous catalysts in terms of product yield. "However, because of metal contamination of products, isolation and reusable homogeneous catalysts are the more problematic disadvantages when used for fine chemical production in the chemical and pharmaceutical industries. Less effective but more appealing heterogeneous catalysts are more appealing due to advantages such as reusability and easier isolation from the medium. Aside from heterogeneous catalysts, nanocatalysts have received increased attention as semi-heterogeneous catalysts due to their large

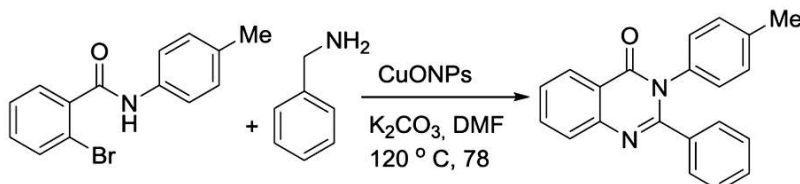
surface-volume ratio, which results in more interactions between the surface of the catalyst and the reactant. Even if the catalyst is filtered using specific filtration methods, it can still be contaminated. Magnetism has recently been used to obtain and extract magnetic nanocatalysts from the medium with an external magnetic field. They have provided a more promising solution for chemical industries, and it appears to be suitable for the active pharmaceutical ingredient (API) industry".⁷

Gerbino and colleagues used a copper-based magnetically recoverable nanocatalyst to synthesize xanthenes in a single step.⁸ Under ligand-free conditions, salicylaldehyde and phenol derivatives were reacted in toluene. When a reusable copper nanocatalyst was tested in the fourth cycle, it was found to be 89 % effective. The substitution of a copper nanocatalyst for a conventional catalyst, CuCl or CuO, reduced the product yield to 65 and 62 %, respectively.



Outfitting of derivative by using copper based nano particles

Patel et al. Synthesized quinazolinones from halo benzamide and benzylamine using copper nanocatalysts (CuONPs). Researchers discovered that traditional copper catalysts such as CuBr, CuCl, and CuI have a lower catalytic effect than copper nanocatalysts. Furthermore, there is no cyclic product without a catalyst.⁹

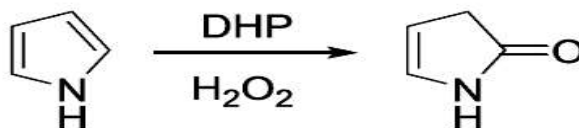


Quinazolinone ring synthesis (Scheme 6)

2. Bio catalysts as a sustainable solution

Biocatalysts are recyclable, reusable, efficient, and stereoselective, which means they are more atom efficient than traditional approaches. They are more effective tools for green chemistry in this regard. A biocatalyst can be an isolated enzyme, a crude cell-free extract, an immobilized enzyme, or enzymes from entire microbial cells. Enzymes are important endogens that play a crucial function in living cells, catalyzing all in vivo metabolic events to produce a required product for the organism. Since a century, enzymes have been used in the laboratory to mimic the venture of enzymes for our reactions. Scientists have employed enzymes such as “oxidoreductases, transferases, hydrolases, lyases, isomerases, and ligases” for a variety of reasons. Enzymes are used in a variety of industries, including food, pharmaceuticals, medicine, and textiles. Enzymes have special qualities that artificial organic products can't always mimic.

Ghiladi et al. developed a biocatalytic green approach for pyrrole ring oxidation to produce pyrroline-2-one. For the biocatalytic reaction, dehaloperoxidase (DHP) was used, and hydrogen peroxide was used as an oxygen source.¹⁰ Finally, 31.7 % conversion yielded pyrroline-2-one. Some pyrrole compounds were oxidized to 100% conversion, according to the authors.

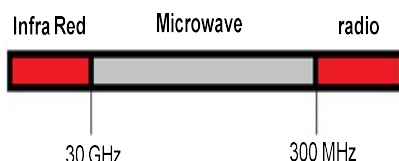


Oxidation of pyrrole by using green catalyst DHP (Scheme 7)

Microwave-assisted Synthetic approach

Organic synthesis has been transformed by microwave-assisted organic synthesis. Small molecules can be created in a fraction of the time that traditional thermal methods require. As a result, this technique has quickly gained acceptance as a valuable tool for speeding up drug discovery and development processes. A microwave is a type of electromagnetic energy that falls at the lower end of the electromagnetic spectrum and has a frequency range of 300 to 300,000 MHz, corresponding to wavelengths of 1 cm to 1 m.¹¹

Microwave-assisted synthesis works via stimulation of the material's dipoles in an external field using microwave electromagnetic radiations, and is usually used in conjunction with a well-known synthesis approach.



Advantages

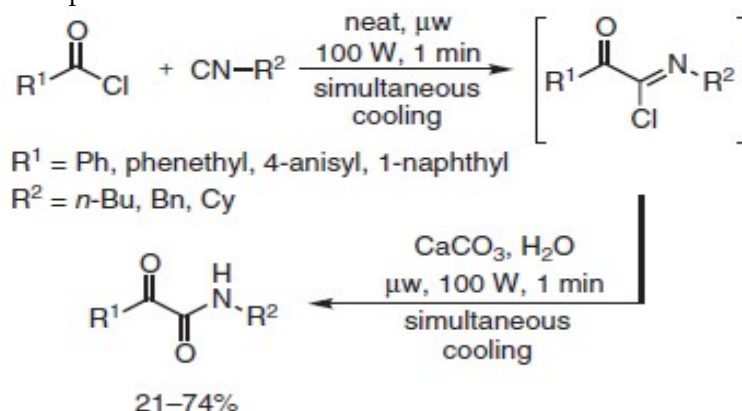
- Uniform heating occurs throughout the material
 - Process speed is increased
 - High efficiency of heating
 - Reduction in unwanted side reaction
- Purity in final product,
Improve reproducibility
Environmental heat loss can be avoided
Reduce wastage of heating reaction vessel
Low operating cost

When a molecule is exposed to microwaves, it aligns with the applied field. The molecule is affected by the rapidly changing electric field (2.45×10^9 Hz), and as a result, the molecule is constantly attempting to align itself with the changing field, and energy is absorbed. The dielectric constant determines a material's ability to convert electromagnetic energy into thermal energy. The stronger the coupling with microwaves, the greater the dielectric constant. When microwaves are used, solvents such as water, methanol, DMF, ethyl acetate, acetone, acetic acid, and others are rapidly heated.¹¹

An alternative method for performing microwave-assisted organic reactions, known as "Enhanced Microwave Synthesis" (EMS), has recently been investigated. More energy can be directly applied to the reaction mixture by externally cooling the reaction vessel with compressed air while simultaneously administering microwave irradiation. The initial microwave power in "Conventional Microwave Synthesis" (CMS) is high, rapidly raising the bulk temperature (TB) to the desired set point. However, once this temperature is reached, the microwave power is reduced or completely turned off in order to maintain the desired bulk temperature without exceeding it.¹²

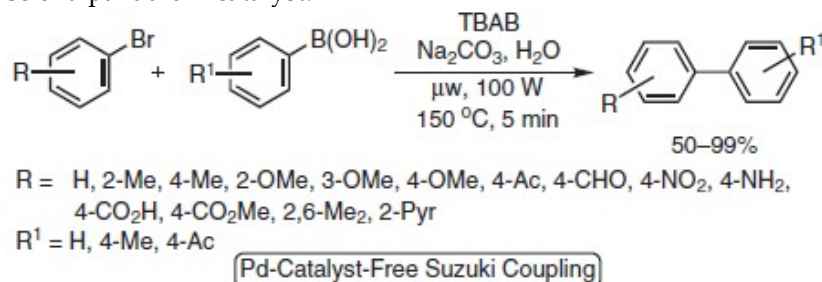
The scientists used an older methodology from the 1960s to combine acyl chlorides with different isonitriles. On hydrolysis, α -ketoimidoyl

chloride intermediates were generated, which were then transformed to α -keto amides. The two steps took 2 minutes and yielded 21–74 percent under conventional heating circumstances; however, under optimal EMS conditions, the two steps took 2 minutes and yielded 21–74 percent.¹²



Enhanced Microwave Synthesis Improves the Synthesis of α -Keto Amides (EMS). (Scheme 8)

Transition-metal-free Suzuki and Sonogashira couplings are two of the most amazing recent findings in organometallic chemistry. Leadbeater and colleagues have demonstrated that reacting an activated aryl bromide with an aryl boronic acid in water with tetrabutylammonium bromide (TBAB) as a phase-transfer catalyst yields an effectively linked biaryl Suzuki product without the use of a palladium catalyst.¹²



(Scheme 9)

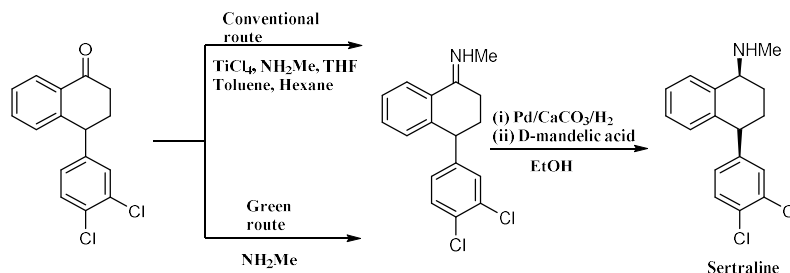
Microwave assisted reactions using solvent, under solvent free conditions, using solid phase and on mineral supports in dry media are reported in various experiments. The majority of peptide

synthesis takes place in the solid state, and microwave irradiation has been shown to improve chemical reactions such as deprotection, coupling, cyclization, condensation, isomerization, oxidation, reduction, cycloaddition, rearrangement, nucleophilic substitution, and cleavage. A series of effective and selective allosteric AKT kinase inhibitors were produced using microwave heating technique, which is highly efficient. A 2,3-diphenylquinoxaline was used to make these inhibitors.

To accelerate the drug discovery and development process, rapid synthesis and building of varied chemical libraries are required. Microwave irradiation heating technique has grown in prominence as a tool in drug discovery programmes for high-speed synthesis. As a result, microwave technology is gaining traction as a potent alternative energy source for completing chemical transformations in minutes rather than hours or days.¹³

Scientific Approaches for Industrial Applications of Green Chemistry

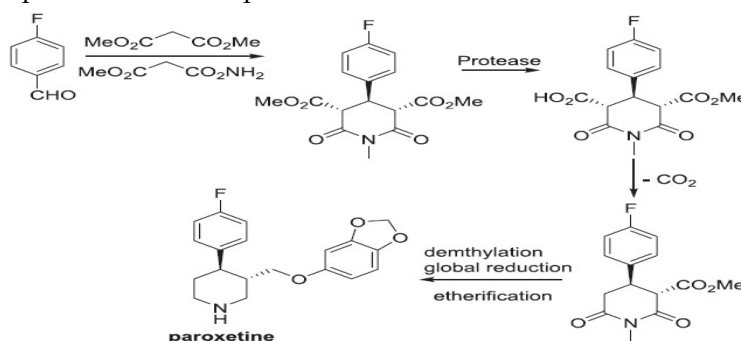
Colberg and colleagues at Pfizer Global Research and Development developed a green sertraline procedure in which harmful solvents including toluene and hexane were removed from the strategy and a collation of solvent usage between the first economical way and the second commercial route was made. The new green approach revealed 76,000 L solvents and 440 tonnes of TiO₂-MeNH₂ every year. HCl waste was avoided, as well as around 40 tonnes of undesirable trans-isomer waste.



Green approach for Sertraline (Scheme 8)

1) GlaxoSmithKline has revealed a green pathway for paroxetine, which is sold as Seroxat and Paxil and is used to treat anxiety disorders. They discussed how the overall yield of the transformation was nearly double that of the conventional route,

resulting in a greener, shorter, and more cost-efficient process. The use of protease enzyme, which regioselectively hydrolyzed an ester group, was a critical step.



Green approach for Paroxetine (Scheme 9)

References:

- [1] Education, F. S.; Scientific, part of T. F. *Green Chemistry Curriculum: An Introduction to Green Chemistry*.
- [2] *Green Chemistry and Technology for Sustainable Development. Basic Principles and Applications 2.1. Green Chemistry from Theory to Practice*.
- [3] Menges, N.; Şahin, E. Metal- and Base-Free Combinatorial Reaction for C-Acylation of 1,3-Diketo Compounds in Vegetable Oil: The Effect of Natural Oil. *ACS Sustainable Chemistry & Engineering* 2014, 2 (2). <https://doi.org/10.1021/sc400281h>.
- [4] Safaei, H. R.; Shekouhy, M.; Rahmanpur, S.; Shirinfeshan, A. Glycerol as a Biodegradable and Reusable Promoting Medium for the Catalyst-Free One-Pot Three Component Synthesis of 4H-Pyrans. *Green Chemistry* 2012, 14 (6). <https://doi.org/10.1039/c2gc35135h>.
- [5] Morsch, L. A.; Deak, L.; Tiburzi, D.; Schuster, H.; Meyer, B. Green Aqueous Wittig Reaction: Teaching Green Chemistry in Organic Teaching Laboratories. *Journal of Chemical Education* 2014, 91 (4). <https://doi.org/10.1021/ed400408k>.
- [6] Yang, Z.; Pan, W. Ionic Liquids: Green Solvents for Nonaqueous Biocatalysis. *Enzyme and Microbial Technology* 2005, 37 (1). <https://doi.org/10.1016/j.enzmtec.2005.02.014>.
- [7] Wang, D.; Astruc, D. Fast-Growing Field of Magnetically Recyclable Nanocatalysts. *Chemical Reviews* 2014, 114 (14). <https://doi.org/10.1021/cr500134h>.
- [8] Menéndez, C. A.; Nador, F.; Radivoy, G.; Gerbino, D. C. One-Step Synthesis of Xanthenes Catalyzed by a Highly Efficient Copper-Based Magnetically Recoverable Nanocatalyst. *Organic Letters* 2014, 16 (11). <https://doi.org/10.1021/ol500964e>.
- [9] Modi, A.; Ali, W.; Mohanta, P. R.; Khatun, N.; Patel, B. K. CuO Nanoparticle Catalyzed Synthesis of 2,3-Disubstituted Quinazolinones via Sequential N-Arylation and Oxidative C-H Amidation. *ACS Sustainable Chemistry & Engineering* 2015, 3 (10).

- [10] McCombs, N. L.; Smirnova, T.; Ghiladi, R. A. Oxidation of Pyrrole by Dehaloperoxidase-Hemoglobin: Chemoenzymatic Synthesis of Pyrrolin-2-Ones. *Catalysis Science & Technology* 2017, 7 (14). <https://doi.org/10.1039/C7CY00781G>.
- [11] Ravichandran, S.; Karthikeyan, E. *Microwave Synthesis-A Potential Tool for Green Chemistry*; Vol. 3, pp 466–470.
- [12] Hayes, B. L. *Recent Advances in Microwave-Assisted Synthesis*.
- [13] Sahoo, B. M. Microwave Assisted Drug Synthesis (MADS): A Green Technology in Medicinal Chemistry. *Journal of Applied Pharmacy* 2016, 08 (01). <https://doi.org/10.4172/1920-4159.1000e106>.

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Chapter: 5

Removal of total hardness from different samples of water by using a coconut shell as an adsorbent

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Abstract Water hardness is a conventional indicator of water's ability to react with soap, with hard water necessitating significantly more soap to generate lather. It leaves a visible film of precipitate (insoluble metals, soaps, or salts) in the drain. Activated carbon was prepared from the coconut shell for the analysis of hardness from the different samples of water. The current study investigates the use of prepared adsorbent for a contact period of 4 hours in order to turn the sample neutral. From the results, it was observed that the prepared adsorbent from agriculture waste was proved better as it turned sample to neutral. The hardness of wastewater and dying water were found as 870 and 720 mg/L respectively after using an adsorbent. The findings suggested that the prepared adsorbent has a positive effect and can be used as an adsorbent.

Keywords: Adsorbent, Adsorption, Hardness, Coconut Shell

1.1 INTRODUCTION

The quantity of calcium and magnesium in water is the primary determinant of its hardness. Hard water is caused by high amounts of these and other minerals. Water softening systems operate by lowering the mineral content in the water. Soft water, rather than having higher amounts of calcium and magnesium, has a larger concentration of sodium, or salt. Water hardness is an issue that has been observed in many areas throughout the world, including Tanzania. This problem is particularly severe in Tanzania's coastal and central areas, due to the rock type, sedimentary rock, which is high in calcium and magnesium (Knivslund 2012; Napacho and Manyele 2010). Hard water causes a variety of problems in everyday life, including scaling in boilers, washing machines, and pipelines (Seo et al., 2010). Water softening applications employ a variety of approaches, ranging from traditional procedures to cutting-edge

technology; Ion-exchange membrane filtration, electrochemical approaches, and adsorption by natural adsorbents are some of the most widely used methods calcium and magnesium ions in water are exchanged with sodium ions in the resins in the ion exchange technique. The primary disadvantage of such resins is that sodium ions discharged into the medium create significant health issues on the other hand, while ion-exchange membrane methods are highly efficient, they use a lot of energy (Pentamwaet al., 2011; Manhan 2011; Karabacakoglu et al.,2015; Su et al.,2010; Yang 2016; Yangali et al.,2015; Gharehchahi et al.,2014; Sepehr et al., 2013; Idris et al., 2013). Water softening by adsorption utilizing agricultural wastes-based activated carbon as an adsorbent appears to have potential because agricultural wastes are readily available and inexpensive Coconut shells are agricultural wastes that are often discarded once the interior contents have been extracted. These wastes may be turned into usable activated carbon, which can then be used to purify water (Grassi et al., 2012). Furthermore, different agriculture-based adsorbents have been utilized to remove Ca^{2+} and Mg^{2+} from normal drinking water; nevertheless, the greatest adsorption of these ions was seen at acidic pHs, suggesting some practical limits owing to natural hard water's basicity (Muyibi et al., 1996). Although most of the methods developed so far are effective in removing hardness from water, their high energy consumption is a key disadvantage that makes them unsustainable in many areas. As a result, there is a growing scientific interest in developing more environmentally friendly, long-term, and cost-effective ways for removing water hardness, despite the fact that this area of study has received little attention thus far. To this end, an adsorbent was prepared from a coconut shell for the removal of hardness from the different samples of water. In addition, an analysis was done for different samples of water with and without adsorbent for a contact period of 4 hours.

1.3 MATERIAL METHODOLOGY

1.3.1 Material

The coconut shell was obtained from the local shop of Khanna area Punjab, and then it was cleaned with some distilled water and dried at 102°C . The chemicals like Ethyl diamine tetra acetate and Erichrome black T dye were used to carry out the experimental investigation

1.3.1.2 Method

After the collection of the material the coconut shell was completely cleaned with some distilled water and dried then the material was ground of 2.00mm. Later a 1000ml vessel was taken and filled with

some normal drinking water. After that 200g of coconut shell was added into the water and mixed well by stirrer and left the sample for a contact period of 3 hours. The activated carbon was made from coconut shells using KOH, and it was discovered that it had the ability to remove Pb^{2+} from aqueous solutions (Song et al. 2014).

1.3.1.3 Determination of total hardness (temporary and permanent)

A 30 mL sample of regular drinking water with a pH of 7.1 was collected, and a few drops of ammonia buffer were added to bring the pH up to 10. Also, a few drops of Erichrome black T dye was added to the sample to change the color to wine red, and then the sample was titrated against Ethylene diamine tetra acetate solution until the color changed to blue, and the final reading of the burette was recorded, followed by the initial reading of 0. In addition, several samples of dying water and wastewater were examined before and after a 4-hour interaction with the adsorbent. The total hardness of several water samples was determined using the formula (1)

$$\text{Total hardness (mg/L CaCO}_3 \text{ scale)} = \frac{\text{mL of EDTA} \times 103}{\text{mL of sample taken}} \quad (I)$$

1.4 RESULT AND DISCUSSION

The produced adsorbent had a positive effect on the diverse water samples, causing them to become neutral. In the current investigation, it was discovered that activated carbon made from coconut shell had a smooth texture and a large pore volume, making it appropriate for determining total hardness from various samples after a 4-hour contact period.

1.4.1 Effect of prepared adsorbent on the total hardness

The overall hardness of typical drinking water is 300 mg/L; however, in this investigation, the hardness of wastewater and dying water were originally 870 and 720 mg/l respectively which is extremely high in contrast to normal drinking water. When the adsorbent made from agricultural waste was employed for a 3-hour contact time and the test was repeated, the hardness of the wastewater and dying water was decreased to 514 and 525 mg/L respectively. The prepared adsorbent removes the excess hardness in various samples of water (Cecilia et al. 2016). Fig 1 shows the various effects of adsorbents on different samples of water with and without adsorbents.

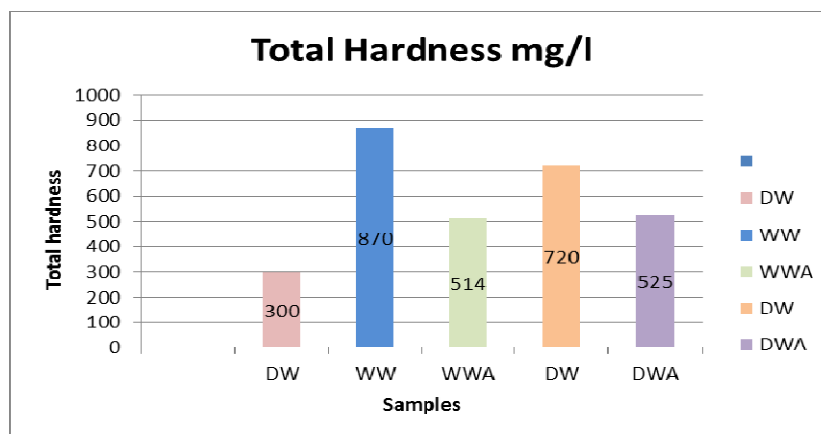


Figure 1. Total hardness of different samples

Conclusion

It is obvious that CSAC (coconut shell activated carbon) is beneficial in water softening based on the findings of this study. Because coconut shells are readily accessible, particularly in coastal areas where hardness problems are prevalent, CSAC adsorbents are predicted to be cost-effective for removing hardness from groundwater. The total hardness of wastewater and dying water were reduced to 514 and 525 mg/l. According to the literature, there are a variety of ways for removing hardness from diverse water samples, each of which takes longer. However, after a 4-hour contact period, the produced adsorbent neutralized the sample, indicating that the method is worthwhile to use in the future. The invention of a low-cost and user-friendly water treatment technology for those who have hard water difficulties is the project's primary accomplishment.

Declaration of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this manuscript.

Acknowledgement

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REFERENCES

- [1] Cecilia and Rolence(2016)Adsorption studies on water hardness removal by using cashew nut shell activated carbon as an adsorbent. African Journal of Science and Research(5)4:78-8.
- [2] Grassi M, Kaykioglu G, Belgiorio V, Lofrano G(2012)Removal of emerging contaminants from water and wastewater by adsorption process. In Emerging compounds removal from wastewater108:15-37

- [3] Gharehchahi E, Mahvi AH, Shahri SM, Davani R(2014)Possibility of application of kenaf fibers (*Hibiscus cannabinus* L.) in water hardness reduction. *Desalination and Water Treatment*52(31-33):6257-62.
- [4] Idris S, Iyaka YA, Dauda BEN, Ndamitso M M,Umar MT(2012) Kinetic study of utilizing groundnut shell as an adsorbent in removing chromium and nickel from dye effluent. *Am Chem Sci J* 2(1):12-24
- [5] Knivslund SM(2012)Water chemistry in the Bahi-Manyoni basin in Tanzania.
- [6] Karabacakoglu B, Tezakıl F, Güvenç A(2015) Removal of hardness by electro dialysis using homogeneous and heterogeneous ion exchange membranes. *Desalination and Water Treatment*54(1):8-14.
- [7] Muyibi SA, Evison LM(1996). Coagulation of turbid water and softening of hardwater with *Moringa oleifera* seeds. *International journal of Environmental studies*49(3):247-59.
- [8] Manahan SE(2011) Fundamentals of environmental chemistry. CRC press.
- [9] Napacho ZA, Manyele SV(2010)Quality assessment of drinking water in Temeke District (part II): Characterization of chemical parameters. *African Journal of Environmental Science and Technology*4(11):775-89.
- [10] Pentamwa P, Thipthara W, Nuangon S(2011) Removal of hardness from groundwater by synthetic resin from waste plastics. *International Journal of Environmental Science and Development*2(6):479-84.
- [11] Seo SJ, Jeon H, Lee JK, Kim GY, Park D, Nojima H, Lee J, Moon SH (2010). Investigation on removal of hardness ions by capacitive deionization (CDI) for water softening applications. *Water research*44(7):2267-75.
- [12] Su Y, Wang J, and Fu L(2010) Pure water production from aqueous solution containing low concentration hardness ions by electrode ionization. *Desalination and Water Treatment*22(1-3):9-16.
- [13] Sepehr MN, Zarrabi M, Kazemian H, Amrane A, Yaghmaian K, Ghaffari HR(2013) Removal of hardness agents, calcium and magnesium, by natural and alkaline modified pumice stones in single and binary systems. *Applied Surface Science* 274:295-305.
- [14] Song C, Wu S, Cheng M, Tao P, Shao M, Gao G(2014) Adsorption studies of coconut shell carbons prepared by KOH activation for removal of lead (II) from aqueous solutions. *Sustainability* 6(1):86-98.
- [15] Yang G, Zhang Y, Guan S(2016)Study on the desalination of high hardness water by electrodeionization reversal. *Desalination and Water Treatment*57(18):8127-8138.
- [16] Yangali-Quintanilla V, Olesen L, Lorenzen J, Rasmussen C, Laursen H, Vestergaard E. and Keiding K, (2015). Lowering desalination costs by alternative desalination and water reuse scenarios. *Desalination and Water Treatment*55(9):2437-2445.

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Chapter: 6

Recent progress in electrogenic microbial communities in microbial fuel cells

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Abstract

The depletion of non-renewable energy has led to the development of pollution free energy resources. Combustion of fossil fuels emits a lot of greenhouse gas like carbon dioxide, which has shown alarming consequences to the environment. Wastewater treatment and electricity generation have been the major concerns for the last few years [1][2]. Microbial fuel cells (MFCs) is lauded for its potentials to solve both energy crisis and environmental pollution [3]. MFCs are energy conversion devices that simultaneously produce electricity while degrading the wastewater's organic materials[4]. MFCs harvests energy through the oxidation of organic substrates and transform into the electric current with the aid of electrogenic microbes [2]. The recent progress in electrogenic microbial communities in microbial fuel cells is discussed and reported.

Keywords: Microbial fuel cells (MFCs), Electrogenic microbes, Energy generation, Environmental pollution.

Microbial fuel cell & Electrogenic microbes

Electricity production by using microbial cultures was first observed over 90 years ago by Potter [5,6,7]. MFCs harvests energy through the oxidation of organic substrates and transform into the electric current with the aid of microorganisms as catalysts[2]. The main factors of a MFC are the anode and the microorganisms around it that produce electrons [8]. Electrogenic bacteria which, as the name suggests, can transfer electrons from the microorganisms to electron acceptor at a higher electrochemical potential, leading to development of sustainable means of power generation [9].

Recent developments

Sumin KIM (2021) reported the change of voltage along with the growth of *Bacillus megaterium* in a plant MFC. Guar gum was the base structure as it can culture microorganisms and create a hydrogel by cross-linking with borax. *Bacillus megaterium* was added to the hydrogel as it can survive under the basic conditions of borax while producing electrons. Glucose was added as well to help culture the bacteria. Then, the change of voltage was observed along with the growth of *B. megaterium* [10].

A study of promoting extracellular electron transfer of *Shewanella oneidensis* MR-1 by optimizing the periplasmic Cytochrome c Network by was reported (Weining Sun et.al.) The low efficiency of extracellular electron transfer is a major bottleneck for *Shewanella oneidensis* MR-1 acting as an electroactive biocatalyst in bioelectrochemical systems [11]. A periplasmic c-type cytochrome (c-Cyt) network plays a critical role in regulating EET efficiency[11]. *Shewanella oneidensis* exchanges electrons between cellular metabolism and external redox partners. The critical component of this pathway is the outer membrane spanning MTR complex, a biomolecular wire formed of the MtrA, MtrB, and MtrC proteins [12].

The recent study on Electrochemical Characterization (in situ) of a Microbial Fuel Cell Biocathode Running on Wastewater was reported (Sudarsu V. Ramanaiah et.al.). The bacteria presence, in particular when biofilms are allowed to develop, was related with the enhanced active redox processes associated with an improved catalytic activity, namely for oxygen reduction, when compared with the results attained for an abiotic microbial fuel cell cathode [13].

Brian J. Eddie et.al, studied the *Marinobacter atlanticus* electrode biofilms which differentially regulate gene expression depending on electrode potential and lifestyle. Like other *Marinobacter* spp., *M. atlanticus* generates small amounts of electrical current when grown as a biofilm on an electrode, which is enhanced by the addition of redox mediators [14].

The study reported by Aakash Singh et al. (2021) provided insights into the dynamics of the MFCs substrate utilization. This study reported the effects of ionic conductivity on electrical energy production. Power generation at the low conductivities of less than 7.7 mS/cm was restricted by the competition between fermentative bacteria (e.g., *Lactobacillus*) and exoelectrogens (e.g., *Pseudomonas* and *Shewanella*) for substrate utilization [15].

Anh Tuan Hoang et al. (2021) detailed the treatment of pharmaceutical wastewater along with energy production using bioaugmentation of halophilic consortium in air cathode microbial fuel cell (ACMFC) under saline condition (4%). *Ochrobactrum*, *Marinobacter*, *Bacillus* and *Rhodococcus* were the dominant halophilic electrogenic strain in ACMFC at different organic load [16].

The electrical performance and wastewater treatment efficiency were evaluated for Microbial Fuel Cells treating unsterile palm oil mill effluent with chemical oxygen demand, reported by Tabbi Wilberforce et al. (2021). Pure electrogenic (*Shewanella* sp.) inoculation led to a diversification process, resulting in a lower current generation. MFC inoculation tends to a microbial equilibrium wherein generation of high current density was achieved by gradual microbial enrichment rather than external electrogenic invasion [2].

Obinna Markraphael Ajunwa et al. (2021) studied the influence of enhanced electrogenicity on anodic biofilm and bioelectricity production by a novel microbial consortium. Biofilms of test electrogens were grown on anodes of microbial fuel cells fed with glucose-based media. In this study, electrogens used were anodophilic *Enterobacter aerogenes* 102, flavinogenic *Bacillus* sp. 101, *Pichia kudriavzevii* 103 and four pyocyanogenic *Pseudomonads*. Bioelectricity production using metabolically-enhanced electrogens was carried out in a modified MFC and optimum yields were achieved using a consortium of all electrogens exposed to metabolic enhancements [17].

The outcome of the study conducted by Lukasz Szydlowski et al. (2021) indicated that the application of electrogenic bacteria can be expanded by genome engineering. Electrogenic bacteria metabolize organic substrates by transferring electrons to the external electrode, with subsequent electricity

generation [18]. The study presented a novel strain of a known, electrogenic *Arcobacter butzleri* that can grow primarily on acetate and lactate and its electric current density is positively correlated to the COD concentrations up to 200 ppm.

Electrogenic bacteria are organisms that can transfer electrons to extracellular electron acceptors and have the potential to be used in devices such as bioelectrochemical systems [19]. In the study by Natalia J. Sacco et.al, *Dietzia* sp. RNV-4 bacterium has been isolated and identified based on its biochemical, physiological and morphological characteristics, as well as by its 16S rRNA sequence analysis. The current density production and electron transfer mechanisms were investigated using bioelectrochemical methods. This study identified Canthaxanthin as the main compound involved in charge transfer between the bacteria and the solid electrodes. This is the first time that *Dietzia* sp. RNV-4 has been electrochemically characterized and identified as a new electrogenic strain [19].

Mehdi Tahernia et.al,(2020)characterized microbial extracellular electron-transfer capabilities and capacities of five gut bacteria: *Staphylococcus aureus*, *Enterococcus faecalis*, *Streptococcus agalactiae*, *Lactobacillus reuteri*, and *Lactobacillus rhamnosus*[20].

Cheng L et.al.(2021) reported that a group of uncultured *Desulfobulbaceae* were greatly enriched on electrode surfaces. These *Desulfobulbaceae* appeared to form filaments with morphological features ascribed to cable bacteria, but the majority were taxonomically distinct from recognized cable bacteria genera [21]. This study provides new information about a group of *Desulfobulbaceae* that can exhibit filamentous morphologies and respire on the oxidative electrodes.

Conclusion

In future, the advancement of MFC technology for sustainable electricity production using electrogenic bacterial species would benefit the entire human race with cleaner energy and the environment.

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Conflict of Interest

The author declares that no conflict of interest with regard to this study.

References

- ❖ Sidra Mohyudina, et al.(2022). Microbial fuel cells a state-of-the-art technology for wastewater treatment and bioelectricity generation. *Environmental Research*, Vol. 204, Part D,112387.<https://doi.org/10.1016/j.envres.2021.112387>
- ❖ Tabbi Wilberforce, et al.(2021). Role of carbon-based nanomaterials in improving the performance of microbial fuel cells.*Energy*,122478.<https://doi.org/10.1016/j.energy.2021.122478>
- ❖ Anh TuanHoang, et al.(2022). Microbial fuel cells for bioelectricity production from waste as sustainable prospect of future energy sector.*Chemosphere*,Vol. 287, Part 3,132285. <https://doi.org/10.1016/j.chemosphere.2021.132285>
- ❖ Aakansha Singh,SumitDahiyam& Brijesh KumarMishra,(2021). Microbial fuel cell coupled hybrid systems for the treatment of dye wastewater: A review on synergistic mechanism and performance. *Journal of Environmental Chemical Engineering*,Vol. 9, Issue 6, 106765. <https://doi.org/10.1016/j.jece.2021.106765>
- ❖ Titon Chandra Saha, et al.(2019). Microbial Fuel Cell (MFC) Application for Generation of Electricity from Dumping Rubbish and Identification of Potential Electrogenic Bacteria. *Advances in Industrial Biotechnology*. <http://dx.doi.org/10.24966/AIB-5665/100010>
- ❖ Potter M (1910) On the difference of potential due to the vital activity of microorganisms. *Proc Univ Durham Phil Soc*.
- ❖ Potter MC (1911) Electrical effects accompanying the decomposition of organic compounds. *J Proc R Soc Lond B* 84: 260-276.
- ❖ Sumin KIM, et al.(2021). Guar gum hydrogel microbial fuel cell using *b.megaterium*. *European journal of materials science and engineering*, Vol. 6, Issue 2, 089-098.http://ejmse.ro/articles/06_01_04_EJMSE-21-125.pdf
- ❖ Weining Sun, et al.(2021). Promoting Extracellular Electron Transfer of *Shewanella oneidensis* MR-1 by Optimizing the Periplasmic Cytochrome c Network. *Frontiers in microbiology*. <https://doi.org/10.3389/fmicb.2021.727709>
- ❖ Weining Sun, et al.(2021). Promoting Extracellular Electron Transfer of *Shewanella oneidensis* MR-1 by Optimizing the Periplasmic Cytochrome c Network. *Frontiers in microbiology*. <https://doi.org/10.3389/fmicb.2021.727709>
- ❖ Samuel E. H. Piper, et al.(2021). Bespoke Biomolecular Wires for Transmembrane Electron Transfer: Spontaneous Assembly of a Functionalized Multiheme Electron Conduit. *Microbiol*,Volume 12. <https://doi.org/10.3389/fmicb.2021.714508>
- ❖ Sudarsu V. Ramanaiah, et al.(2021). In Situ Electrochemical Characterization of a Microbial Fuel Cell Biocathode Running on Wastewater. *Catalysts*, 11(7), 839. <https://doi.org/10.3390/catal11070839>

- ❖ Brian J.Eddie, et al.(2021). *Marinobacter atlanticus* electrode biofilms differentially regulate gene expression depending on electrode potential and lifestyle. *Biofilm*, Vol. 3,100051.<https://doi.org/10.1016/j.biofilm.2021.100051>
- ❖ Lukasz Szydlowski, et al.(2020). Metabolic engineering of a novel strain of electrogenic bacterium *Arcobacter butzleri* to create a platform for single analyte detection using a microbial fuel cell. *Enzyme and Microbial Technology*, Vol.139,109564.<https://doi.org/10.1016/j.enzmictec.2020.109564>
- ❖ Natalia J Sacco, M Celina Bonetto & Eduardo Cortón,(2017). Isolation and Characterization of a Novel Electrogenic Bacterium, *Dietzia* sp. RNV-4. *PLoSOne*,12(2):e0169955.<https://doi.org/10.1371/journal.pone.0169955>
- ❖ Mehdi Tahernia, et al.(2020). Characterization of Electrogenic Gut Bacteria. *Enzyme and Microbial Technology*, ACS Omega 2020, 5, 45, 29439–29446.<https://doi.org/10.1021/acsomega.0c04362>
- ❖ Cheng Li, Clare E Reimers , Yvan Alleau ,(2021). Using Oxidative Electrodes to Enrich Novel Members in the *Desulfobulbaceae* Family from Intertidal Sediments, *Microorganisms*, 9(11):2329. <https://doi.org/10.3390/microorganisms9112329>.

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Chapter: 7

Glucose Oxidase immobilized Platinum Doped SBA-15 nanoparticle for the application of glucose biosensor

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Abstract

Combining platinum nanoparticles (PtNP) doped SBA-15 (Pt@SBA-15) with glucose oxidase yielded a new electrochemical glucose biosensor (GOX). Due to the high surface area of these catalysts, the resultant Pt@SBA-15-GOX displayed remarkable stability and reactivity for catalyzing glucose electroreduction. With a linear range up to 16 mmol L⁻¹, this glucose biosensor was capable of determining glucose without interference. It also has some significant advantages, such as ease of preparation and stability. The proposed method for determining glucose in a human serum sample appears to be promising.

Keywords: Platinum modified; glucose oxidase; cyclic voltammetry, immobilization; biosensor.

Introduction

In recent years, over 5% of the world's population has developed diabetes as a result of glucose metabolism abnormalities, making it critical to monitor blood glucose levels for diabetes treatment and control [1]. As a result, over the last decade, researchers have focused increasingly on developing glucose monitoring systems to aid in the management of diabetes [2]. Fiber optic, electrochemical, chemiluminescence, and fluorescence glucose biosensors [7-13] are just a few of the biosensors that have been reported for glucose analysis [3-6]. Electrochemical glucose biosensors, for instance, play a

key part in the monitoring process [14] due to their ease of use, high sensitivity, and great selectivity.

The use of nanomaterials and bioactive materials in the design of electrochemical glucose biosensors has gotten a lot of attention in recent years because of their unique physical and chemical properties, which offer great potential for developing new sensing systems and amplifying recognition event transduction. Due to their unique electrocatalysis and conductive capabilities led by their specific surface area, platinum nanoparticles (PtNP) play a crucial role in the production of electrochemical biosensors [15]. It also drew a lot of attention because of its prospective application in enzyme immobilization, which improved enzyme stability.

SBA-15 [16-19], which possesses enormous surface areas and homogeneous, controllable pore sizes ranging from 2 to 50 nm, has recently piqued interest in the production of biosensors. Enzyme and other nanoparticles can be encapsulated into SBA-15 by adsorption or capillary filling. Furthermore, by modifying the organic components throughout the SBA-15 synthesis process, the surface characteristics and composition of SBA-15 can be easily customized.

The enzyme chosen for this study was glucose oxidase (GOX), which catalyzes the electron transfer from glucose to oxygen that occurs during the generation of gluconolactone and hydrogen peroxide. For the immobilization of GOX, SBA-15 was used as effective support for PtNP to produce a Pt@SBA-15 composite. Pt@SBA-15-GOX, the resultant nanoparticle, was deposited onto the electrode surface to create a glucose biosensor. Using thionine as an electron mediator, the manufactured Pt@SBA-15-GOX biosensor provided an outstanding electrical signal for glucose with high sensitivity and quick reaction, and the results demonstrated that the glucose biosensor had high sensitivity, stability, and selectivity. When compared to GOX-free glucose biosensors, the high density of PtNP and GOX immobilized onto SBA-15 provides a larger amino-group to greatly improve sensitivity, as well as operational stability, ease of separation from the product, more convenient handling, greater resistance to environmental changes, and reusability [20-21]. Furthermore, the glucose biosensor had the potential to be used in clinical analysis as well as in a wide range of commercial applications.

Experiments

Apparatus and reagents

Glucose oxidase (GOX), $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (P123), Poly (vinylpyrrolidone) (PVP) provided the glucose (99 percent),

H₂PtCl₆•6H₂O, Tetraethylorthosilicate (TEOS), and thionine was obtained from Spectrum Chemicals, India. 0.1 mol L⁻¹ Na₂HPO₄ and 0.1 mol L⁻¹ KH₂PO₄ stock solutions were used to make phosphate-buffered solutions (PBS). All other compounds were analytical reagent grade and were not purified further. For all electrochemistry measurements, PBS (0.1 mol L⁻¹, pH 6.4) buffer solution was utilized as an electrolyte. Throughout the studies, (double distilled) DD water was used.

All the electrochemical measurements were performed on a CHI608D electrochemical workstation (CH Instruments, USA). A conventional three-electrode system was used for all electrochemical measurements: a glassy carbon electrode (GCE, 3 mm) as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire electrode as the counter electrode. All electrochemical experiments were carried out in the PBS solution containing 5 mmol L⁻¹ thionine in the presence of different glucose concentrations by cyclic voltammetry between -0.4 V and +0.7 V at a scan rate of 10 V s⁻¹. SBA-15 and Pt@SBA-15 were characterized by a JOEL model 3010 transmission electron microscope.

Synthesis of Platinum nanoparticle doped SBA-15

PtNP was synthesized using methods described in the literature [22-23]. PVP (133 mg) was dissolved in a 20 mL aqueous solution of 6.0 mmol L⁻¹ H₂PtCl₆•6H₂O and 180 mL ethanol combination. The mixture was heated to 433 K for 3 hours as N₂ bubbled around it. The solvent was ejected, and the residue was re-distributed in water. SBA-15 was made following a process described in the literature [24].

Pluronic P123 6 g was dissolved in 45 g water and 180 g 2 mol L⁻¹ HCl solution at 308 K for 30 minutes with stirring. TEOS (12.75 g) was added to the solution and stirred for 20 hours at 308 K. For 24 hours, the mixture was heated to 373 K. Filtration was used to recover the white powder, which was completely cleaned with water and ethanol before being dried in the air. SBA-15 was created by calcinating the substance at 823 K for 12 hours.

PtNP colloidal aqueous solution (25.6 mL, 3×10⁻³ mol L⁻¹) was combined with 74.4 mL water and 100 mL ethanol in a mixture of 74.4 mL water and 100 mL ethanol. A commercial ultrasonic cleaner was used to sonicate the slurry for 3 hours at room temperature after promptly adding the mixture to 1.5 g of SBA-15. Centrifugation was used to separate the brown precipitates, which were then extensively washed with water and ethanol before being dried in a 373 K oven.

By calcining the precipitates at 723 K for 12 hours with O₂ flow, Pt@SBA-15 was produced [25].

Immobilization of glucose oxidase onto Platinum nanoparticle doped SBA-15

2 mg of Pt@SBA-15 was dispersed in 1 mL of 2.5 percent (v/v) glutaraldehyde solution for 1 hr then centrifuged and washed three times. Pt@SBA-15 treated with glutaraldehyde was then added to 1 mL of GOX solution (10 mg mL⁻¹) and incubated overnight at 277 K. After centrifuging and washing, the Pt@SBA-15-GOX was obtained. In 1 mL H₂O, 2 mg of Pt@SBA-15-GOX was disseminated and sonicated for 30 seconds. Ultimately, the resulting modified Pt@SBA-15-GOX was constructed.

Fabrication of GCE modified Pt@SBA-15-GOX glucose biosensor

A GCE was polished with 1, 0.25, and 0.05 µm alumina powders in order, then fully sonicated with ethanol for 3 minutes. 6 µL of the Pt@SBA-15-GOX mixture was put onto the electrode surface after it had been cleaned with double distilled water and dried at 277 K. To eliminate unbound particles, the electrode was washed with PBS. Before electrochemical testing, the modified electrode was kept in PBS at 277 K.

Results and discussion

Characterization of the material

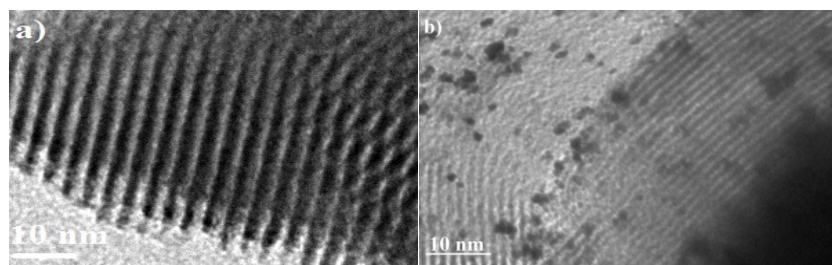


Fig. 2HR-TEM image of SBA-15(a) and Pt@SBA-15 (b)

HR- TEM image of SBA-15 is shown in Fig. 1(a), demonstrating that the channel diameter was around 10-15 nm. The as-prepared product had a startlingly consistent shape, according to the results. HR-TEM image of the commonly produced Pt@SBA-15 is shown in Fig. 1(b). A considerable portion of the active PtNP could be found on the SBA-15 outer surface as well as inside the channels, and the maximal PtNP size incorporated in the mesopores was limited by the SBA-15 channel diameter, making PtNP with a large surface area for glucose detection extremely effective.

Electrochemical characterization of modified electrodes

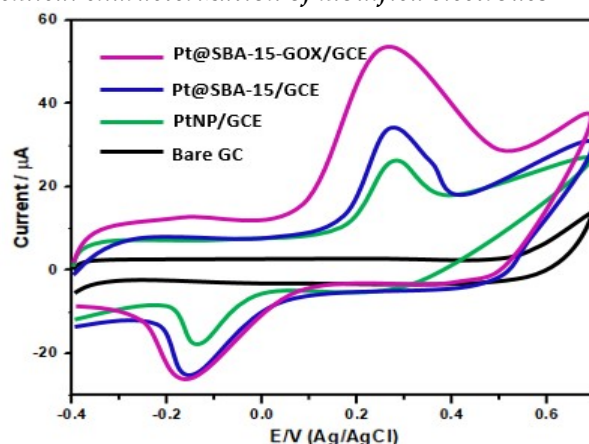


Fig. 2 Cyclic voltammograms obtained at Pt@SBA-15-GOX/GCE, Pt@SBA-15/GCE and PtNP/GCE in 0.1 mol L⁻¹ PBS solution containing 5 mmol L⁻¹ thionine. Scan rate: 10 V s⁻¹

Figure 2 depicts cyclic voltammograms of GCEs coated with various materials in PBS containing 5 mmol L⁻¹ thionine at a scan rate of 10 V s⁻¹ in PBS containing 5 mmol L⁻¹ thionine. At PtNP/GCE, a well-defined redox peak was seen, which was attributed to thionine activity. The cathodic current at the redox potential of thionine increased significantly after the electrode was modified by Pt@SBA-15, indicating that Pt@SBA-15 was successfully loaded on the GCE owing to its large amount of grafted amino groups, large surface area, and distinctive nanostructures. The backdrop current of Pt@SBA-15-GOX/GCE is greater than that of Pt@SBA-15/GCE, which can be attributed to the Pt@SBA-15-GOX film's extensive surface area. However, after the Pt@SBA-15-GOX alteration, the peaks current rose, showing that GOX was successfully loaded on Pt@SBA-15.

The cyclic voltammogram response of the Pt@SBA-15-GOX/GCE in the absence of substrate and the presence of varied additions of glucose ranging from 10 to 50 mmol L⁻¹ is shown in Fig. 3. This figure shows that when glucose was introduced to the substrate solution, the cathodic and anodic currents increased significantly, demonstrating that this glucose biosensor had outstanding electrocatalytic activity towards glucose. It should be mentioned that for the amperometric studies, a working potential of 0.25 V was used since a low potential would help to reduce background current and diminish the reactions of common interference species.

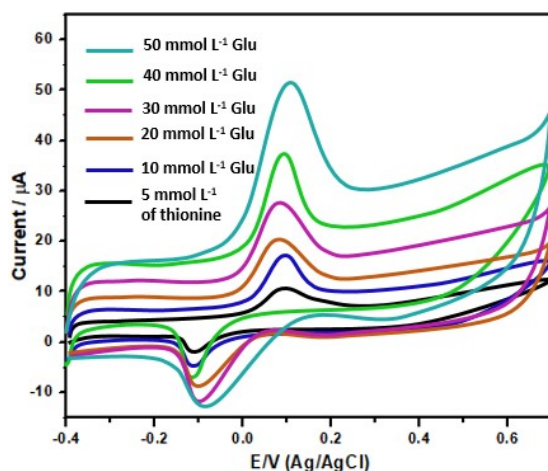


Fig. 3 Cyclic voltammograms of Pt@SBA-15-GOX/GCE in 0.1 mol L⁻¹ PBS solution containing 5 mmol L⁻¹ thionine before and after the various addition of glucose from 10 to 50 mmol L⁻¹ at the scan rate of 10 V s⁻¹.

Optimization of experimental conditions

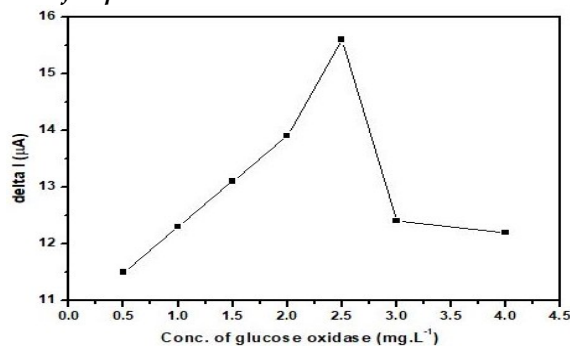


Fig. 4 Cyclic voltammetric peak currents of Pt@SBA-15-GOX/GCE to GOX concentration at -0.25 V in 0.1 mol L⁻¹ PBS solution containing 5 mmol L⁻¹ thionine in the presence of 5 mmol L⁻¹ glucose at the potential of -0.25 V.

The effect of GOX concentration on the glucose biosensor response was examined and displayed in Fig. 4. The current response of the electrode was first increased to the maximum at 2.5 mg mL⁻¹ and subsequently dropped as the GOX concentration was increased from 0.5 to 2.5 mg mL⁻¹. This result indicates that when the concentration of GOX grew, the sensitivity of the glucose biosensor improved, assisting in the improvement of electrocatalytic performance.

However, increasing the quantity of GOX could degrade the conductivity of the modification coating, obstructing electron transport. In the next study, a GOX concentration of 2.5 mg mL^{-1} was employed.

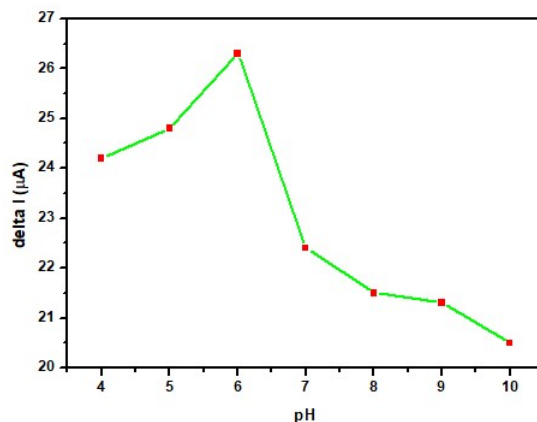


Fig. 5 Cyclic voltammetric peak currents of Pt@SBA-15-GOX/GCE to pH at -0.25 V in 0.1 mol L^{-1} PBS solution containing 5 mmol L^{-1} thionine in the present of 10 mmol L^{-1} glucose at potential of -0.25 V .

To generate an appropriate electrochemical signal, the pH value of the substrate solution was studied. With pH values ranging from 4 to 10, the curve of current response was obtained, as shown in Fig. 5, with the largest current response occurring at pH of 6. Higher and lower pH levels were found to impair protein activity and shorten the lifespan of the glucose biosensor. As a result, the pH of 6 was chosen as the best for further research.

Performance of the glucose biosensor

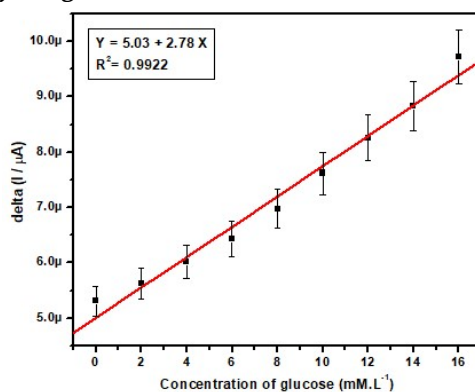


Fig. 6 Calibration curve of the glucose biosensor for different concentrations of glucose.

The manufactured glucose biosensor's cyclic voltammograms current response toward varied concentrations of glucose has been studied systematically in PBS solution containing thionine at the ideal condition. As can be seen in Fig. 6, an increase in current has been noticed as glucose concentration has increased. The current value stabilized after an average of 25 seconds in each case for varying glucose concentrations, showing a quick reaction of the manufactured biosensor to glucose. The detection limit was determined to be $0.001 \text{ mmol L}^{-1}$ based on $S/N = 3$ and the biosensor had a wide linear range of 0 to 16.0 mmol L^{-1} glucose (Fig. 7). The calibration curve's equation was $Y = 5.03 + 2.78 X$, $R^2 = 0.9922$. The sensitivity of the constructed biosensor was $0.8965 \mu\text{A}/\text{mM}$. The biosensor's sensitivity can be due to its wide surface area and excellent GOX contact with both PtNP and SBA-15, which allows for quick electron transfer with a low barrier between the enzyme and the electrode. Because of the high number of grafted amino groups, broad surface area, and distinctive nanostructures, considerable amounts of GOX are expected to be immobilized in the nanocomposites. These good qualities were also important in boosting the performance of the glucose biosensor that resulted. The huge linear range suggested that a considerable amount of PtNP and GOX had been immobilized onto the electrode; second, the direct immobilization of GOX onto Pt@SBA-15 aided in the detection of the enzyme reaction's product.

Reproducibility, selectivity and stability

Seven electrodes were created for the detection of 10 mmol L^{-1} glucose to test the glucose biosensor's repeatability. The relative standard deviation (RSD) of the data for the seven electrodes was 5.8 percent, indicating that the suggested glucose biosensor's precision and reproducibility were quite good. These findings suggested that immobilising GOX in the Pt@SBA-15-GOX composite film was an efficient and repeatable technique.

Figure 7 shows the specificity of the built glucose biosensor by comparing cyclic voltammetric peak currents after 10 mmol mL^{-1} glucose with every 10 mmol mL^{-1} of dopamine (DA), ascorbic acid, fructose, uric acid, lactose and sucrose added respectively. When compared to glucose alone, the current fluctuation owing to the presence of interfering chemicals was less than 7.5 percent, indicating that the glucose biosensor's selectivity was satisfactory.

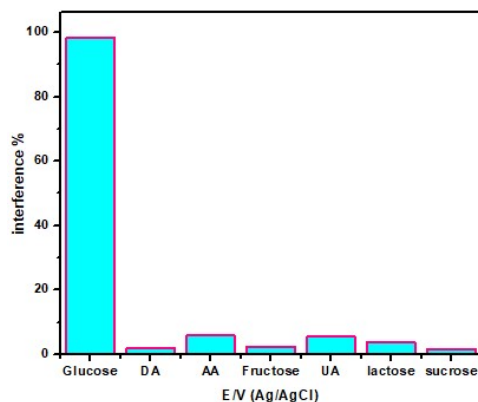


Fig. 7 Cyclic voltammetric peak currents of the glucose biosensor to 10 mmol mL⁻¹ glucose with each 10 mmol mL⁻¹ of dopamine (DA), ascorbic acid, fructose, uric acid, lactose and sucrose at potential of 0.25 V.

The glucose biosensor's stability was further tested by measuring its current response regularly. When the glucose biosensor wasn't in use, it was kept at 277 K in the air. The glucose biosensor's current response for detecting 1.0 mmol L⁻¹ glucose in substrate solution was 6.486 μ A, and it kept roughly 94% and 80% of its initial value after 2 weeks and 1 month, respectively, indicating that the glucose biosensor was highly stable. As a result, the repeatability, selectivity, and stability of this as-prepared biosensor showed that it may be used to determine human blood glucose concentrations.

Conclusions

Immobilizing GOX on a Pt@SBA-15 nanocomposite resulted in the creation of a glucose biosensor. Pt@SBA-15-GOX/GCE has exceptional electrochemical characteristics, which can be attributed to SBA-15's high biocompatibility and PtNP's high catalytic activity. The constructed Pt@SBA-15-GOX glucose biosensor has a high electrocatalytic activity for glucose reduction, which might be attributed to the nanocomposite's wide surface area and unique and stable nanostructures. Furthermore, the fabricated Pt@SBA-15-GOX glucose biosensor had good sensitivity and reproducibility for measuring glucose, as well as a wide linear range, high selectivity, and long-term stability, suggesting that it could be a promising approach for determining glucose in real serum samples in clinical applications that is comparable to or better than the current practical method.

Reference

- [1] R. Fu, Y. Lu, Y. Ding, L. Li, Z. Ren, X. Si, Q. Wu, A novel non-enzymatic glucose electrochemical sensor based on CNF@Ni-Co layered double hydroxide modified glassy carbon electrode, *Microchem. J.* 150 (2019) 104106/1-104106/6.
- [2] J.D. Newman, A.P.F. Turner, Home blood glucose biosensor: a commercial perspective, *Biosens. Bioelectron.* 20 (2005) 2435-2453.
- [3] L. Meng, J. Jin, G. X. Yang, T. H. Lu, H. Zhang, C. X. Cai, Nonenzymatic Electrochemical Detection of Glucose Based on Palladium-Single-Walled Carbon Nanotube Hybrid Nanostructures, *Anal. Chem.* 81 (2009) 7271-7280.
- [4] H. Muguruma, A. Hiratsuka, I. Karube, Thin-Film Glucose Biosensor Based on Plasma-Polymerized Film: Simple Design for Mass Production, *Anal. Chem.* 72 (2000) 2671-2675.
- [5] T. W. Tsai, G. Heckert, L. F. Neves, Y. Q. Tan, D. Y. Kao, R. G. Harrison, D. E. Resasco, D.W. Schmidtke, Adsorption of Glucose Oxidase onto Single-Walled Carbon Nanotubes and Its Application in Layer-By-Layer Biosensors, *Anal. Chem.* 81 (2009) 7917-7925.
- [6] H. Muguruma, A. Hiratsuka, I. Karube, Thin-Film Glucose Biosensor Based on Plasma-Polymerized Film: Simple Design for Mass Production, *Anal. Chem.* 72 (2000) 2671-2675.
- [7] M. M. Ward Muscatello, L. E. Stunja, S. A. Asher, Polymerized Crystalline Colloidal Array Sensing of High Glucose Concentrations, *Anal. Chem.* 81 (2009) 4978-4986.
- A. Diouf, N.E. Bari, B. Bouchikhi, A nonenzymatic electrochemical glucose sensor based on molecularly imprinted polymer and its application in measuring saliva glucose, *Mater. Sci. Eng. C*, 98 (2019) 1196-1209.
- [8] A.K. Minkstiene, L. Glumbokaite, A. Ramanaviciene, A. Ramanavicius, Reagentless amperometric glucose biosensor based on nanobiocomposite consisting of poly(1,10-phenanthroline-5,6-dione), poly(pyrrole-2-carboxylic acid) gold nanoparticles and glucose oxidase, *Microchem. J.* 154 (2020) 104665/1 - 104665/7.
- [9] B.C. Kang, B.S. Park, T.J. Ha, Highly sensitive wearable glucose sensor system based on functionalized single-wall carbon nanotubes with glucose oxidase- nafion composites, *Applied Surf. Sci.* 470 (2019) 13-18.
- [10] P.N. Asrami, S.A. Mozaffari, M.S. Tehrani, P.A. Azar, A novel impedimetric glucose biosensor based on immobilized glucose oxidase on a CuO-chitosan nanobiocomposite modified FTO electrode, *Int. J. Biol. Macromol.* 118 (2018) 649-660.
- [11] L. Jiansin, B. Xiang, S. Tamulevicius, D. Erts, C.F. Chang, G. Yesong, Fabrication of a biocompatible and continuous glucose biosensor with the poly(3,4-ethylenedioxythiophene) modified electrode, *J. Taiwan Inst. Chem. Eng.* 104 (2019) 1-7.
- [12] C. Wei, X. Zou, Q. Liu, S. Li, C. Kang, W. Xiang, A highly sensitive non-enzymatic glucose sensor based on CuS nanosheets modified Cu₂O/CuO nanowire arrays, *Electrochim. Acta*, 334 (2020) 135630/1-135630/10.
- [13] K.E. Tohill, R.G. Compton, Electrochemical non-enzymatic glucose sensor: a perspective and an evaluation, *Int. J. Electrochem. Sci.* 5 (2010) 1246-1301.
- [14] C. Nana, Y. Zhanga, G. Zhanga, C. Donga, S. Shuanga, M.M.F. Choi, Activation of nylon net and its application to a biosensor for determination of glucose in human serum, *Enzyme Microb. Technol.* 44 (2009) 249-253.
- [15] Q. Hu, J. J. Li, Z. P. Hao, L. D. Li, S. Z. Qiao, Dynamic adsorption of volatile organic compounds on organofunctionalized SBA-15 materials, *Chem. Eng. J.* 149 (2009) 281-288.

- [16] Y. J. Li, G. W. Zhou, C. J. Li, D. W. Qin, W. T. Qiao, B. Chu, Adsorption and catalytic activity of Porcine pancreatic lipase on rod-like SBA-15 mesoporous material, *Colloids Surf., A* 341 (2009) 79-85.
- [17] M. Moritz, M. Łaniecki, SBA-15 mesoporous material modified with APTES as the carrier for 2-(3-benzoylphenyl) propionic acid, *Appl. Surf. Sci.* 258 (2009) 7523-7529.
- [18] A.Z. Abdullah, N.S. Sulaiman, A.H. Kamaruddin, Biocatalytic esterification of citronellol with lauric acid by immobilized lipase on aminopropyl-grafted mesoporous SBA-15, *Biochem. Eng. J.* 441 (2009) 263-270.
- [19] E. Drockenmuller, I. Colinet, D. Damiron, F. Gal, H. Perez, G. Carrot, Efficient Approaches for the Surface Modification of Platinum Nanoparticles via Click Chemistry, *Macromolecules* 43 (2010) 9371-9375.
- [20] S. Mandal, D. Roy, R.V. Chaudhari, M. Sastry, Pt and Pd Nanoparticles Immobilized on Amine-Functionalized Zeolite: Excellent Catalysts for Hydrogenation and Heck Reactions, *Chem. Mater.* 16 (2004) 3714-3724.
- [21] Y. Wang, J. Ren, K. Deng, L. Gui, Y. Tang, Preparation of Tractable Platinum, Rhodium, and Ruthenium Nanoclusters with Small Particle Size in Organic Media, *Chem. Mater.* 12 (2000) 1622-1627.
- [22] T. Teranish, M. Hosoe, T. Tanaka, M. Miyake, Size Control of Monodispersed Pt Nanoparticles and Their 2D Organization by Electrophoretic Deposition, *J. Phys. Chem. B* 103 (1999) 3818-3827.
- [23] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G. D. Stucky, Nonionic Triblock and Star Diblock Copolymer and Oligomeric Surfactant Syntheses of Highly Ordered, Hydrothermally Stable, Mesoporous Silica Structures, *J. Am. Chem. Soc.* 120 (1998) 6024-6036.
- [24] R. M. Rioux, H. Song, J. D. Hoefelmeyer, P. Yang, G. A. Somorjai Rioux, R. M. Song, H. Hoefelmeyer, J. D. Yang, P. D. Somorjai, High-Surface-Area Catalyst Design: Synthesis, Characterization, and Reaction Studies of Platinum Nanoparticles in Mesoporous SBA-15 Silica, *J. Phys. Chem. B* 109 (2005) 2192-2202.

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Chapter: 8

Synthesis of Nanomaterials: An Overview of Preparation Methods

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Abstract

In recent years, nanomaterials have become increasingly popular because, in the realm of material science, unanticipated variations in surface characteristics are caused by particle size. Particle diameter reduction to the nanoscale results in novel and improved characteristics such as particle diameter and form. In recent years, there has been a dramatic increase in the usage of nanomaterials in a range of areas, including energy, medical, and nutrition. Nanoparticles have an important function in pharmacological and medical sciences. For the synthesis of nanostructured materials, several strategies are employed, which are split into two categories based on the starting material of nanoparticle preparation: bottom-up methods and top-down methods. The application metal nanomaterials are increasingly being used in biomedicine and other fields throughout the world. Because of their striking features, metal nanoparticles, nanostructures, and nanomaterial production are now attracting the attention of researchers. The current study focuses on several techniques of nanomaterials production and their benefits, drawbacks, and applications. The synthesis of nanomaterials via bottom-up and top-down methods will be the emphasis of this chapter.

1. Introduction

Nanomaterials have been developed into a fascinating class of materials [1] that includes a diverse range of samples with at least one dimension ranging from 1 to 100 nm. [2]. The sensible design of nanoparticles can result in extremely large surface areas [3]. It is feasible to construct nanostructures with remarkable magnetic, mechanical, optical, electrical, and catalytic properties that differ

significantly from their bulk counterparts [4-6]. Nanomaterials' properties are fine-tuned by precisely controlling their shape, size, synthesis parameters, and appropriate functionalization [7]. This chapter provides a brief history of nanomaterials and their usage in triggering developments in nanotechnology development throughout history [8]. Depending on the kind and nature of the nanomaterials, multiple processes are used to create them [9]. The two most popular methods of fabrication are "top-down" and "bottom-up" [10]. Bulk materials are converted to nanoparticles in the top-down strategy, whereas nanomaterials are produced from the ground up in the bottom-up method [11]. Some of the processes used to manufacture nanomaterials include vapour deposition, micropatterning method, sputtering method, mechanical milling, laser ablation method, nanolithography method, sol-gel method, electro-spinning method, pyrolysis method, and electrochemical method [12-16]. Nanoparticles' physicochemical qualities are critical for their behaviour, bio-distribution, safety, and effectiveness. As a result, characterization of nanomaterials is essential for determining the functional features of the particles generated [17]. UV-vis spectroscopy, FTIR spectroscopy, X-ray diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), dynamic light scattering (DLS), and atomic force microscopy (AFM) are all used in the identification process. [18-21]. Several peer-reviewed publications and review sites have detailed the concepts and applications of several types of analysis methodologies for nanomaterial structural characterization. Nonetheless, the principles of the most essential methodologies for identifying synthesised nanomaterials are explained for clarity in the broad subject of nanotechnology [22,23].

2. Nanomaterial classification- nanoparticles are broadly classed as carbon-based nanoparticles, inorganic nanoparticles, and organic nanoparticles [24,25].

2.1. Carbon nanomaterials- Carbon-based nanomaterials are those that are entirely composed of carbon [26]. As shown in Figure 1, these materials include carbon nanotubes, carbon nanofibers, fullerenes, activated carbon, and carbon nanodots at nanoscale[27,28].

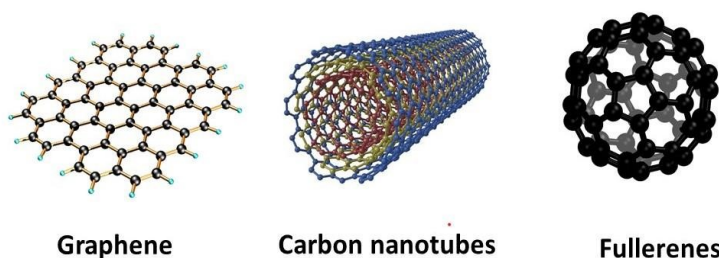


Figure1- Carbon nanoparticles – 1.Graphene 2. Carbon nanotube 3. Fullerenes

2.2. Organic nanomaterials- Organic nanomaterials or polymeric materials are often aptamers, dendrimers, micelles, ferritin, and liposomes are some of the terms used to describe these materials[29,30]. These nanomaterials are non-toxic and disposable. Some certain particles, such as nanocapsules (hollow core), liposomes, micelles, and dendrimers, are heat and chemically sensitive[31].

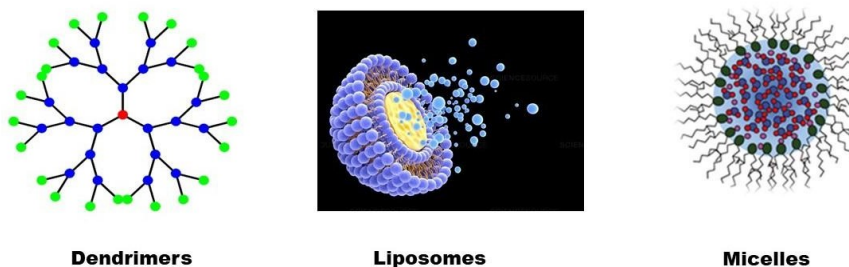


Figure 2- Organic nanoparticles- 1. Dendrimers 2. Liposomes 3. Micelles

2.3. Inorganic nanomaterials- Inorganic nanomaterials include metal and metal oxide nanomaterials. Silver, gold, zinc, iron, copper and cobalt are the most widely employed metals for the synthesis of nanomaterials. The most frequently synthesised oxides are zinc oxide (ZnO), cerium oxide (CeO₂), magnetite (Fe₃O₃), titanium oxide (TiO₂), [32-35].

3. Synthesis of nanomaterials- Nanoparticles are created via a variety of processes, which are classified as bottom-up or top-down. Figure:3 illustrates a simplified illustration of the procedure [36].

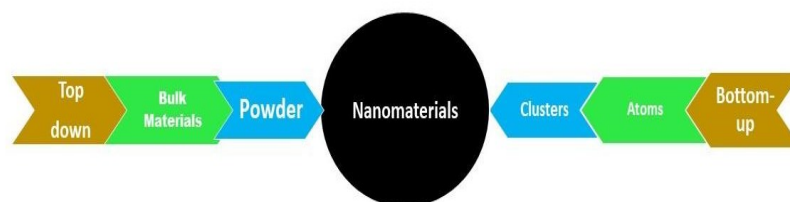


Figure 3- Demonstration of top-down and bottom-up synthesis processes

The top-down or disruptive approach of reducing a bulk substance to nanometrically sized particles [37]. The mechanical milling method, the laser ablation method, the sputtering method, the micropatterning method, the nanolithography method, and the method are some of the most typical nanomaterial manufacturing procedures. Bottom-up or constructive methods of material formation range from atoms to clusters to nanomaterials [38]. Chemical vapour deposition, sol-gel method, electro-spinning method, pyrolysis method and electrochemical are examples of bottom-up processes for creating nanoparticles (Figure:4).

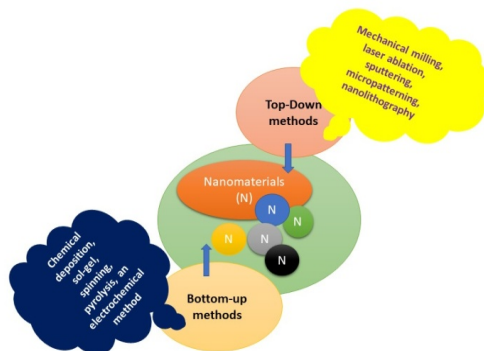


Figure 4-Top-down and bottom-up methods are separated into two categories

3.1. Top-down Synthetic methods

3.1.1 Mechanical milling- A significant powder charge (usually an elemental blend) is placed in a high energy mill, which is coupled to a

suitable milling medium in mechanical milling (MM). Milling is a technique used to reduce particle size and combine particles. Ball milling may be used in a variety of ways at a new level. Balls assaulted with a powder charge may roll down the table's surface during the manufacturing of nanomaterials. They can either fall freely or be confined in a chamber with parallel layers. They have an effect on the powder and balls underneath them. To scale manufacturing for big quantities, mechanical millings and nano-sized grain are used. The dynamics of mechanical milling or alloying are energy-dependent. Energy is transmitted from the balls to the powder during milling [39].

3.1.2 Laser ablation method-In the manufacturing of nanoparticles, laser ablation is utilised. The temperature of the irradiation zone quickly accelerates when laser light is targeted on the surface of the substrate target material in the surrounding atmosphere (gas or liquid), vaporising the target material. Electron state excitation, light emission, and electron and ion generation come from collisions between condensing species and adjacent molecules, culminating in a laser-induced plasma plume [40]. The target substance, ambient medium (liquid or gas), absolute pressure, and laser parameters all influence plasma structures (plume size and emission spectrum). Typical electron surface morphology of nanoparticles created by laser ablation of diverse materials. Laser ablation in a low-pressure background gas is often favourable for creating a large plume and performs well enough for manufacturing small particles. Nanomaterials such as c - dots, nanotubes, nanorods, and core-shell nanoparticles are created via laser ablation. By nucleating and growing laser-vaporized species in a background gas, this method creates nanoparticles. [41]

3.1.3 Sputtering method-Sputter deposition is a popular method for depositing thin films on surfaces. The approach is based on ion bombardment of a target material, which is source material. Ion bombardment produces vapour as a result of a purely physical process, namely the sputtering of the target material. This approach falls under the category of physical vapour deposition techniques, which also includes thermal evaporation and pulsed laser deposition[42]. The most popular method for developing thin films

by sputter deposition is to employ a magnetron source, which bombards the target with positive ions contained in the plasma of a magnetically accelerated glow discharge[43]. The platinum nanoparticles have been synthesized by sputter deposition on polymer and ionic liquid substrates [44].

3.1.4 Micropatterning method - Micropatterning is a popular technique in biomedical engineering research that is being used more and more[45]. This is a simple, low-temperature, non-vacuum synthetic process of developing metal nanoparticles on a variety of surfaces. Metal nanoparticle ink was produced utilizing the micropatterning method with thermocapillary flow generated by a focused laser. This approach is used to produce nanoparticles by using suitable starting materials that have been cut to the required size by a laser or electron beam[46].

3.1.5 Nanolithography method- Nanolithography is the technique of fabricating nanometric-scale objects having a minimum of one dimension between 1 and 100 nm in size. Examples of nanolithographic methods include optical, electron-beam, multiphoton, nanoimprint, and scanning probes, to name a few. Shape and texture are produced by a light-sensitive substance that preferentially removes a piece of material. The fundamental advantage of nanolithography is its ability to create any type of nanoparticle or cluster, despite of shape or size. Limitations include the need for specialised equipment and the big investment [47].

3.2. Bottom-up synthetic methods

3.2.1 Chemical deposition method- This method, also known as vacuum deposition, entails depositing the gaseous reactant as a thin layer on a substrate, which, when mixed with other gas molecules, causes the substrate to overheat. The substrate comes into contact with the mixed gases during the process, resulting in ion reduction. This reaction usually results in the formation of a coating, from which the nanoparticles must be scraped. The approach has become increasingly important in the electronics and semiconductor sectors because to its capacity to produce exceptionally pure, homogeneous, and nonporous nanoparticles. Despite these considerable benefits, there are some significant downsides to this method, including the

requirement for specialised equipment to make the films and reaction chambers, as well as the fact that the gaseous by-products of this reaction are extremely toxic [48].

3.2.2 Sol-gel method- Sol-gel processing techniques, in addition to the procedure described above, have been widely used. Colloidal particles are far larger in size than molecules or nanoparticles. When colloids are mixed with a liquid, they appear bulky, whereas nanomolecules are always thin. It requires the construction of a continuous liquid phase network using colloidal suspension production (sol) and gelatin (gel). Metal alkoxides and alkoxysilane ions are the precursors to the creation of these colloids. Tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) are the most commonly utilised silica gel-forming chemicals (TEOS). Organic substances are alkoxides [49]. They are indistinguishable in water. They are organometallic precursors of silica, aluminium, titanium, and zirconium, as well as many alcohols utilised as mutual solvents. A homogeneous solution is used to start the sol-gel process [50]. An organic precursor for silica, alumina, titania, and other minerals is a solution of one or more alkoxides of choice.

3.2.3 Electro-Spinning method- Spinning is a near-net-shape forming technology often used to produce axisymmetric, thin-walled-thickness, and hollow circular cross-section components. To achieve the desired outcome, one or more rollers are fed against a metal blank or tube that rotates in parallel with a machine's main spindle. Axisymmetric and hollow geometries can be generated by inducing continuous and localised plastic deformation on the blank[51]. Because of the nature of localised material deformation, this technique provides inherent benefits such as low forming loads, simplified tooling, excellent material usage, low manufacturing costs, and enhanced mechanical qualities, as well as an increased likelihood of obtaining lightweight components with manufacturing flexibility [52].

3.2.4 Pyrolysis method- Thermal degradation is another key approach for Nanoparticle's synthesis that is widely utilized alone or in conjunction with other physical processes [53]. This is the chemical decomposition method endothermic in nature, which employs the disruption of chemical bonds by heat. As a result of the breakdown of

the precursor, a chemical reaction occurs, producing Nanoparticles and ash as by-products, and these nanoparticles can be recovered by additional processing of solid ash. Pyrolysis is a common method for producing noble Nanoparticles [54]. One of the most significant disadvantages of this technology is its excessive energy usage.

3.2.5 Electrochemical method- Electrochemical techniques are widely used in the production of nanomaterials and nanostructured materials. They are typically employed for catalysis, but have recently been exploited as biosensors in biological applications [55]. In 1994, Reetz and Helbig pioneered the electrochemical technique by dissolving a pure metal sheet from the anode and depositing metal salts on the cathode of an electrochemical cell in the presence of an electrolyte [56]. The type of reducing agent used, the purity of the metal and stabiliser, the electrolyte used, the concentration ratio, and the temperature, all of which have a direct influence on the physical properties of the nanoparticles, all have an impact on the success of this operation [57]. The electrochemical synthesis of nanocomposites is currently preferred over the fabrication of nanoparticles [58].

3.2.6. Green synthesis method- The goal of green nanomaterials is to reduce waste and establish a long-term procedure. In the production of nanomaterials for ecological sustainability, green techniques employing moderate process parameters and nontoxic precursors have indeed been stressed throughout time[59]. Green synthesis is a biological technique that may be used in place of physical and chemical processes. Biological organisms like bacteria, actinobacteria, algae, plants, moulds, and yeasts, or their products, also do this synthesis in a single step. Plants and microbes produce nanomaterials by reducing molecules like proteins, amines, phenolic compounds, enzymes, and alkaloids. Nanomaterials are created using this process by fragmenting or extracting precursors via biogenic reduction[60].

References-

1. Stark, W.J., Stoessel, P.R., Wohlleben, W. and Hafner, A.J.C.S.R., 2015. Industrial applications of nanoparticles. *Chemical Society Reviews*, 44(16), pp.5793-5805.
2. Rauch, J., Kolch, W., Laurent, S. and Mahmoudi, M., 2013. Big signals from small particles: regulation of cell signaling pathways by nanoparticles. *Chemical reviews*, 113(5), pp.3391-3406.

3. Ai, J., Biazar, E., Jafarpour, M., Montazeri, M., Majdi, A., Aminifard, S., Zafari, M., Akbari, H.R. and Rad, H.G., 2011. Nanotoxicology and nanoparticle safety in biomedical designs. *International journal of nanomedicine*, 6, p.1117.
4. Baig, N., Kammakam, I. and Falath, W., 2021. Nanomaterials: a review of synthesis methods, properties, recent progress, and challenges. *Materials Advances*, 2(6), pp.1821-1871.
5. Darabdhara, G., Das, M.R., Singh, S.P., Rengan, A.K., Szunerits, S. and Boukherroub, R., 2019. Ag and Au nanoparticles/reduced graphene oxide composite materials: synthesis and application in diagnostics and therapeutics. *Advances in colloid and interface science*, 271, p.101991.
6. Kannan, K., Radhika, D., Sadasivuni, K.K., Reddy, K.R. and Raghu, A.V., 2020. Nanostructured metal oxides and their hybrids for photocatalytic and biomedical applications. *Advances in Colloid and Interface Science*, 281, p.102178.
7. Wu, D., Li, B.L., Zhao, Q., Liu, Q., Wang, D., He, B., Wei, Z., Leong, D.T., Wang, G. and Qian, H., 2020. Assembling Defined DNA Nanostructure with Nitrogen-Enriched Carbon Dots for Theranostic Cancer Applications. *Small*, 16(19), p.1906975.
8. Patra, J.K., Das, G., Fraceto, L.F., Campos, E.V.R., del Pilar Rodriguez-Torres, M., Acosta-Torres, L.S., Diaz-Torres, L.A., Grillo, R., Swamy, M.K., Sharma, S. and Habtemariam, S., 2018. Nano based drug delivery systems: recent developments and future prospects. *Journal of nanobiotechnology*, 16(1), pp.1-33.
9. Niu, L., Coleman, J.N., Zhang, H., Shin, H., Chhowalla, M. and Zheng, Z., 2016. Production of two-dimensional nanomaterials via liquid-based direct exfoliation. *Small*, 12(3), pp.272-293.
10. Zhu, C., Yang, G., Li, H., Du, D. and Lin, Y., 2015. Electrochemical sensors and biosensors based on nanomaterials and nanostructures. *Analytical chemistry*, 87(1), pp.230-249.
11. Zhang, W., Li, J., Zhang, J., Sheng, J., He, T., Tian, M., Zhao, Y., Xie, C., Mai, L. and Mu, S., 2017. Top-down strategy to synthesize mesoporous dual carbon armored MnO nanoparticles for lithium-ion battery anodes. *ACS applied materials & interfaces*, 9(14), pp.12680-12686.
12. Rane, A.V., Kanny, K., Abitha, V.K. and Thomas, S., 2018. Methods for synthesis of nanoparticles and fabrication of nanocomposites. In *Synthesis of inorganic nanomaterials* (pp. 121-139). Woodhead Publishing.
13. Ataei, F., Dorrarian, D. and Motakef-Kazemi, N., 2020. Bismuth-based metal-organic framework prepared by pulsed laser ablation method in liquid. *Journal of Theoretical and Applied Physics*, 14(1), pp.1-8.
14. Mirgane, N.A., Shivankar, V.S., Kotwal, S.B., Wadhawa, G.C. and Sonawale, M.C., 2021. Degradation of dyes using biologically synthesized zinc oxide nanoparticles. *Materials Today: Proceedings*, 37, pp.849-853.
15. Low, Z.H., Chen, S.K., Ismail, I., Tan, K.S. and Liew, J.Y.C., 2017. Structural transformations of mechanically induced top-down approach BaFe₂O₁₉ nanoparticles synthesized from high crystallinity bulk materials. *Journal of Magnetism and Magnetic Materials*, 429, pp.192-202.
16. Arole, V.M. and Munde, S.V., 2014. Fabrication of nanomaterials by top-down and bottom-up approaches-an overview. *J. Mater. Sci*, 1, pp.89-93.
17. Yang, J., Ling, T., Wu, W.T., Liu, H., Gao, M.R., Ling, C., Li, L. and Du, X.W., 2013. A top-down strategy towards monodisperse colloidal lead sulphide quantum dots. *Nature communications*, 4(1), pp.1-6.
18. Bello, S.A., Agunsoye, J.O. and Hassan, S.B., 2015. Synthesis of coconut shell nanoparticles via a top down approach: Assessment of milling duration on the particle sizes and morphologies of coconut shell nanoparticles. *Materials Letters*, 159, pp.514-519.
19. Li, C., Yin, C., Mu, X. and Maier, J., 2013. Top-down synthesis of open framework fluoride for lithium and sodium batteries. *Chemistry of Materials*, 25(6), pp.962-969.

20. Xu, T., Lin, C., Wang, C., Brews, D.L., Ito, Y. and Lu, J., 2010. Synthesis of Supported Platinum Nanoparticles from Li- Pt Solid Solution. *Journal of the American Chemical Society*, 132(7), pp.2151-2153.
21. Din, M.I. and Rehan, R., 2017. Synthesis, characterization, and applications of copper nanoparticles. *Analytical Letters*, 50(1), pp.50-62.
22. Feng, J., Guo, L.Q., Xu, X., Qi, S.Y. and Zhang, M.L., 2007. Hydrothermal synthesis and characterization of Mn_{1-x}Zn_xFe₂O₄ nanoparticles. *Physica B: Condensed Matter*, 394(1), pp.100-103.
23. Palazzolo, S., Bayda, S., Hadla, M., Caligiuri, I., Corona, G., Toffoli, G. and Rizzolio, F., 2018. The clinical translation of organic nanomaterials for cancer therapy: a focus on polymeric nanoparticles, micelles, liposomes and exosomes. *Current medicinal chemistry*, 25(34), pp.4224-4268.
24. Lombardo, D., Kiselev, M.A. and Caccamo, M.T., 2019. Smart nanoparticles for drug delivery application: development of versatile nanocarrier platforms in biotechnology and nanomedicine. *Journal of Nanomaterials*, 2019.
25. Veerakumar, P., Sangili, A., Manavalan, S., Thanasekaran, P. and Lin, K.C., 2020. Research progress on porous carbon supported metal/metal oxide nanomaterials for supercapacitor electrode applications. *Industrial & Engineering Chemistry Research*, 59(14), pp.6347-6374.
26. Ealia, S.A.M. and Saravanakumar, M.P., 2017, November. A review on the classification, characterisation, synthesis of nanoparticles and their application. In *IOP Conference Series: Materials Science and Engineering* (Vol. 263, No. 3, p. 032019). IOP Publishing.
27. Sharma, S., Bhatia, A. and Gakkhar, N., Nanotechnology in cancer therapy: An overview and perspectives.
28. Hobbs, R.G., Petkov, N. and Holmes, J.D., 2012. Semiconductor nanowire fabrication by bottom-up and top-down paradigms. *Chemistry of Materials*, 24(11), pp.1975-1991.
29. Kumar, R. and Lal, S., 2014. Synthesis of organic nanoparticles and their applications in drug delivery and food nanotechnology: a review. *J Nanomater Mol Nanotechnol* 3: 4. of, 11, p.2.
30. Bae, K.H., Chung, H.J. and Park, T.G., 2011. Nanomaterials for cancer therapy and imaging. *Molecules and cells*, 31(4), pp.295-302.
31. Lombardo, D., Kiselev, M.A. and Caccamo, M.T., 2019. Smart nanoparticles for drug delivery application: development of versatile nanocarrier platforms in biotechnology and nanomedicine. *Journal of Nanomaterials*, 2019.
32. Veerakumar, P., Sangili, A., Manavalan, S., Thanasekaran, P. and Lin, K.C., 2020. Research progress on porous carbon supported metal/metal oxide nanomaterials for supercapacitor electrode applications. *Industrial & Engineering Chemistry Research*, 59(14), pp.6347-6374.
33. Jiang, H., Ma, J. and Li, C., 2012. Mesoporous carbon incorporated metal oxide nanomaterials as supercapacitor electrodes.
34. Das, R., Pachfule, P., Banerjee, R. and Poddar, P., 2012. Metal and metal oxide nanoparticle synthesis from metal organic frameworks (MOFs): finding the border of metal and metal oxides. *Nanoscale*, 4(2), pp.591-599.
35. Ealia, S.A.M. and Saravanakumar, M.P., 2017, November. A review on the classification, characterisation, synthesis of nanoparticles and their application. In *IOP Conference Series: Materials Science and Engineering* (Vol. 263, No. 3, p. 032019). IOP Publishing.
36. Hobbs, R.G., Petkov, N. and Holmes, J.D., 2012. Semiconductor nanowire fabrication by bottom-up and top-down paradigms. *Chemistry of Materials*, 24(11), pp.1975-1991.
37. Biswas, A., Bayer, I.S., Biris, A.S., Wang, T., Dervishi, E. and Faupel, F., 2012. Advances in top-down and bottom-up surface nanofabrication: Techniques, applications & future prospects. *Advances in colloid and interface science*, 170(1-2), pp.2-27.

38. Jia, X., Khan, W., Wu, Z., Choi, J. and Yip, A.C., 2019. Modern synthesis strategies for hierarchical zeolites: Bottom-up versus top-down strategies. *Advanced Powder Technology*, 30(3), pp.467-484.
39. Yadav, T.P., Yadav, R.M. and Singh, D.P., 2012. Mechanical milling: a top down approach for the synthesis of nanomaterials and nanocomposites. *Nanoscience and Nanotechnology*, 2(3), pp.22-48.
40. Dell'Aglio, M., Gaudiuso, R., De Pascale, O. and De Giacomo, A., 2015. Mechanisms and processes of pulsed laser ablation in liquids during nanoparticle production. *Applied Surface Science*, 348, pp.4-9.
41. Kim, M., Osone, S., Kim, T., Higashi, H. and Seto, T., 2017. Synthesis of nanoparticles by laser ablation: A review. *KONA Powder and Particle Journal*, p.2017009.
42. An, Z., Jia, H., Wu, Y., Rack, P.D., Patchen, A.D., Liu, Y., Ren, Y., Li, N. and Liaw, P.K., 2015. Solid-solution CrCoCuFeNi high-entropy alloy thin films synthesized by sputter deposition. *Materials Research Letters*, 3(4), pp.203-209.
43. Yap, F.L. and Zhang, Y., 2007. Protein and cell micropatterning and its integration with micro/nanoparticles assembly. *Biosensors and Bioelectronics*, 22(6), pp.775-788.
44. Hynes, W.F., Doty, N.J., Zarembinski, T.I., Schwartz, M.P., Toepke, M.W., Murphy, W.L., Atzet, S.K., Clark, R., Melendez, J.A. and Cady, N.C., 2014. Micropatterning of 3D microenvironments for living biosensor applications. *Biosensors*, 4(1), pp.28-44.
45. Valsecchi, C., Gomez Armas, L.E. and Weber de Menezes, J., 2019. Large area nanohole arrays for sensing fabricated by interference lithography. *Sensors*, 19(9), p.2182.
46. Sotelo-Lerma, M., Zingaro, R.A. and Castillo, S.J., 2001. Preparation of CdTe coatings using the chemical deposition method. *Journal of Organometallic Chemistry*, 623(1-2), pp.81-86.
47. Lu, C. and Liu, J., 2006. Controlling the diameter of carbon nanotubes in chemical vapour deposition method by carbon feeding. *The Journal of Physical Chemistry B*, 110(41), pp.20254-20257.
48. Dehghanghadikolaie, A., Ansary, J. and Ghoreishi, R., 2018. Sol-gel process applications: A mini-review. *Proc. Nat. Res. Soc.*, 2(1), p.02008.
49. Parashar, M., Shukla, V.K. and Singh, R., 2020. Metal oxides nanoparticles via sol-gel method: a review on synthesis, characterization and applications. *Journal of Materials Science: Materials in Electronics*, 31(5), pp.3729-3749.
50. Feinle, A., Elsaesser, M.S. and Huesing, N., 2016. Sol-gel synthesis of monolithic materials with hierarchical porosity. *Chemical Society Reviews*, 45(12), pp.3377-3399.
51. Mirjalili, F., Danafar, F. and ZareiMahmodabadi, A., 2020. The effect of adding different amount of spinning additives on preparation of nano Alumina fibers using a combined method of sol gel and electrospinning. *Journal of Nanoanalysis*, 7(3), pp.210-220.
52. Franchin, G., Wahl, L. and Colombo, P., 2017. Direct ink writing of ceramic matrix composite structures. *Journal of the American Ceramic Society*, 100(10), pp.4397-4401.
53. Bilisik, K., 2019. Braiding and Recent Developments. *Fibres to Smart Textiles*, pp.131-152.
54. Rao, B.G., Mukherjee, D. and Reddy, B.M., 2017. Novel approaches for preparation of nanoparticles. In *Nanostructures for novel therapy* (pp. 1-36). Elsevier.
55. Chakraborty, S., Sarkar, I., Behera, D.K., Pal, S.K. and Chakraborty, S., 2017. Experimental investigation on the effect of dispersant addition on thermal and rheological characteristics of TiO₂ nanofluid. *Powder Technology*, 307, pp.10-24.
56. Liu, S., Sun, S. and You, X.Z., 2014. Inorganic nanostructured materials for high performance electrochemical supercapacitors. *Nanoscale*, 6(4), pp.2037-2045.
57. Gurrappa, I. and Binder, L., 2008. Electrodeposition of nanostructured coatings and their characterization – a review. *Science and Technology of Advanced Materials*.
58. Tiwari, J.N., Tiwari, R.N. and Kim, K.S., 2012. Zero-dimensional, one-dimensional, two-dimensional and three-dimensional nanostructured materials for advanced electrochemical energy devices. *Progress in Materials Science*, 57(4), pp.724-803.

59. Zhu, C., Yang, G., Li, H., Du, D. and Lin, Y., 2015. Electrochemical sensors and biosensors based on nanomaterials and nanostructures. *Analytical chemistry*, 87(1), pp.230-249.
60. Amer, M.W. and Awwad, A.M., 2021. Green synthesis of copper nanoparticles by Citrus limon fruits extract, characterization and antibacterial activity. *Chem Int*, 7(1), pp.1-8.
61. Ghidan, A.Y., Al-Antary, T.M. and Awwad, A.M., 2016. Green synthesis of copper oxide nanoparticles using Punica granatum peels extract: Effect on green peach Aphid. *Environmental Nanotechnology, Monitoring & Management*, 6, pp.95-98.

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Chapter: 9

Nano Technology and Environment: A Critical Analysis

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Abstract:

Nanoscaled particles have a relatively larger surface area per unit mass which is the critical factor to increase mechanical modulus and other physical and chemical properties. Nanotechnology increases the strengths of many materials and devices, as well as enhances efficiencies of monitoring devices, remediation of environmental pollution, and renewable energy production. In general, nanotechnology devices consume less energy, reduce material wastes, and help in monitoring devices. Nanotechnology can also be used to reduce and prevent the toxicity of nanoparticles in an environment more efficiently. Nanoparticles have higher surface areas than bulk materials which can cause more damage to the human body and environment compared to the bulk particles. Therefore, concern for the potential risk to society due to nanoparticles has attracted national and international attention. The present paper discusses the positive and negative impacts of nanotechnology on man and the environment.

Key Words: Nano Particles, Toxicity, Environment

Introduction:

‘Nanotechnology’ is the science of studying phenomena and the manipulation of materials at atomic, molecular and macromolecular scale. Use of the prefix ‘nano’ in this context refers to a nano metre (nm). A nanometer is one-billionth of a meter. A sheet of paper is about 1,00,000 nanometers thick; a single gold atom is about one third of a nanometer in diameter. Dimensions between approximately 1 and 100 nanometers are known as the ‘nanoscale’. Nanomaterials are generally defined as materials that are <100 nm (0.1 mm) at least one dimension. This means that nanomaterials can be three-dimensional particles of almost any shape, ultrathin films (two-dimensional-like) or fine rods (essentially one-dimensional).

Ecological Perspective:

Ecologists have good reason to believe that even this shape difference will play a big role in their environmental and specifically, their

biological influences. But most importantly and far beyond this simple classification with respect to size, nanomaterials are so fascinating because their properties and therefore their environmental/biological behavior, depend on their size. This is to say that their chemical (reactivity, solubility etc), mechanical (elasticity, hardness etc), electronic (conductivity, redox behavior etc) and nuclear (magnetic) properties often change as a function of size. These changes can be and often are dramatic. Finally, through desertification, biomass burning, industrial combustion, engine exhaust, mining and other anthropogenic activities, humans have vastly increased the global supply and variety of incidental nanoparticles that is those nanoparticles unintentionally produced by humans.

Role of Nano - Technology:

Nanotechnology has revolutionary changes in commerce will transform daily life of consumer products in many ways.

1. Nanotechnology has been heralded as a “revolution” in science, for two reasons: first, because of its revolutionary view of the way in which chemicals and elements, such as gold and silver, behave, compared to traditional scientific understanding of their properties. Second, the impact of these new discoveries, as applied to commerce, can transform the daily life of consumer products ranging from sun tan lotions to cosmetics, food packaging, paints and coatings for cars, housing and fabrics, medicine and thousands of industrial processes. Beneficial consumer use of nanotechnologies, already in the stream of commerce, improves coatings on inks and paints in everything from food packaging to car paintings.

2. Additionally, ‘Nano medicine’ offers the promise of diagnosis and treatment at the molecular level in order to detect and treat pre symptomatic disease or to rebuild neurons in Alzheimer’s and Parkinson’s disease. There is a possibility that severe complications such as stroke or heart attack may be avoided by means of prophylactic treatment of people at risk and bone regeneration may keep many people active who never expected rehabilitation. Miniaturizations of diagnostic equipment can also reduce the amount of sampling materials required for testing and medical surveillance.

3. Miraculous developments that sound like science fiction to those people who eagerly anticipate these medical products, combined with the emerging commercial impact of nanotechnology applications to consumer products will reshape civil society - permanently. Thus, everyone within the jurisdiction of the Council of

Europe is an end-user of nanotechnology, even without realizing that nanotechnology has touched daily life.

Engineered Nanoparticles:

Engineered nanoparticles are defined simply as any intentionally produced particle that has a characteristic dimension between 1 and 100 nm and possesses properties that are not shared by no nanoscale particles with the same chemical composition (USNTC, 2004). As a result of their small size, nanomaterials possess unique properties, this is particularly true for nanoparticles <20 to 30 nm in size, which are generally characterized as having an excess of energy at the particle surface that makes them highly reactive and thermodynamically unstable (Auffan et al., 2009). Those nanomaterials that have the most unique characteristics (e.g., the fluorescence properties of quantum dots, the tensile strength of Carbon NanoTubes [CNTs], the photocatalytic properties of TiO₂) have proven to be the most economically profitable (Wiesner et al., 2009).

Number of laboratory trials has measured acute toxicity and sublethal effects of Engineered Nano Particles (ENPs) on organisms (Kahru and Dubourguier, 2009). Yet, the absence of evidence should not be taken as proof that environmental impacts will not occur. As a community, ecologists are primed to be concerned about the consequences of new technologies for the environment. One need only mention asbestos, tetraethyl lead, DDT and PCBs or chlorofluorocarbons to conjure up the lung disease, lead poisoning, bird population declines, contaminated fisheries, and Antarctic ozone hole environmental disasters caused by these technological innovations (Rattner, 2009; Rowland, 1991).

Scientists recognize that Engineered Nano Particles (ENPs) can enter the environment directly through intentional environmental additions (e.g., zero-valent Fe for remediation [Yantasee et al., 2007] or unintentional spills: (i) as the waste byproducts of ENP manufacture; (ii) through the liquid waste stream as they are leached from industrial and consumer products; (iii) as constituents of solid wastes from bio solids; and (iv) through landfill leaching of disposed products or bio solids.

Once ENPs enter the environment, their impact on organisms will be mediated by abiotic reactions that influence their solubility, shape and chemistry. Engineered nanoparticles that remain soluble or that are in high concentrations in the environment are more likely to have (i) direct effects on the organisms they encounter. Engineered nanoparticles may also (ii) indirectly affect organisms by altering the

chemical environment or by (iii) increasing or decreasing the solubility, transport, or membrane transfer of co-occurring contaminants. Regardless of whether any organism experiences lethal or sub lethal effects, if the ENP is incorporated into tissues or into detritus it is susceptible to trophic transfer and bioaccumulation into higher trophic levels.

Positive Impacts:

Nanotechnology increases the strengths of many materials and devices, as well as enhances efficiencies of monitoring devices, consumes less energy, reduces material waste, prevents toxicity, remediation of environmental pollution, and renewable energy production. While, these are considered to be the positive effect of nanotechnology. The use of nanomaterials and nanoparticles can also lead to significant savings in resources and efficiency increases in manufacturing and energy related applications.

Nanotechnology offers potential economic, societal and environment benefits. It has the potential to help reduce the human footprint on the environment by providing solutions for energy consumption, pollution, and green gas emissions.

Nanotechnology holds the promise of meeting global challenges of the twenty-first century regarding providing alternative energy, protecting the human right to clean water, ensuring wildlife protection, clean-up of brownfields and reducing the global disease burden.

It offers the potential for significant environmental benefits, including:

- Cleaner, more efficient industrial processes
 - Improved ability to detect and eliminate pollution by improving air, water, and soil quality
 - High precision manufacturing by reducing amount of waste
 - Clean abundant power via more efficient solar cells
 - Removal of greenhouse gases and other pollutants from the atmosphere
 - Remediating environmental damages
- The nanoscale products that utilize graphene in an industrial use or research can benefit the environment in several ways:
- Graphene based nanocomposites reduce the weight of airplanes by substituting traditional metals and composites and the consequence of the weight saving results in a reduction of a thousand tons of gasoline.
 - Graphene thin films or graphene buck papers can be substituted in place of metal meshes around the fuselage of

- airplane used to prevent the direct and indirect effects of lightning strikes.
- The eminent properties of graphene increase the efficiency of advanced renewable energy processes, such as reducing the weight of a wind turbine blades and increasing the energy converse efficiency.

Energy Consumption:

The use of graphene into a coating material resulting in the need for only one layer, which does not require a multifunctional film coating. Two applications for a graphene based coating are to apply it to a blade used in wind turbines or on the body of an airplane. It saves the weight increasing efficiency.

Cost Saving on Materials:

An alternative energy method such as hybrid automobiles will decrease the price by novel developments in nanotechnology.

Less Waste on Raw Materials:

Large sample testing will be done on a smaller scale and simultaneously use of raw materials will become more efficiency. Nanoscale chemical reagents (or catalysts) increase the reaction rate and other efficiency of chemical reactions.

Environmental Monitoring and Protection:

Utilizing advanced nanotechnology, a detector was made to detect a nuclear leak faster and more accurate at the Fukushima Daiichi Nuclear Power Plant. Which is one of the best radiation detector in Washington and can sense the faintest amount of radiation.

Cheap and Clean Energy:

Prototype solar panels incorporating nanotechnology are more efficient than standard designs when converting sunlight into electricity. Nanotechnology is in use in batteries, nanomaterials may improve hydrogen storage materials and catalysts for fuel cells. By creating more surface area and lighter storage units, nanotechnology can enhance energy generation, conversion and storage for: fuel cell, solar cell, thermo-to-electric, biomass energy, hydrogen storage, secondary batteries, super-capacitors, and thermal storage fluids.

Protecting the human right to clean water:

Nanotechnology offers inexpensive water purification due to rapid, low cost impurity detection. Magnetic interactions using ultra small rust can help remove arsenic from drinking water. Nanotechnology may also improve air and water quality monitoring, by developing more sensitive detection devices that can measure a broad range of pollutants and toxic agents simultaneously. Rapid detection allows

for swift response, thereby minimizing damage and reducing remediation costs.

Clean-up of Brown Fields:

Antimicrobial properties of nano-silver may clean up oil spills and hazardous chemicals.

Pollution Reduction and Environmental Progress:

Lighter cars and machinery that require less fuel; alternative fuel and energy sources; and materials that detect and clean up environmental contaminants all seem possible. The University College of Dublin (UCD) Center for Bio-Nano Interactions (CBNI) studies the impact of nanoparticles dispersed in environmental milieu, where decaying plant and animal matter becomes natural organic matter, typically composed of polysaccharides, interact with nanoparticles, and examines how this interaction affects organic stability, dispersability, environmental fate and behavior.

Reducing the Global Disease Burden:

Improvements in health care through enhanced diagnosis and treatment will increase personal wellbeing worldwide.

Mitigating Economic Crisis:

Investment in nanotechnology will stimulate economic growth that supports development of ancillary industries, such as marketing for new products, recycling and disposal of waste and litigation regarding intellectual property and liability.

Applications:

Nanotechnology, which involves materials and processes on an ultra-small scale, is currently an area of intense scientific research due to the wide variety of potential applications in the biomedical, optical, and electronic fields. Nanotechnology can also provide solutions for certain environmental problems. Nevertheless, little is known about the potential impacts of nanoparticles on the environment and human health, even though in some cases chemical composition, shape and size have been shown to contribute to the toxicological effects. Nanoparticles can be beneficial in catalytic and remediation application.

Biological applications:

The Development of ultra-small probes on planetary surfaces for agricultural applications and control of soil, air, and water contamination. Biomedical applications: This includes the medical diagnostic and treatments. Polymer composite materials when compared to traditional structural materials made out of metals have a reduced weight, high specific modulus and high resistance to environmental effects.

Negative Impacts:

Nanoparticles have higher surface areas than the bulk materials which can cause more damage to the human body and environment compared to the bulk particles there are certain negative impacts of nanotechnology on environment in many ways, such as increased toxicological pollution on the environment due to the uncertain shape, size, and chemical compositions of some of the nanotechnology products (or nanomaterials). Carbon nanotubes appear to cause health effects similar to asbestos when they come into contact with lung epithelia (Poland et al., 2009), but it is less clear what effect Carbon Nano Tubes (CNTs) will have when they are present at low concentrations in soils, sediments, and natural waters. Nano materials vary by shape and size which are important factors in determining the toxicity. Lack of information and methods of characterizing nanomaterials make existing technology extremely difficult to detect the nanoparticles in air for environmental protection. Also, information of the chemical structure is a critical factor to determine how toxic a nanomaterial is, and minor changes of chemical function group could drastically change its properties. Full risk assessment of the safety on human health and environmental impact need to be evaluated at all stages of nanotechnology. The risk assessment should include the exposure risk and its probability of exposure, toxicological analysis, transport risk, persistence risk, transformation risk and ability to recycle. Life cycle risk assessment is another factor that can be used to predict the environmental impacts. As current nanoscale materials are becoming smaller, it is more difficult to detect toxic nanoparticles from waste which may contaminate the environment. There are few ways that nanoparticles or nanomaterials can become toxic and harm the surrounding environment:

- **Hydrophobic and Hydrophilic Nanoparticles:** Nano coating researchers are currently working on TiO_2 powder as a coating inclusion that will reduce the weathering effects, such as salt rain degradation on composite materials.
- **Mobility of Contaminants:** There are two general methods that nanoparticle can be emitted into atmosphere. Nanoparticles are emitted into air directly from the source called primary emission, and are the main source of the total emissions. However, secondary particles are emitted naturally, such as homogeneous nucleation with ammonia and sulfuric acid presents.

Environmental Analysis:

Several nanoscale inclusions have been used for various applications. Among these nanoscale inclusions, graphene has the higher priority for various reasons. Graphene is one of the most advanced materials for structural improvement, substitution of silicon for electronic devices, as well as thermal transferring, and fire retardant.

Environmental Effects & Risks:

The risks associated with current consumer and industrial uses remain unknown and therefore unquantified. CBNI has begun research regarding plants, animals, and micro-organisms in order to understand the potential impact of nanoparticles upon ecosystems.

Environmental effects and risks associated with nanotechnology is very limited and inconsistent. The potential environmental harm through nanotechnology can be summarized as follows:

- High energy requirements for synthesizing nanoparticles causing high energy demand
- Dissemination of toxic, persistent nano substances originating environmental harm
- Lower recovery and recycling rates
- Environmental implications of other life cycle stages also not clear

Discussion:

Ecological research on ENPs can take advantage of the wealth of oceanic, terrestrial, and atmospheric earth science research involving naturally occurring nanoparticles. In particular, there are significant physical and chemical similarities between the most widely manufactured ENPs and naturally occurring nanoparticles, although in a number of cases the exact size, shape, and coatings/surface functional groups may be quite different from ENPs. Also, while the term nanoparticle may not yet be widely used in ecology, earth scientists have been studying at least some major classes of natural nanoparticles for many decades.

This is because an exceptionally wide variety of nanoparticles exist on earth, and are in fact ubiquitous in both the biotic and abiotic compartments of earth (Gilbert and Banfield, 2005; Hochella et al., 2008). The most abundant of these particles include ash from volcanoes and forest fires, sea salt aerosols, and the iron and other transition metal oxides in soils, rivers, and oceans (Hochella, 2008; Buseck and Adachi, 2008; Kulmala and Kerminen, 2008; Hassellöv and von der Kammer, 2008; and references therein). It has also been demonstrated that naturally occurring nanoparticles have important

local, regional, and even global consequences. (Chadwick et al., 1999; Jickells et al., 2005; Prospero, 1999; Simonson, 1995). We now know that naturally occurring nanoparticles are even present in interplanetary and interstellar space (Hochella, 2008). They have also been abundant on earth since its formation, were part of its formation (Becker et al., 2006), and life from the beginning has evolved in their presence. Emerging research is suggesting that many organisms synthesize nanomaterials. Bacteria in sediments may synthesize electrically conductive pilli, called nanowires, for sensing neighbors or for transferring electrons and energy (Blango and Mulvey, 2009; Gorby et al., 2006). Bacterial reduction of uranyl, $U^{6+}(aq)$, to U(IV) oxide (uraninite) is an important bioremediation strategy (Bargar et al., 2008). Manceau et al. (2008) found that wetland plants, or their symbionts, synthesize copper (Cu) nanoparticles in their rooting zone when grown in contaminated soils, thereby reducing Cu uptake. As analytical tools for the detection of nanoparticles improves, that biogenic nanoparticles are ubiquitous and bio geochemically vital across the living planet. Multiple characteristics contribute to the toxicity of many nanomaterials; they include not just mass or number of particles but also the shape of the particles, the electrical charge at the particle surface, the coating of the particle with another material and numerous other characteristics.

Conclusion:

There is no doubt that nanotechnology will continue to be developed, be a benefit to society and improve the environment in various ways. Nanoscale materials will make the products better in terms of functionality, weight savings, less energy consumption and a cleaner environment. Shortcomings always exist when new unproven technology is released. Nanomaterial may help clean certain environmental wastes, but contaminate environment in other ways. Choosing the right nanoscale materials is one of the key parameters for the future direction of nanotechnology. Engineering ethics need to be defined before the commercial use of nanotechnology. Risk assessment on new nanomaterial based application is important to evaluate potential risk to our environment when the products are in use. Full life cycle evaluation and analysis for all different applications should be conducted with constant attention. A major concern regarding nanoparticles is that they might not be detectable after release into the environment, which in turn can create difficulties if remediation is needed. Therefore, analysis methods need to be developed to detect nanoparticles in the environment that

accurately determine the shape and surface area of the particles (two of the factors that define their toxic properties).

- More information is needed regarding the structure-function relationships and in relating surface area and chemistry to functionality and toxicity.
- Full risk assessments should be performed on new nanomaterials that present a real risk of exposure during manufacture or use. Such assessments should take into consideration the toxicological hazard, the probability of exposure and the environmental and biological fate, transport, persistence, transformation into the finished product and recycling.
- Life cycle analysis will be a useful tool for assessing the true environmental impacts.
- When the use of scarce material is inevitable for the elaboration of the nanoparticles, an effective strategy for recycling and recovery is necessary.

References:

1. Auffan, M., J. Rose, J.-Y. Bottero, G.V. Lowry, J.-P. Jolivet, and M.R. Wiesner. 2009. Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective. *Nat. Nanotechnol.* 4:634-641.
2. B. Zhang¹, H. Misak¹, P.S. Dhanasekaran¹, D. Kalla² and R. Asmatulu¹. Environmental Impacts of Nanotechnology and Its Products. Proceedings of the 2011 Midwest Section Conference of the American Society for Engineering Education. P. No. 1-9.
3. Bargar, J.R., R. Bernier-Latmani, D.E. Giammar, and B.M. Tebo. 2008. Biogenic uraninite nanoparticles and their importance for uranium remediation. *Elements* (Chantilly, VA, U.S.) 4:407-412.
4. Becker, L., R.J. Poreda, J.A. Nuth, F.T. Ferguson, F. Liang, and W.E. Billups. 2006. Fullerenes in meteorites and the nature of planetary atmospheres. p. 95-121. In F.J.M. Rietmeijer (ed.) *Natural fullerenes and related structures of elemental carbon*. Vol. 6. Springer, Dordrecht, Netherlands.
5. Blango, M.G., and M.A. Mulvey. 2009. Bacterial landlines: Contact-dependent signaling in bacterial populations. *Curr. Opin. Microbiol.* 12:177-181.
6. Buseck, P.R., and K. Adachi. 2008. Nanoparticles in the atmosphere. *Elements* (Chantilly, VA, U.S.) 4:389-394.
7. Chadwick, O.A., L.A. Derry, P.M. Vitousek, B.J. Huebert, and L.O. Hedin. 1999. Changing sources of nutrients during four million years of ecosystem development. *Nature* 397:491-497.
8. D. F. Emerich and C. G. Thanos, "Nanotechnology and medicine," *Expert Opinion on Biological Therapy*, vol. 3, pp. 655-663, 2003.
9. D. G. Rickerby and M. Morrison, "Nanotechnology and the environment: A European perspective," *Science and Technology of Advanced Materials*, vol. 8, pp. 19-24.
10. Emily S. Bernhardt, Benjamin P. Colman, Michael F. Hochella, Jr. Bradley J. Cardinale and Roger M. Nisbet, Curtis J. Richardson and Liyan Yin. An Ecological Perspective on Nanomaterial Impacts in the Environment. *Journal of Environmental Quality*. Volume 39. November-December 2010. *J. Environ. Qual.* 39:1-12 (2010).

11. F. Kim, J. Luo, R. Cruz-Silva, L. J. Cote, K. Sohn, and J. Huang, "Self-Propagating Domino-like Reactions in Oxidized Graphite," *Advanced Functional Materials*, vol. 20, pp. 2867-2873, 2010.
12. For more information on the EU action Plan on Nanotechnology: ftp://ftp.cordis.europa.eu/pub/nanotechnology/docs/nano_action_plan2005_en.pdf. Source: D.G. Rickerby and M. Morrison (2007) "Nanotechnology and the environment: A European perspective", *Science and Technology of Advanced Materials* 8(1-2): 19-24.
13. Gilbert, B., and J.F. Banfield. 2005. Molecular-scale processes involving nanoparticulate minerals in biogeochemical systems. *Rev. Mineral. Geochem.* 59:109-155.
14. Gorby Y.A., S. Yanina, J.S. McLean, K.M. Rosso, D. Moyles, A. Dohnalkova, T.J. Beveridge, I.S. Chang, B.H. Kim, K.S. Kim, D.E. Culley, S.B. Reed, M.F. Romine, D.A. Saffarini, E.A. Hill, L. Shi, D.A. Elias, D.W. Kennedy, G. Pinchuk, K. Watanabe, S. Ishii, B. Logan, K.H. Nealson, and J.K. Fredrickson. 2006. Electrically conductive bacterial nanowires produced by *Shewanella oneidensis* strain MR-1 and other microorganisms. *Proc. Natl. Acad. Sci. USA* 103:11358-11363.
15. Hassellöv, M., and F. von der Kammer. 2008. Iron oxides as geochemical nanovectors for metal transport in soil-river systems. *Elements (Chantilly, VA, U. S.)* 4:401-406.
16. Hochella, M.F., Jr. 2008. Nanogeoscience: From origins to cutting-edge applications. *Elements (Chantilly, VA, U. S.)* 4:373-379.
17. Hochella, M.F., S.K. Lower, P.A. Maurice, R.L. Penn, N. Sahai, D.L. Sparks, and B.S. Twining. 2008. Nano minerals, mineral nanoparticles, and Earth systems. *Science* 319:1631-1635.
18. Bhatt and B. N. Tripathi, "Interaction of engineered nanoparticles with various components of the environment and possible strategies for their risk assessment," *Chemosphere*, vol. 82, pp. 308-317, 2011.
19. Fenoglio, G. Greco, S. Livraghi, and B. Fubini, "Non-UV-Induced Radical Reactions at the Surface of TiO₂ Nanoparticles That May Trigger Toxic Responses," *Chemistry - A European Journal*, vol. 15, pp. 4614-4621, 2009.
20. Jickells, T.D., Z.S. An, K.K. Andersen, A.R. Baker, G. Bergametti, N. Brooks, J.J. Cao, P.W. Boyd, R.A. Duce, K.A. Hunter, H. Kawahata, N. Kubilay, J. laRoche, P.S. Liss, N. Mahowald, J.M. Prospero, A.J. Ridgwell, I. Tegen, and R. Torres. 2005. Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science* 308:67-71.
21. Kahru, A., and H.-C. Dubourguier. 2009. From ecotoxicology to nanoeotoxicology. *Toxicology*. doi:10.1016/j.tox.2009.08.016.
22. Kulmala, M., and V.-M. Kerminen. 2008. On the formation and growth of atmospheric nanoparticles. *Atmos. Res.* 90:132-150.
23. M. A. H. Hyder, "NANOTECHNOLOGY AND ENVIRONMENT: Potential Applications and Environmental Implications of Nanotechnology," Master of Science Master's Thesis, Environmental Engineering, Technical University of Hamburg-Harburg, German, 2003.
24. Manceau, A., K.L. Nagy, M.A. Marcus, M. Lanson, N. Geoffroy, T. Jacquet, and T. Kirpichtchikova. 2008. Formation of metallic copper nanoparticles at the soil-root interface. *Environ. Sci. Technol.* 42:1766-1772.
25. Patrick Hunziker "Nanomedicine: The Use of Nano-Scale Science for the Benefit of the Patient" European Foundation for Clinical Nanomedicine (CLINAM) Basel, Switzerland 2010.
26. Poland, C.A., R. Duffin, I. Kinloch, A. Maynard, W.A.H. Wallace, A. Seaton, V. Stone, S. Brown, W. MacNee, and K. Donaldson. 2009. Carbon nanotubes introduced into the abdominal cavity of mice show asbestoslike pathogenicity in a pilot study. *Nat. Nanotechnol.* 3:423-428.

27. Prospero, J.M. 1999. Long-range transport of mineral dust in the global atmosphere: Impact of African dust on the environment of the southeastern United States. *Proc. Natl. Acad. Sci. USA* 96:3396–3403.
28. R. E. Hester, R. M. Harrison, and C. Royal Society of, Nanotechnology : consequences for human health and the environment. Cambridge: Royal Society of Chemistry, 2007.
29. Rattner, B.A. 2009. History of wildlife toxicology. *Ecotoxicology* 18:773–783.
30. Rowland, F.S. 1991. Stratospheric ozone in the 21st-century: The chlorofluorocarbon problem. *Environ. Sci. Technol.* 25:622–628.
31. Science for Environment Policy, DG Environment News Alert Service. European Commission. 26 July 2007. Positive and Negative Effects of Nano Technology on Environment.
32. Simonson, R.W. 1995. Airborne dust and its significance to soils. *Geoderma* 65:1–43.
33. UNEP
http://www.unep.org/yearbook/2007/PDF/7_Emerging_Challenges72dpi.pdf
34. USNTC (U.S. National Science and Technology Council). 2004. The National Nanotechnology Initiative: Strategic plan. Available at http://www.nano.gov/NNI_Strategic_Plan_2004.pdf (verified 4 Aug. 2010). Nanoscale Science, Engineering, and Technology Subcommittee, Nat.Technol. Coord.Office, Arlington, VA.
35. Valeriy Sudarenkov “Nanotechnologies, a new danger to the environment?” Preliminary draft report.
36. Valeriy SUDARENKOV. Nanotechnology: balancing benefits and risks to public health and the environment. Committee on Social Affairs, Health and Sustainable Development. AS/Soc/Inf (2013) 03. January 2013. Asocdocinf03_2013. P.no. 1-16.
37. Wiesner, M.R., G.V. Lowry, K.L. Jones, M.F. Hochella, R.T. Di Giulio, E. Casman, and E.S. Bernhardt. 2009. Decreasing uncertainties in assessing environmental exposure, risk, and ecological implications of nanomaterials. *Environ. Sci. Technol.* 43:6458–6462.
38. Yantasee, W., C.L. Warner, T. Sangvanich, R.S. Addleman, T.G. Carter, R.J. Wiacek, G.E. Fryxell, C. Timchalk, and M.G. Warner. 2007. Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles. *Environ. Sci. Technol.* 41:5114–5119.

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Chapter: 10

Climate change and its effects on environment

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Abstract

Human activity has degraded the earth's atmosphere severely. It has a drastic effect on land and ocean area. The quicker change in the earth's atmosphere is due to anthropogenic pollutants. It has several impacts on human health and livelihood. The change in the earth's atmosphere is due to a change in glacier mass which is due to global warming. Uncontrolled forest fire is also one of the causes of the increase of greenhouse gases in the atmosphere. The melting of Glaciers in the last 100 to 200 years is due to the addition of greenhouse gases to the earth's atmosphere. The melting of glaciers has had a great impact on the human population. They are at risk of flood, drought, and deficiency of drinking water, and loss of biodiversity. Due to global warming, it is expected that the global temperature will rise to 1.4-8 degrees by the end of the 20th century. Another projection shows that an increase in temperature of 4 degrees Centigrade would eliminate all the world's glaciers. In the past 100 years, the global mean sea level has been rising at an average rate of 1 to 2 millimeters annually. Hence it is highly needed to know the cause and effect of global warming and glacier melting so that we can save our earth.

Keywords: Glaciers, Global warming, Biodiversity, anthropogenic pollutants, Greenhouse gases, ecosystem

Introduction

Ice acts like a protective cover over the earth and ocean. It helps to keep the planet cool by reflecting excess heat to the space. It has been found that about 10% of land area on earth is covered with ice and 90% in Antarctica. Glaciers are the most visible evidence of climate change. Glaciers not only contribute in the rise of sea level but also accumulate and release pollutants. Due to industrialization and human interference the concentration of greenhouse gases in the atmosphere is increasing which is the primary cause of global rise of temperature. As a result of greenhouse gases the world's average temperature has increased 0.3 and 0.6 degree centigrade over the past

100 years. There is expectation of global average temperature increase by 1.4 to 5.8 degree centigrade in 2100. Global warming will effect human health, economy and the ecosystems upon which humans and other species depends. Nationwide efforts to be carried out to save our earth.

Impact of global warming

Highlights of the global warming impacts studied by various scientists

1. Arctic amplification

Arctic sea ice plays an essential role in ecosystems. Its melting may render many species homeless. Study found that most polar bear populations are at risk of dying out by 2100 because of a loss of sea ice. As global temperature rise and more sea ice melts it may cause more disastrous. In a recent study by (Maria and Louise, 2020) have warned that Arctic sea ice could be non-existent by 2035. Researchers found that during the warm interglacial period, intense spring time sunshine created pools of water as ice melted. These melt water pools cause more ice to melt. Most of the sun rays and energy are absorbed by the water due to climate change, warming more ice contributing to a phenomenon known as Arctic amplification. The study carried out by Jianjun Yin and Jonathan Overpeck (2018) observed that the global temperature will rise more 0.43 degrees F by the end of 2016, Jonathan Overpeck a climate scientist said that the Arctic warms much faster due to increase in level of carbon dioxide and other greenhouse gases in the atmosphere and this leads to melting of ice and increase of wild fire. Warming is leading to a rapid meltdown and increase in wild fires. The record increase in global temperature is 8 degree Celsius above average.

Antarctica is considered one of the Earth's largest, most pristine remaining wildernesses. The study by Dr Bernard Coetzee and team (2020) claimed that the human impact on Antarctica is increasing especially in ice free and coastal areas where most of its biodiversity is found. The teams of researchers are able to show how extensive human use of Antarctica happened between the years 1819 and 2018. This work will help to conserve the biodiversity. The study by scientists show that high emission of greenhouse gases leads to ice loss in Antarctica which in turn rise the sea level 30cm by 2100, with Greenland contributing an additional 9cm. The rise in earth's

temperature of one degree Celsius will rise 2.5 meters sea level in Antarctica and more three degrees rise in temperature may lift oceans 6.5 meters. This increase in temperature would have a negative impact on human being. It will have also great impact on coastal city like Mumbai.

2. Glaciers melting in Jammu, Kashmir

A group of researchers (Tariq Abdullah et al. 2020) studied the Glaciers in Jammu and Kashmir. The satellite data reveals that Glaciers in Jammu, Kashmir and Ladakh are melting at a significant rate. According to the data over 1200 glaciers in the Himalayan region shows reduction in mass of 35 centimetre from 2000-2012. The researchers continuously monitoring the melting of glacier and reduction in mass of glaciers in different regions. They observed that the melting of glacier is a continuous process. Due to unavailability of satellite data it is not possible to record continuously. The researchers observed that the region has lost about 70.32 gigatonne of glacier mass in one decade. The scientists revealed that the cause of melting is due to increase in temperature and decrease in precipitation. This is due to emission of greenhouse gases from industries and burning of fossil fuels. The continuous melting of glaciers have adverse impact on economic condition of the region.

3. Impact of climate change on Himalayan glaciers

Tayal and Sarkar (2019) studied the impact of climate change on Himalayan glaciers and energy security of country. They noticed that the climate change has strong impact on melting of snow and glaciers and precipitation over Himalayas. This in turn affects the runoff patterns of rivers of that region. These Rivers are the main source of livelihood for the 500 million people inhabiting in Gangetic plain. They also support many industries of that area. They also influence the economy of the region by producing energy sources. It helps in production of hydro and thermal energy through dams and power plants. Due to global warming and emission of greenhouse gases the temperature is increasing which in turn melts the glacier and changes flow pattern of rivers in Himalayan region that can have adverse impact on energy security of country. India, one of the biggest investors in renewal energy in the world is always concerned to tackle global warming. Temperature plays a dominant role in influencing the glaciers in Himalayan region. Glaciers in Himalayan region are influenced by Indian and Asian monsoon. It is decreasing from west to east and from eastern Himalayas to west (Burbank et

al.2003; Bookhagen and Burbank 2006, 2010).The diversity of climate across the region have different pattern of glacier response across different river basins (Fujita and Nuimura 2011, Scherler et al.2011, Bolch et al. 2012, Gardelle et al. 2013, Gardener et al. 2013).The variation in temperature and melting pattern of ice in Himalayan region is studied by many scientists (Singh et al.2015, Joshu Maurer, 2019).

4. World meteorological organization (WMO-2020)

The world meteorological organization (WMO-2020) states that the La Nina event is not enough to counter act the impact of human induced climate change. Due to the impact of climate change the global temperature will increase despite of a La Nina weather phenomenon. The result of greenhouse effect will be extreme weather ranging from scorching temperature and wild fires to devastating floods and marine heat waves. A major international study concluded that sustained greenhouse gas emission could see global sea levels rise nearly 40centimetres this century as ice sheets in Antarctica and Greenland continue to melt.

5. Emission drop and its impact on climate change

Piers Forster (2020) studied the emission drop and its impact on climate change. The lockdown due to pandemic situation has slowed down the emission of greenhouse gases to the atmosphere but it has no effect on climate change. Due to government restrictions the emission of greenhouse gases from industries, automobiles and fossil fuels has reduced to eight percent in 2020.The study shows that during lockdown period the pollutants like carbon dioxide and nitrogen oxide also reduced in between ten and thirty percent. Hence it can reduce 0.01 degree Celsius of warming by3030.The 2015 Paris climate deal commit to reduce the emission and limit temperature rise to below two degree Celsius. It has been decided to maintain the temperature to 1.5 degree Celsius. In order to keep1.5 degree Celsius global emissions must fall 7.6percent annually this decade. In this regard India has announced 2070 as its net zero cut-off. India has also made significant commitments to boost its non-fossil energy capacity to 500GW by 2030, and that year ensuring that half of its energy needs are met through renewable sources. Hence rigours steps to be taken to cut down emission of greenhouse gases.

Conclusion

In the past thousand years the earth's climate fluctuates. It has experienced warming and cooling. Global warming has serious concerned and it should be discussed among scientists. Warming is one of the factors for faster melting of mountain glaciers. The slow rise in sea level is caused by thermal expansion of oceanic water and melting of ice. All this happens due to emission of greenhouse gases especially CO₂. CO₂ is the worst enemy of environment. So we should reduce the use of appliances that release CO₂. India has launched a new climate equity website. As the sixth largest economy and the fourth largest source of greenhouse emissions, India's concerns are critical to the future of the global warming debate. It is a simple fact that developed countries have contributed to a vast majority of emissions which triggered global warming. Climate equity is the first step towards climate justice, towards an era where a fair distribution in responsibility and resource spending is allocated to countries that have contributed for a long time to global emissions on that basis.

References

- [1] Abdullah, T., Romshoo, S.A., Rashid, I. (2020). The satellite observed glacier mass changes over the upper Indus Basin during 2000-2012. *Scientific Reports*- 10, 14285.
- [2] Bookhagen, B., Burbank, D.W. (2006). Topography, relief, and TRMM derived rainfall variations along the Himalaya. *Geophysical Research Letters*- 33, L08405.
- [3] Bookhagen, B., Burbank, D.W. (2010). Toward a complete Himalayan hydrological budget: Spatiotemporal distribution of snowmelt and rainfall and their impact on river discharge. *J. Geophysics. Res*- 115, F03019.
- [4] Burbank, D.W., Blythe, A.E., Putkonen, J., Sitaula, B.P., Gabet, E., Oskin, M., Barros, A., Ojha, T.P., (2003). Decoupling of erosion and precipitation in the Himalayas. *Nature* 426: 652-655.
- [5] Bolch, T., Kulkarni, A., Kaab, A., Huggel, C., Paul, F., Cogley, J.G., Frey, H., Kargel, J.S., Fujita, K., Scheel, M., Bajracharya, S., Stoffel, M. (2012). The state and fate of Himalayan glaciers. *Science* 336.6079: 310-314.
- [6] Fujita, K., Takayuki, N. (2011). Spatially heterogeneous wastage of Himalayan glaciers. *Proceedings of the National Academy of Sciences* 108.34: 14011-14014.
- [7] Gardner, A.S., Moholdt, G., Cogley, J.G., Wouters, B., Arendt, A.A., Wahr, J., Berthier, E., Hock, R., Pfeffer, W.T., Kaser, G., Ligtenberg, S.R.M., Bolch, T., Sharp, M.J., Hagen, J.O., van den Broeke, M.R., Ligtenberg, S.R. (2013). A reconciled estimate of glacier contributions to sea level rise: 2003 to 2009. *Science* 340.6134: 852-857.
- [8] Gardelle, J., Berthier, E., Arnaud, Y., Kaab, A. (2013). Region wide glacier mass balances over the Pamir-Karakoram Himalaya during 1999-2011, *The Cryosphere* 7: 1263- 1286.
- [8] Guarino, M., Sime, L.C., Schroeder, D. et al. (2020). Sea-ice-free Arctic during the last interglacial supports fast future loss. *Nat. Clim. Chang.* 10: 928-932.
- [9] Jianjun, Y., Jonathan, O., Cheryl, P., Ronald, S. (2018). Big jump of record warm global mean surface temperature in 2014-2016 related to unusually large oceanic heat releases. *Geophysical research letters*.
- [10] Maurer, J.M., Schaefer, J.M., Rupper, S., Corley, A. (2019). Acceleration of ice loss across the Himalayas over the past 40 years. *Science advances* Vol-5, no. 6: 7266.
- [11] NOAA National Centers for Environmental information

- [12] Piers, M., Forster, Harriet, I. Forster, Steven, T. Turnock (2020). Current and future global climate impacts resulting from COVID-19. *Nature climate change*, 10:913-919.
- [13] Rachel, I., Leihy, Bernard, W.T., Coetzee, Fraser Morgan, Ben Raymond, Justine, D. Shaw, Aleks Terauds, Kees Bastmeijer, Steven L. Chown. (2020). Antarctica's wilderness fails to capture continents biodiversity. *Nature*, 41586-020-2506-3.
- [14] Scherler, D., Bookhagen, B., Strecker, M.R. (2011). Spatially variable response of Himalayan glaciers to climate change affected by debris cover. *Nature geo science* 4.3: 156-159.
- [15] Schrama, E.J.O., Wouters, B., Rietbroek, R. (2014). A mascon approach to assess ice sheet and glacier mass balances and their uncertainties from GRACE data. *J Geophys Res Solid Earth* 119: 6048– 6066.
- [16] Singh, D., Gupta, R.D., Jain, S.K. (2015). Statistical analysis of long term spatial and temporal trends of temperature parameters over Sutlej river basin, India. *J. Earth Syst. Sci.* 124.1: 17–35.
- [17] Tayal, S., Sarkar, S.K. (2019). Climate change impacts on Himalayan glaciers and implications on energy security of the country, TERI Discussion paper, New Delhi: The energy and resources institute.
- [18] WMO-World meteorological organization

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Chapter: 11

Advances in Catalytic Conversion of Benzene to Phenol using N₂O as Oxidant

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Abstract

Nitrous oxide serves as a potential oxidant due to its low N₂-oxygen affinity and this potency of N₂O can be utilized in production of phenol from benzene. Phenol is a very important commodity chemical and produced via well-known cumene process which is energy-intensive and not environmentally friendly. Therefore, there is a demand for an alternative single-step gas-phase catalysis process. Fe-ZSM-5 is the classical catalyst for phenol production and AlphOx technology demonstrated a successful path for industrialization with N₂O as oxidant. In this chapter we have tried to provide a comparative study between classical mechanism of selective benzene oxidation to phenol with N₂O as oxidant, involved with Fe-ZSM-5 catalysts and that of acid-base catalysts involved with the alkali metals incorporated in zeolites in a nutshell.

Keywords: N₂O oxidant, benzene C-H functionalization, selective phenol synthesis, catalysis

8. Introduction

Nitrous oxide (N₂O), owing to its low N₂-oxygen affinity (40 kcal/mol) serves as an O-donor molecule and this potency of N₂O is responsible for ozone depletion [1,2] Thus N₂O is nearly 300 times more potent than carbon dioxide as a greenhouse gas. N₂O emissions totaling 33,046 metric tons from the plant in 2018, the most recent year for which data is available, equal the annual greenhouse gas emissions of 2.1 million automobiles, according to company data reported to the Environmental Protection Agency and the agency's greenhouse gas equivalencies calculator [3]. In the late 1970s-early 1980s, N₂O has attracted a significant attention of

researchers involved in searching for new ways in selective transformation of methane. First practical interest to N_2O as an oxidant has appeared in relation to phenol production.

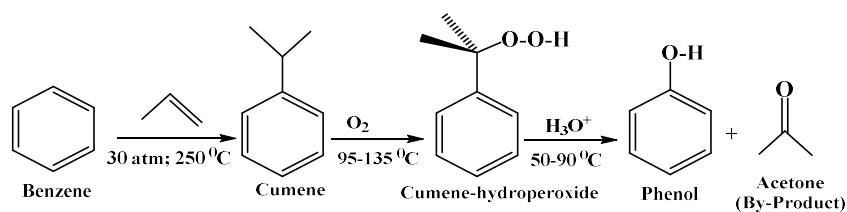
Phenol is an important commodity chemical and its production by hydroxylation of the C-H bond in benzene has received much attention. Despite significant progress in C-H functionalization chemistry in recent years, catalytic benzene hydroxylation still remains a challenge since C-H bonds are not only thermodynamically stable but also kinetically inert [4-6].

9. Niche uses of Phenol

Phenol (worldwide production: 14 million MT/year) is an important industrial commodity as it serves as precursor to many materials and useful compounds. It is used to synthesize plastics and related materials. Phenol and its chemical derivatives are essential for production of polycarbonates, epoxies, Bakelite, nylon, detergents, herbicides such as phenoxy herbicides, and pharmaceutical drugs [7,8]. Some other phenol derivatives are somewhat local in application, e.g. aniline is produced from phenol at only two plants, one in Japan and the other in the USA. Likewise, phenol is used in the production of nylon, via caprolactam or adipic acid by only one United States producer and one European producer.

10. Industrial Process of Phenol Production

In industrial practice, phenol is obtained from benzene via the three-step cumene process. The oxidation of cumene (Hock process) continues to be the dominant synthetic route to produce phenol accounting for more than 6.7 million t/a of phenol and about 4.1 million t/a of acetone as coproduct [7]. The Hock process consists of two steps: cumene is first oxidized with oxygen to cumene hydroperoxide (CHP). CHP is then cleaved to phenol and acetone by using a strong mineral acid as catalyst. Both reactions are very exothermic with heats of reaction of -117 kJ/mol for the oxidation of cumene and -252 kJ/mol for the cleavage of the peroxide. Further, the oxidation occurs at conditions close to the flammable limits. Furthermore, the CHP is a potentially unstable material which can violently decompose under certain conditions. Today the biggest producers of phenol using cumene oxidation are INEOS Phenol (Europe and USA), Mitsui (Japan, Singapore), Shell (USA), Polymeri Europa (Italy), and Ertisa (Spain, now CEP SA). Approximately 45% of the world production capacity resides in China.



Scheme 1. Industrial production of phenol from benzene

Although all these companies are based on the Hock process, there are differences in the technical design of the reaction and fractionation sections. The key issue influencing the overall process yield is the formation of the byproducts dimethyl benzyl alcohol (DMBA) and acetophenone (ACP) in the oxidation step. ACP is separated as a high boiling component in the distillation. DMBA is dehydrated during the cleavage step to α -methylstyrene (AMS), which forms high-boiling dimers and cumylphenols in the acid-catalyzed process step. The unconverted methylstyrene is hydrogenated back to cumene later in the process. Typical phenol yield from CHP cleavage is > 98 mol % [7]. The drawback of the current process is the fluctuating demand of Bisphenol A which is highly dependent on the demand for polycarbonate a commodity polymer. Thus, the global demand for phenol is expected to increase during the coming decade; therefore, there is potential interest in developing new, environmentally benign and coproduct-free routes to phenol, i.e. selective phenol production via direct oxidation of benzene.

11. Catalysts for Hydroxylation of Benzene to Phenol using N₂O

Direct synthesis of phenol from benzene and O₂ using a solid catalyst is preferred but its commercial viability remains a challenge. In 1983, Iwamoto et al. were the first to use N₂O [9]. This reaction over a vanadia catalyst allowed achieving much better selectivity as compared to the oxidation by dioxygen. At 550 °C, the reaction selectivity exceeded 70%. These results were recognized as a promising lead to a long-awaited one-step direct process. However, a pilot test performance did not meet the expectations since the selectivity proved to be too low for a commercial development. In 1988, three groups of researchers [10,11] independently distinguished the ZSM-5 zeolites to be the best catalysts for reaction. The catalysts

allowed the reaction to proceed at much lower temperature and, which is even more important, with the selectivity approaching 100%. Panov et. al. reported the AlphOx technology based on the use of Fe-containing ZSM-5 zeolites for benzene hydroxylation to phenol using N_2O as oxidant [12-17]. The catalyst operates at 300-450 °C and provides 100% selectivity towards phenol at 25-30% benzene conversion. In 1996, Solutia started a pilot plant based on the AlphOx technology in Pensacola, Florida. On this basis, a new phenol process has been developed jointly by Solutia Inc. (formerly a chemical business of Monsanto separated in 1997) and the Boreskov Institute of Catalysis (BIC) in Russia [7]. N_2O is a major component in the off-gas from adipic acid production plants. Solutia produces 400,000 t/a of adipic acid from cyclohexane which is associated with the formation of about 200,000 t/a of N_2O [7]. The oxidation is carried out in the gas phase with zeolites of the ZSM-5 type as the catalyst. The heat of reaction is 286 kJ/mol [7]. The oxidation is performed at 300-450 °C at atmospheric pressure. Reported benzene conversion is upto 40% with phenol selectivities being > 95 %. Although this approach constitutes an interesting alternative to the cumene process; however, it was never commercialized owing to some serious issues from industrial perspectives. The strongly adsorbed phenolate intermediate, generated in this process considered as a precursor of coke, contributing to pore plugging [18]. Another side-reaction involves the oxidation of phenol into dihydroxybenzenes and their condensation into high-molecular weight aromatic compounds, which slowly migrate through the micropores and may also deposit there [19]. Brønsted acid sites in zeolite channels are believed to be another cause of coke formation in these Fe/ZSM-5 zeolites [20,21]. All of these cooking mechanisms account for rapid deactivation of Fe/ZSM-5 catalysts in benzene oxidation. Apart from the high price of N_2O , rapid deactivation of Fe/ZSM-5 catalysts are a serious challenge in realizing a commercial process for the direct oxidation of benzene using N_2O . Various strategies have been employed to sort out these issues e.g., by synthesizing zeolites with extra-large micropores, by introducing intracrystalline mesopores in zeolite particles and reducing the zeolite crystal size, etc. [21-27]. But so far, and so forth, no group could have reported >20% conversion of benzene, maintaining 99.9% selectivity towards phenol.

Very recently, Iwasawa and his group reported that the single alkali and alkaline earth metal cations incorporated in β -zeolite pores selectively promote benzene C-H activation toward direct phenol

synthesis from benzene and N_2O [28]. Among the alkali and alkaline earth metal ions, Cs^+ and Rb^+ with ion diameters greater than 300 pm provided the pivotal single metal ion site platform with a sufficiently large coordination sphere at a confined cross-channel in a β -zeolite pore for the selective inter-coadsorbate concerted reaction pathway. The most active catalyst was Rb/β , which showed benzene conversions of 25.5% at 340 °C, maintaining the 99.9% phenol selectivity. N_2O consumption on Rb/β and Cs/β was nearly stoichiometric to the phenol production.

12. Benzene Hydroxylation Mechanism

The mechanism of the benzene oxidation to phenol reaction with $\text{Fe}/\text{ZSM-5}$ zeolite catalysts proceed on active iron centers (“ α -sites”) to form a surface oxygen species that is often called “ α -oxygen”; “ α -oxygen” is able to oxidize benzene to phenol. Although the exact structure of the “ α -sites” in $\text{Fe}/\text{ZSM-5}$ zeolites for N_2O decomposition and oxidation of benzene to phenol remains unclear, most studies agree that on the role of cationic extraframework Fe complexes in $\text{Fe}/\text{ZSM-5}$ zeolites. It has been found that only a fraction of these “ α -oxygen” are able to oxidize benzene to phenol [21]. Steaming of isomorphously substituted $\text{Fe}/\text{ZSM-5}$ zeolite is crucial to enhance the number of extraframework Fe ions. During steaming, Fe-O-Si bonds in $\text{Fe}/\text{ZSM-5}$ crystals are broken, resulting in the migration of Fe from the zeolite framework to extraframework locations. In this process, a range of extraframework Fe species are usually formed including isolated Fe cations, oligomeric cationic Fe complexes, and neutral Fe-oxide clusters (Fe_xO_y) as well as larger Fe-oxide aggregates. Bulk Fe-oxides species display very low activity in the decomposition of N_2O .

On the other hand, Iwasawa and his group established a new mechanism of benzene hydroxylation using N_2O over single alkali and alkaline earth metal cations incorporated in β -zeolite pores, in the light of DFT studies [28]. The detailed computational reaction profile for the reaction mechanism demonstrates the involvement of associative coadsorption states: The first step of the process is associated with benzene adsorption on the Cs^+ ion coordinated by a β -zeolite cluster through the π -bond. N_2O also adsorbs molecularly, which is rather in contrast to the typical redox catalysis. The next step involves the dissociation of $\text{O-N}(\text{N}_2\text{O})$ bond and formation of $\text{O-C}(\text{benzene})$ bond that proceeds concertedly via two transition states, followed by migration of the H atom to the O atom (O-C

carbon in the coordinated benzene on the Cs⁺ ion) to form phenol. The single Cs⁺ ion site with a large ion diameter provides an active platform capable of interadsorbate reaction, resulting in the molecular transformation from benzene with N₂O to phenol without the Cs⁺ site undergoing a redox reaction.

13. Conclusions and Outlook

Industrially phenol is obtained from benzene via the three-step cumene process. Since last couple of decades N₂O has attracted a significant attention to researchers in utilizing N₂O as an oxidant in selective production of phenol. Solutia process demonstrated some optimistic phenol production in terms of yield, but, however, the process never commercialized. Several researchers came forward to sort out the issues involved in the process but no group could have reported >20% conversion of benzene, maintaining 99.9% selectivity towards phenol. Major groups reported phenol production from benzene using N₂O as oxidant using Fe- based catalysts with the involvement of active iron centers ("α-sites") to form a surface oxygen species (α-oxygen). Contrarily, Iwasawa and his group reported phenol production from benzene using N₂O with the involvement of associative coadsorption states, entirely different from classical mechanism. However, there are several difficulties associated with these catalytic systems that should be overcome to make it appropriate at industrial scale level. Therefore, there is still a big room for further studies and improvements in this field.

14. References

- [1]. S. G. Lias, J. E. Bartmess, J. F. Liebmann, J. L. Holmes, R. D. Levin, W. G. Mallard, Gas-phase ion and neutral thermochemistry, *J. Phys. Chem. Ref. Data* 17 (1988) 1–861.
- [2]. S. Wannakao, T. Nongnual, P. Khongpracha, T. Maihom, J. Limtrakul, Reaction Mechanisms for CO Catalytic Oxidation by N₂O on Fe-Embedded Graphene, *J. Phys. Chem. C* 116 (2012) 16992–16998.
- [3]. <https://insideclimatenews.org/news/24032020/plant-florida-emits-vast-quantities-greenhouse-gas-nearly-300-times-more-potent-carbon/>
- [4]. E. Roduner, W. Kaim, B. Sarkar, V. B. Urlacher, J. Pleiss, R. Glaser, W. D. Einicke, G. A. Sprenger, U. Beifuß, E. Klemm, C. Liebner, H. Hieronymus, S. F. Hsu, B. Plietker, S. Laschat, Selective catalytic oxidation of C-H bonds with molecular oxygen, *ChemCatChem* 5 (2013) 82–112.
- [5]. S. S. Acharyya, S. Ghosh, R. Tiwari, C. Pendem, T. Sasaki, R. Bal, Synergistic effect between ultrasmall Cu(II) oxide and CuCr₂O₄ spinel nanoparticles in selective hydroxylation of benzene to phenol with air as oxidant, *ACS Catal.* 5 (2015) 2850–2858.

- [6]. S. S. Acharyya, S Ghosh, Y Yoshida, T Kaneko, T Sasaki, Y Iwasawa, NH_3 -driven benzene C–H activation with O_2 that opens a new way for selective phenol synthesis, *Chem. Rec.* 9 (2019) 2069–2081.
- [7]. M. Weber, M. Weber, V. Weber, Phenol, *Ullmann's Encyclopedia of Industrial Chemistry*, 2020, pp.1–20; Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim ; DOI: 10.1002/14356007.a19_299.pub3.
- [8]. J. Wallace, Phenol, *Kirk-Othmer Encyclopedia of Chemical Technology* 2005; <https://doi.org/10.1002/0471238961.1608051423011212.a01.pub2>.
- [9]. M. Iwamoto, K. Matsukami, S. Kagawa, Catalytic oxidation by oxide radical ions. 1. One-step hydroxylation of benzene to phenol over Group 5 and 6 oxides supported on silica gel, *J. Phys. Chem.* 87 (1983) 903–905.
- [10]. M. H. Gubelmann, P. J. Tirel, *Fr. Pat.* 2630735 (filed May 2, 1988).
- [11]. S. Kharitonov, T. N. Aleksandrova, L. A. Vostrikova, V. I. Sobolev, K. G. Ione, G. I. Panov, *USSR Pat.* 1805127 (filed June 22, 1988).
- [12]. G. I. Panov, G. A. Sheveleva, A. S. Kharitonov, V. N. Romannikov, L. A. Vostrikova, Oxidation of benzene to phenol by nitrous oxide over Fe-ZSM-5 zeolites, *Appl. Catal. A* 82 (1992) 31–36.
- [13]. G. I. Panov, A. S. Kharitonov, V. I. Sobolev, Oxidative hydroxylation using dinitrogen monoxide: a possible route for organic synthesis over zeolites, *Appl. Catal. A* 98 (1993), 1–20.
- [14]. G. I. Panov, *Advances in Oxidation Catalysis; Oxidation of Benzene to Phenol by Nitrous Oxide. CATTECH* 4 (2000) 18–31.
- [15]. D. P. Ivanov, M. A. Rodkin, K. A. Dubkov, A. S. Kharitonov, G. I. Panov, Mechanism of coke influence on the catalytic activity of FeZSM-5 in the reaction of benzene oxidation into phenol, *Kinet. Catal.*, 41 (2000), 771–775.
- [16]. K. A. Dubkov, N. S. Ovanesyan, A. A. Shteinman, E. V. Starokon, G. I. Panov, Evolution of iron states and formation of α -Sites upon activation of FeZSM-5 zeolites, *J. Catal.* 207 (2002) 341–352.
- [17]. L.V. Pirutko, V. S. Chernyavsky, A. K. Uriarte, G. I. Panov, Oxidation of benzene to phenol by nitrous oxide: Activity of iron in zeolite matrices of various composition, *Appl. Catal. A* 227 (2002) 143–157.
- [18]. G. Li, E. A. Pidko, R. A. van Santen, Z. Feng, C. Li, E. J. M. Hensen, Stability and reactivity of active sites for direct benzene oxidation to phenol in Fe/ZSM-5: A comprehensive periodic DFT study, *J. Catal.* 284 (2011) 194–206.
- [19]. D. P. Ivanov, L. V. Pirutko, G. I. Panov, Effect of steaming on the catalytic performance of ZSM-5 zeolite in the selective oxidation of phenol by nitrous oxide, *J. Catal.* 311 (2014) 424–432.
- [20]. J. Jia, K. S. Pillai, W. M. H. Sachtler, One-step oxidation of benzene to phenol with nitrous oxide over Fe/MFI catalysts, *J. Catal.* 221 (2004) 119–126.
- [21]. L. Meng, X. Zhu, E. J. M. Hensen, Stable Fe/ZSM-5 nanosheet zeolite catalysts for the oxidation of benzene to phenol, *ACS Catal.* 7 (2017) 2709–2719.
- [22]. J. Jiang, J. Yu, A. Corma, Extra-large-pore zeolites: bridging the gap between micro and mesoporous structures, *Angew. Chem.* 49 (2010) 3120–3145.
- [23]. K. Na, M. Choi, R. Ryoo, Recent advances in the synthesis of hierarchically nanoporous zeolites, *Microporous Mesoporous Mater.* 2013, 166, 3–19.
- [24]. H. Xin, A. Koekkoeck, Q. Yang, R. van Santen, C. Li, E. J. M. Hensen, A hierarchical Fe/ZSM-5 zeolite with superior catalytic performance for benzene hydroxylation to phenol, *Chem. Commun.* (2009) 7590–7592.

- [25]. J. J. Koekkoek, H. Xin, Q. Yang, C. Li, E. J. M. Hensen, Hierarchically structured Fe/ZSM-5 as catalysts for the oxidation of benzene to phenol, *Microporous Mesoporous Mater.* 145 (2011) 172-181.
- [26]. S. Rana, B. Singh, R. Kumar, D. Verma, M. K. Bhunia, A. Bhaumik, A. K. Sinha, Hierarchical mesoporous Fe/ZSM-5 with tunable porosity for selective hydroxylation of benzene to phenol, *J. Mater. Chem.* 20 (2010) 8575–8581.
- [27]. M. K. Al Mesfer, M. Danish, S. M. Ahmed, Catalytic conversion of benzene to phenol, *Russ. J. Appl. Chem.* 89 (2016) 1869–1878.
- [28]. S. Ghosh, S. S. Acharyya, T. Kaneko, K. Higashi, Y. Yoshida, T. Sasaki, Y. Iwasawa, Confined single alkali metal ion platform in a zeolite pore for concerted benzene c–h activation to phenol catalysis, *ACS Catal.* 8 (2018), 11979–11986.

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Chapter: 12

SYNTHESIS CHARACTERIZATION AND APPLICATIONS OF IMIDAZOLINIUM BASED CATIONIC SURFACTANTS

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Abstract

Surfactants are substances that reduce the surface tension of liquids and increase their ability to spread. Surfactants are substances found in cleaning products that aid in the removal of debris from the surface being cleaned. Gemini and monomeric surfactants were made by esterifying halogenated carboxylic acids with short-chain fatty alcohols or acids with 2-chloroethanol, creating appropriate esters, and then treating them with spacers (1-methylimidazole). Surfactants based on imidazolium are particularly essential components in a variety of cosmetics. Proton NMR experiments were used to identify these surfactants. A number of factors are considered, including surfactant chemical structure, critical micelle concentration (CMC), melting point, and BOD analysis. The surfactant was synthesized using long-chain fatty acid and haloalcohol at 60 C.

Introduction

Cationic surfactants are an important class of surfactants that have found countless applications in various industries. Imidazolium surfactants particularly are important ingredients of several cosmetic products [1-3]. They are often utilized as corrosion inhibitors [4-5] as well as being used in emulsion polymerization [6-7]. The flotation of minerals [8] and textile processing [9]. Biological applications of these surface-active agents include their antimicrobial activity [10-13], as well as their use as drugs [14-15] and gene delivery agents [16-17]. Several cationic surfactants are also used in DNA extraction methods [18-21]. One major challenge that industry faces in the 21st century is to get the desired molecule not only in a cost-effective manner but also via environmentally friendly means. Furthermore, environmental aspects, such as the biodegradability of the surfactants, must be further improved, so that the surfactants can be easily degraded in the environment. Cationic surfactants due to their

biocide activity and emulsification properties are resistant, to some extent, to biological agents and undergo slow biodegradation [22]. They are neither good detergent nor foaming agents, but tremendously useful for some certain uses, because of their peculiar properties. Cationic surfactants belong to class 8 corresponds i.e. nitrogen compounds like quaternary ammonium compounds and fatty amine salts with one or several long chains of the alkyl type, often coming from natural fatty acids. These surfactants are synthesized by hydrogenation reaction high pressure that is the reason cationic surfactants are more expensive than anionic surfactants. Due to this cause they are only used in two cases, i.e. (1) as bactericide, (2) as the positively charged substance in both cases there is no less expensive substitute. On dissolution in water, positively charged substances are capable of adsorb on negatively charged substrates to produce antistatic and hydrophobic effects, regularly of extraordinary significance such as in corrosion inhibition. Cationic surfactants yield a positively charged surfactant ion and a negatively charged counter ion upon dissolution in water. When Domagk tinted the bactericidal properties of the Cationic surfactants, commercial use of these surfactants increased. From this originated the production of hundreds of commercial products. Now a day, cationic surface-active agents play an important role as sanitizing and antiseptic agents, as components in cosmetic formulations, and as germicides and fungicides. Synthesis of some characteristic cationic surfactants has new applications consisting of their use as antistatic agents, textile softeners, corrosion inhibitors, foam depressants, flotation chemicals, and petroleum derivatives. Two common types of cationic surfactants are long-chain amines and quaternary amine salts. The long chain amine types are made from natural fats and oils or from synthetic amines. They are soluble in strongly acidic medium but become uncharged and insoluble in water having pH greater than 7. Quaternary amine type cationic surfactants are significantly used as fabric softeners. They adsorb on the outside of filaments with their hydrophobic gatherings arranged away from the fibers. This reduces the friction between fibers and imparts a soft, fluffy feel to the fabric. This same mechanism accounts for the behavior and use of cationic surfactants as hair conditioners. Quaternary ammonium salts are effective in neutral and alkaline as well as acidic mediums. Four properties of the cationic surfactants are the basis for their widespread use of surface activity, adsorption onto negatively charged solids, biocidal activity, and their reaction with anionic. Because of these properties, the cationic surfactants are used in large

amounts in a number of applications such as fabric softeners, disinfectants, demulsifiers, emulsifiers, wetting agents, and processing aids.

Cationic surfactants possess many industrial applications and constitute almost 7% of the total industrial surfactant market potential [23]. The overall production of cationic surfactants amounts to 7 lakhs tonnes per annum. A new class of cationic surfactants is a response to the increasing consumer demand for products that are both greener and more efficient.

In order to achieve these objectives, it is necessary to use renewable low-cost materials that are available in quantities and to design molecular structures that show improved performance properties and reduced environmental impact. Demand for new-generation surfactants is growing in relation to their many potential industrial applications. The nature of the polar head group and its charge is an important structural variable in a surfactant molecule that governs its applications and such structure-activity study is essential. In view of the above, the present work is the synthesis and evaluation of imidazolium-based cationic surfactants by renewable raw materials like fatty acids and halogenated alcohols. Here we have chosen the greener approach to make the process environment friendly and cost-effective, too. The purpose of this work was to prepare and characterize the cationic imidazole-based monomeric surfactants from renewable raw materials and to evaluate their surface-active properties. These surfactants have been found to have better surface properties as compared to conventional cationic surfactants. Further investigations by TGA established superior thermal stability of these new surfactants.

Experimental Section

Materials/Methods. Chloroethanol, bromoethanol and 1-methyl imidazole were purchased from Sigma-Aldrich Chemical Co. USA. Lauric acid, Myristic acid, Palmitic acid and silica gel for T.L.C were purchased from S. D. Fine Chemicals Ltd; Mumbai, India. Sulphuric acid was purchased from Merck, Germany. Amyl alcohol (3-methyl butane-1-ol), decanol, benzyl alcohol, methyl benzoate, octanol, ethyl acetate, Ethanol - (C_2H_5OH), acetone (CH_3COCH_3), and toluene (C_7H_8) were obtained from S.D. fine chemicals.

Instrumentation

IR spectra were recorded as a thin film on KBr Pellet on a Shimadzu 8400s FT-IR (Kyoto, Japan) instrument. Mass spectra were recorded

on Waters Q-T of Micro mass using ESI as an ion source at a sophisticated analytical instrumentation facility (SAIF), Panjab University, Chandigarh. ^1H , DEPT, and ^{13}C NMR spectra were recorded on a JEOL AL-300 (JEOL, Japan) system as a solution in CDCl_3 , using tetramethylsilane (TMS) as an internal standard.

Conductivity measurements [24-25]: The critical micelle concentrations (CMC) of these surfactants [7-12] were determined by the conductivity method. The conductance as a function of surfactant concentration was measured at 25°C . Measurements were performed with an Equiptronic Conductometer (Auto temperature conductivity meter model E.Q.661) with stirring to control the temperature. The solutions were thermostated in the cell at 25°C . For each series of measurements, an exact volume of 25ml Millipore water (resistivity $18\text{ M}\Omega$) was introduced into the vessel, and the specific conductivity of the water was measured. For the determination of CMC, adequate quantities of concentrated stock surfactant solutions were added in order to change the surfactant concentration from concentrations well below the critical micelle concentration (CMC) and repeated to verify our results. The curve of conductivity versus surfactant concentration was taken as the CMC. The degree of counterion binding (β) was calculated as $(1 - \alpha)$, where $\alpha = S_{\text{micellar}}/S_{\text{premicellar}}$, i.e., ratio of the slope before and after CMC.

Surface Tension Measurements. Surface tension values were used to calculate CMC using a CSC Du Nouy interfacial tensiometer (Central scientific Co., Inc.) equipped with a platinum-iridium ring (circumference 5.992 cm) at 25°C . The tensiometer was calibrated using triple distilled water. For the determination of CMC and surface tension, adequate quantities of a concentrated stock solution were used. The data of this determination is presented in Table 1.

Thermal stability Measurements The thermal stability of the present cationic surfactants was measured with SDT Q600 Thermal Gravimetric Analyzer (TGA), using a nitrogen atmosphere. All samples were run in aluminum pans under a nitrogen atmosphere at a heating rate of 10°C per minute.

General synthesis procedure

Synthesis of 2 - Chloro/ Bromo ethyl(dodecanoate, tetradecanoate, hexadecanoate). The synthesis of these esters from fatty acid has been reported earlier. Here, we report the Method of preparation with

excellent yield in short time fatty acid like palmitic, lauric, Myristic mole; (2.28 gram or 2.56gm; 0.01 mol, 2 gram) was poured in a halogenated alcohol like Bromo ethanol and chloro ethanol (0.080 gram and 1.23 gm; 0.01 mole) followed by the addition of a catalytic amount of sulphuric acid and stirred all the reactants for 2-3 hours at 60 °C. The progress of the reaction was determined by thin-layer chromatography (silica gel G coated 0.25 mm thick) glass plates using hexane; ethyl acetate (98:2) as mobile phase, In iodine the spots were visualized. In 3 hours reaction gets completed. In every case the impure reaction mixture was extracted with 50 ml of CHCl_3 and washed with water repeatedly (3*25 ml) and dried it over sodium Sulphate (Na_2SO_4) then under reduced pressure in rotary flash chloroform was removed from the impure reaction mixture, then purified an individual impure product using aqueous methanol i.e. (In a separating funnel the crude compound was taken and added 2-3 drops of water with Methanol. The purest form of product settled down at the bottom of the funnel). The resulting esters yield are reported in 2-chloroethyl hexadecanoate (1,92%) i.e. parenthesis, 2-chloroethyl tetradecanoate (2,92%) 2- chloroethyl dodecanoate (3,91%) , 2-bromoethyl hexadecanoate (4,90.1%) , 2- bromoethyl tetradecanoate (5,94.4%) and 2- bromoethyl dodecanoate (6,92%).

With 1- methyl imidazole in 1:1 molar ratio (0.01 mol) at 60 °C for 2 hour (for chloro esters) and 30 minutes (for bromo esters) each resulting esters (1-6) was immediately reacted i.e for 1, 3.19 g; for 2, 2.90 g; for 3, 2.62g ; for 4, 3.63 g; for 5, 3.35 g; for 6, 3.06 g and 1-methyl imidazole (0.082 g) were taken. In every case the impure product was crystallized with ether and subsequently recrystallized in cold acetone to get the pure compounds [7-12] which were characterized on the basis of ^1H , ^{13}C NMR IR experiments and mass spectral analysis as 3-(2-(hexadecanoyloxy) ethyl)-1- methyl - 1H-imidazol-3-ium chloride (8) 3-(2-dodecanoyloxy) ethyl -1-methyl - 1H-imidazol-3-ium chloride (9), 3-(2-(hexadecanoyloxy) ethyl) - 1-methyl - 1H-imidazol-3-ium bromide (10), 3-(2-tetradecanoyloxy) ethyl)-1-methyl-1H-imidazol -3-ium bromide (11), 3-(2-(dodecanoyloxy) ethyl - 1-methyl- 1H- imidazol-3-ium bromide (12).(scheme -1).

Spectral Results

3-(2-(hexadecanoyloxy)ethyl)-1-methyl-1H-imidazol-3-ium chloride [7]. White solid, Yield, 92%. Melting point 128 °C. IR (KBr pellet, cm^{-1}) 2910, 1744, 1643, and 1570. ^1H NMR (δ ppm CDCl_3): 0.89 (t, 3H, CH_3),

1.26 (br,s, chain 24H, (-CH₂)₁₂), 1.67 (t, 2H, CH₂ next to terminal methyl groups), 2.12 (t, 2H, 2XCH₂CO₂), 4.04 (s, 3H NCH₃), 4.15 (t, 2H, CO₂CH₂), 5.43 (t, 2H, N⁺CH₂), 7.43 (s, 2H, α CH to +ve Nitrogen of imidazole), 7.99 (s, 1H, β CH to +ve Nitrogen of imidazole), 9.56 (s, 1H, sand witched proton between to nitrogen of imidazole). ESI-MS positive ions m/z 393.3(100 %) {(M- 2Cl)-1)}⁺, 394.4 (90%) (M-2Cl)⁺ .

3-(2-(tetradecanoyloxy)ethyl)-1-methyl-1H-imidazol-3-ium chloride [8] - white solid, Yield, 95.5%. Melting point 122 °C. IR (KBr pellet, cm⁻¹): 2871, 1743, 1643, and 1570. ¹H NMR (δ ppm CDCl₃): 0.88 (t, 3H, CH₃), 1.26 (br, s, chain 20H, (-CH₂)₁₀), 1.64 (t, 2H, CH₂ next to terminal methyl groups), 2.32 (t, 2H, 2XCH₂CO₂), 4.11 (s, 3H NCH₃), 4.21 (t, 2H, CO₂CH₂), 5.51 (t, 2H, N⁺CH₂), 7.33 (s, 2H, α CH to +ve Nitrogen of imidazole), 7.49 (s, 1H, β CH to +ve Nitrogen of imidazole), 10.46 (s, 1H, sand witched proton between to nitrogen of imidazole). ESI-MS positive ions m/z 365.3 (100 %) {(M- 2Cl)-1)}⁺, 366.3 (90%) (M-2Cl)⁺ .

3-(2-(dodecanoyloxy)ethyl)-1-methyl-1H-imidazol-3-ium chloride (9) - white sticky solid, Yield, 92.5%. Melting point 117 °C. The IR (KBr Pellet, cm⁻¹): 2915, 1746, 1639, and 1570. ¹H NMR (δ ppm, CDCl₃): 0.85 (t, 3H, CH₃), 1.26 (br, s, chain 16H, (-CH₂)₈), 1.61 (t, 2H, CH₂ next to terminal methyl groups), 2.02 (t, 2H, 2XCH₂CO₂), 4.05 (s, 3H NCH₃), 4.16 (t, 2H, CO₂CH₂), 5.44 (t, 2H, N⁺CH₂), 7.29 (s, 2H, α CH to +ve Nitrogen of imidazole), 7.41 (s, 1H, β CH to +ve Nitrogen of imidazole), 10.52 (s, 1H, sand witched proton between to nitrogen of imidazole). ESI-MS positive ions m/z 337.2 (100 %) {(M- 2Cl)-1)}⁺, 338.2 (90%) (M-2Cl)⁺

3-(2-(hexadecanoyloxy)ethyl)-1-methyl-1H-imidazol-3-ium bromide [10] - white solid, Yield, 95.5%. Melting point 145 °C, IR (KBr pellet, cm⁻¹): 2870, 1741, 1641, 1570 and 1514. ¹H NMR (δ ppm CDCl₃): 0.84 (t, 3H, CH₃), 1.22 (br, s, chain 24H, (-CH₂)₁₂), 1.63 (t, 2H, CH₂ next to terminal methyl groups), 2.02 (t, 2H, 2XCH₂CO₂), 3.96 (s, 3H NCH₃), 4.19 (t, 2H, CO₂CH₂), 5.43 (t, 2H, N⁺CH₂), 7.24 (s, 1H, α CH to +ve Nitrogen of imidazole), 7.48 (s, 1H, β CH to +ve Nitrogen of imidazole), 10.26 (s, 1H, sand witched proton between to nitrogen of imidazole). ESI-MS Positive ions m/z 393.5 (20 %) {(M- 2Br)-1)}⁺, 394.2 (10 %) (M-2Br)⁺.

3-(2-(tetradecanoyloxy)ethyl)-1-methyl-1H-imidazol-3-ium bromide [11]. White solid, Yield 93.4%, Melting point 139 °C. IR (KBr pellet, cm⁻¹): 2860, 1742, 1642 and 1560. ¹H NMR (δ ppm CDCl₃): 0.88 (t, 3H,

CH₃), 1.26 (br,s, chain 20H, (-CH₂-)₁₀), 1.67(t, 2H, CH₂ next to terminal methyl groups), 2.02 (t, 2H, 2XCH₂CO₂), 4.09 (s, 3H NCH₃), 4.19 (t, 2H, CO₂CH₂), 5.46(t, 2H, N⁺CH₂), 7.42(s, 1H, α CH to +ve Nitrogen of imidazole), 7.54(s, 1H, β CH to +ve Nitrogen of imidazole), 10.18(s, 1H, sandwiched proton between to nitrogen of imidazole). ESI-MS positive ions m/z 365.3 (100%) {(M- 2Br)-1)}⁺, 366.2 (40 %) (M-2Br)⁺.

3-(2-(dodecanoyloxy)ethyl)-1-methyl-1H-imidazol-3-ium bromide [12]. white sticky solid, Yield 93.4%, Melting point 131 °C. IR (KBr pellet, cm⁻¹): 2910, 1746, 1640 and 1574. ¹H NMR (δ ppm CDCl₃): 0.84 (t, 3H, CH₃), 1.22(br,s, chain 16H, (-CH₂-)₈), 1.63(t, 2H, CH₂ next to terminal methyl groups), 2.02 (t, 2H, 2XCH₂CO₂), 3.96 (s, 3H NCH₃), 4.19 (t, 2H, CO₂CH₂), 5.43(t, 2H, N⁺CH₂), 7.24(s, 2H, α CH to +ve Nitrogen of imidazole), 7.48(s, 1H, β CH to +ve Nitrogen of imidazole), 10.26(s, 1H, sandwiched proton between to nitrogen of imidazole). ESI-MS positive ions m/z 337.9 (50%) {(M- 2Br)-1)}⁺, 338.1 (40%) (M-2Br)⁺.

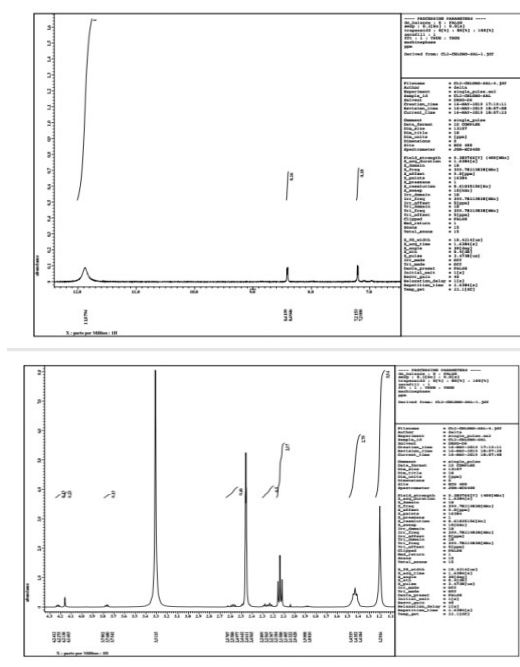
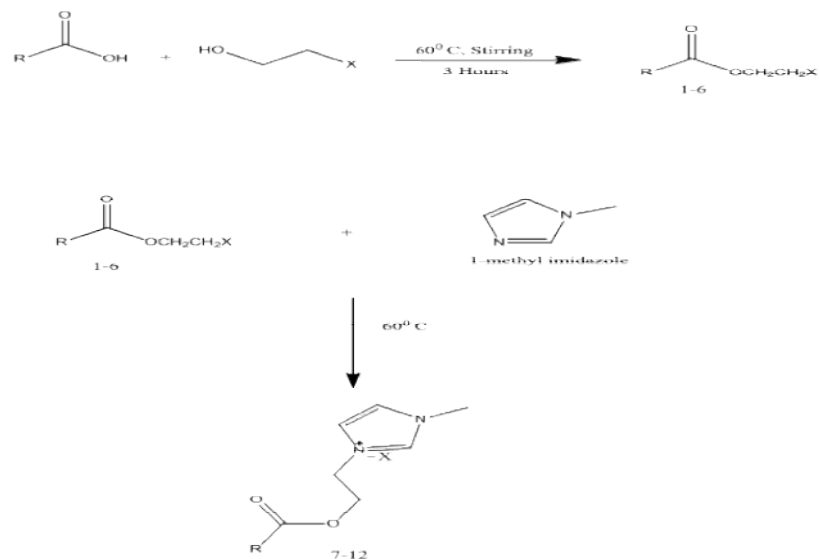


Figure 3.1: NMR spectra of synthesized chloro sol-based cationic based surfactant using 1-methyl imidazole



Reaction's scheme 1st

Where X = Cl, Br and R = CH₃ (CH₂)₁₀-; CH₃(CH₂)₁₂-and CH₃(CH₂)₁₄-.

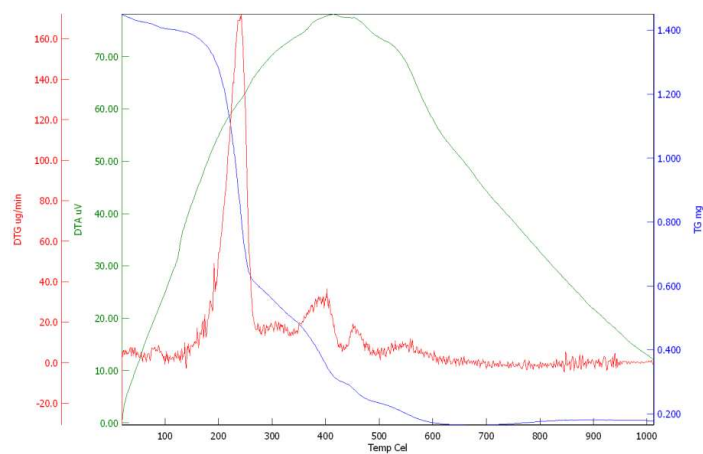


Fig 3.2: TGA and DTA analysis of chloro sol-based cationic based surfactant using methyl imidazole

TGA and DTA analysis was performed to understand the thermal stability of synthesized surfactants. Fig. 3.2 shows three endothermic peaks in differential thermal analysis (DTG) at temperatures of 260 °C, 390 °C and 460 °C respectively. Almost 30 wt% loss at 250 °C attributed to the degradation of methyl imidazole and undergoes rapid degradation at 392°C, indicating a reasonably good thermal stability. This shows that thermal stability of surfactants is up to 500 °C whereas synthesized cationic surfactants are stable up to 262 °C. The TGA measurement indicated that the thermal stability of these long-chain imidazolium-based cationic surfactant increases with an increase in the chain length.

Conclusions

The palmitic acid, chloroethanol and methyl imidazole were used as precursor during surfactant synthesis at moderate temperature. The synthesized cationic surfactant showed biodegradability. These were characterized by TGA, NMR, and by conductometer. The synthesis process followed the quaternization by imidazolium. These surfactants can be used as cleaning agent and disinfectant.

References

- [1] A. Patist, S.S. Bhagwat, K.W. Penfield, P. Aikens, and D.O. Shah (2000) Measurement of Critical Micelle Concentrations of Pure and Technical-Grade Nonionic Surfactants, *Journal of Surfactants and Detergents*: 3, 53-58.
- [2] P. Daripa, S. Dutta, Modeling and simulation of surfactant-polymer flooding using a new hybrid method. *Journal of computational physics*. 15 April 2017, volume 335, 249-282.
- [3] Ali, M. Tariq, R. Patel, A. Firdos, Type and application of some common surfactants. *Journal of Chemical and Pharmaceutical Research, Colloid Polymer Science*, 2008, 183-286.
- [4] B. Giri, K.S. Patel, N.K. Jaiswal, S. Sharma, B. Ambade, W.S. Wang, L.M. Simonich, B.R.T. Simoneit. Type and application of some common surfactants, *Journal of Chemical and Pharmaceutical Research Atmospheric Res.*, 2013, 12(3), 312-324.
- [5] L.L. Schramm, E.N. Stasiuk and D.G. Marangoni, Surfactant and their application, Annual Reports Section C, (Physical Chemistry) August 2003.
- [6] W.K. Tenside, Type and application of some common surfactants, *Journal of Chemical and Pharmaceutical Research, Surfactant Deterg*, 1990, 297-300.
- [7] J.A.V. Costa, V.G. Martins, in Current Developments in Biotechnology and Bioengineering, ScienceDirect Topics, 2018.
- [8] A. Gurao, Ph.d. scholar, Biosurfactants and their application in microbubble preparation, Jan 29, 2014.
- [9] V.C. Ginkel, D.R. Karsa, M.R.P. Blackie, Academic and Professional, Biodegradability of Laundry Detergent Surfactants, *International Journal of Advance Research and Innovation*, 2017, Volume 5, 130-136.
- [10] Van Haesendonck, I.P.H. and E.C.A. Vanzeveren. Rhamnolipids in bakery products, *International Application Patent (PCT)*, Washington, DC., USA, W. O. 2004/040984.
- [11] R.D. Cassia, F.S. Silva, D.G. Almeida, R.D. Rufino, J.M. Luna, V.A. Santos and L.A. Sarubbo, Applications of Biosurfactants in the Petroleum Industry and the

- Remediation of Oil Spills, *International Journal of molecular science*. 2014 Jul; 15(7): 12523–12542.
12. H.C.Speel, Reinhold Publishing Corp, New York, 1952; 227-254.
- [13] M.S.Bakshi, J. Singh, G.Kaur, *Colloid and Interface Science Journal of Chemical and Pharmaceutical Research*, 2005, 284(2), 403-412.
- [14] L.Minhee, K.Hyunmin, D.Wonhong, J. Elsevier, Type and application of some common Surfactants, *Journal of Chemical and Pharmaceutical Research*, 2005, 39(1), 139–146.
- [15] J.C.Fountain, R.C. Starr, T.M. Middleton, M.G.Beikrich, C.Tayler, D.Hodge, *Ground Water*, 1996, 34, 910–916.
- [16] U.Alon, J.C. CRC, P.B. Raton, Type and application of some common Surfactants 1993.
17. P.Bruheim, K. Eimhjellen, Chemically emulsified crude oil as substrate for bacterial oxidation: Differences in species response. *Can. J. Microbiology*, 1998, 442: 195-199.
- [18] L.H.Huber, Type and application of some common surfactants, *Journal of Chemical and Pharmaceutical Research* 1987, 61, 377-382.
- [19] S. K. Khatib, J. Bullon, J. Vivas A. Bahsas Y. R-Oballos, R. Marquez A. Forgiarini J. L. Salager (2019) Synthesis, Characterization, Evaluation of Interfacial Properties and Antibacterial Activities of Dicarboxylate Anacardic Acid Derivatives from Cashew Nut Shell Liquid of *Anacardium occidentale* L, *Journal Surfactant and Detergent*.
- [20] W. Harrison, progress Toward an Artificial Liver Transplant – NIH Research Matters. *National Institutes of Health (NIH)*, Archived from the original on 5 August 2012.
- [21] H.Henau, E. Matthijs, W.D. Hopping, *International Journal of Environment and Analytical Chemistry*, 1986, 26(2) 279-293.
- [22] S. Vijayakumar, V. Saravanan, Biosurfactants-Types, Sources and Applications. *Research Journal of Microbiology*, 2015, 10: 181-192.
- [23] I. Kralova, J. Sjöblom, Surfactants used in food industry: a review, *J. Dispersion Sci. Technol.* 30 (2009) 1363–1383.
- [24] R. Pugh, Foaming, foam films, antifoaming and defoaming, *Adv. Colloid Interface Sci.* 64 (1996) 67-142.
- [25] L.L. Schramm, *Foams: Fundamentals and Applications in the Petroleum Industry*, American Chemical Society, Washington DC, 1994.

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Chapter: 13

Use of Organic Farming for Sustainable Agriculture and Better Environment

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Abstract

Organic farming is a farming techniques that sustains enhance and maintains the quality of the ecosystems. The approach of organic farming is depended upon variety of building elements, organic manures, crop rotation, vermicompost, nitrogen fixing microorganism, organic residue, bio-fertilizer, bio-pesticide, kitchen waste. Organic agriculture can contribute to meaningful socio-economic and ecologically sustainable development, especially in poorer countries. This is due on the one hand to the application of organic principles, which means efficient management of local resources (e.g. local seed varieties, manure, etc.) and therefore cost effectiveness. What can organic agriculture contribute to achieving socially and ecologically sustainable development in poor countries. Central to organic agriculture are promotion of soil fertility, biodiversity conservation (e.g. native flora and fauna), production methods adapted to the locality and avoidance of chemical inputs. These methods, together with cultivation of a diverse range of crops, stabilize the delicate ecosystems in the tropics and reduce drought sensitivity and pest infestation. Organic agriculture reduces the risk of yield failure, stabilizes returns and improves the quality of life of small farmers.

Key Words : Crop management, Nutrient management, Biodiversity, Environmental benefits , organic components

Introduction

India, the beginning of Green Revolution in Indian Agriculture in 1965-66, the fertilizer consumption got a huge momentum for sustaining the needs of burgeoning population. Consequently, we reached our targets and become

self-sufficient in food grain production. However, the hazards of the intensive agricultural system are threatening as they drastically affect the ecological balance. Thus, we started thinking towards organic farming (OF) system approach which was existing earlier (ancient time) in our society.

In modern age, increasing pollution levels in every sphere of life is the key challenge in sustainable development of our environment. Increasing demands and lavish life style of people causes environmental deterioration. Our agricultural system is also affected by pollution. Modern agricultural practices such as use of synthetic fertilizers, pesticides etc. to maximize crop yield contributes in environmental pollution. These approaches ultimately disturb the nutrient balance of soil and therefore reduce soil fertility. To deal with the existing problem, Organic farming provides a natural way of crop cultivation by using environment friendly, animal and plant based local organic resources that are highly enriched in nutrients required for crop plants. It enhances the microbial activities and increases soil health. Organic farming is an efficient and promising agricultural approach for environmental sustainability as it provides yield stability, improved soil health, no environmental concerns, organic food and reduction in the use of synthesized fertilizers. There are different agricultural approaches working on reducing environmental concerns but use of organic farming, no doubt, the best scientifically proved environment friendly approach in maintaining environmental balance of our agriculture.

"Organic agriculture is a holistic production management system which promotes and enhances agro-ecosystem health, including biodiversity, biological cycles, and soil biological activity. It emphasises the use of management practices in preference to the use of off-farm inputs, taking into account that regional conditions require locally adapted systems. This is accomplished by using, where possible, agronomic, biological, and mechanical methods, as opposed to using synthetic materials, to fulfil any specific function within the system." (FAO/WHO Codex Alimentarius Commission, 1999).

riculture and ecological systems.

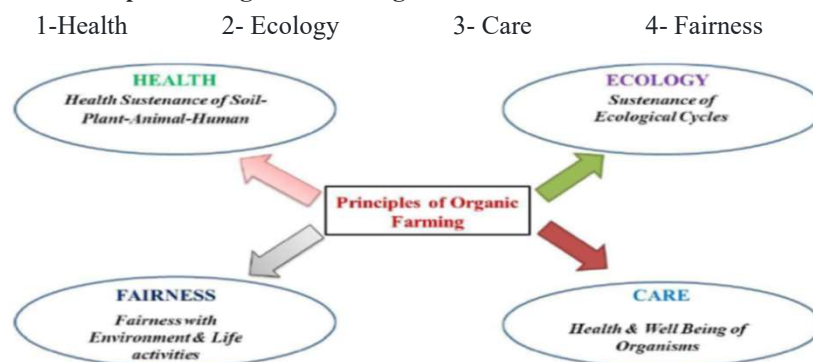
The approach of organic farming is depended upon variety of building elements. Organic manure, Crop rotation, Vermicomposting, Nitrogen fixing microorganisms, organic residue, crop residue, bio fertilizers, bio pesticides, kitchen waste, sludge and biogas are some of the main elements. These are proved to be very useful in maintaining soil health and texture. Their use is ecofriendly and helps in developing sustainable agriculture. Apart from these, the organic agricultural approach follows some basic principles of Health, Ecology, Fairness and Care. These principles are the core of organic

agriculture that ensures sustainable development. In organic farming, more emphasis is given to the environmental health. Due to its nature friendly approach, it helps in reducing soil, water and air pollution. Therefore, acts as natural tool for environmental protection and sustainable development. Farmer's use crop rotation, bio fertilizers etc. to maintain enrichment of nitrogen and other essential crop nutrients. Use of chemicals in the field is prohibited and ecofriendly products are taken into consideration. Vegetables are also grown in the field using the organic farming approach, ensuring availability of organic vegetables in the food markets.

Aims of Organic Farming

- 1- Exclusion of agrochemicals
- 2- Maintenance of natural balance
- 3- Conservation or enhancement of biodiversity and eco-systems services.
- 4- Prevention of pollution.
- 5- Reduction in use of fossil fuel energy in agriculture
- 6- Development of more sustainable and productive agricultural system.

Principals of Organic Farming



Component of Organic Farming

- 1- **Crop and Soil Management:** The systems aim in enhancing the organic matter levels in soil to maintain the long term fertility of soil. In this component, we give stress in selection of variety, timely sowing, crop rotation, green manuring, intercropping with with legumes, etc.
- 2- **Nutrient Management:** This is dealt with the use of organic materials such as farmyard manure, compost, vermicompost, crop residues, green manures, and cover crops. Crop rotation and biofertilizers are also included for their key role in nutrient cycling.

- 3- **Plat Protection:** Insect, pathogens, and other pests are controlled by primarily relying on crop rotations, natural predators resistant variety, diversity and tillage, Thereafter, botanical, thermal, and chemical interventions are applied as a last resort under restricted conditions.
- 4- **Livestock Management:** Livestock are reared by keeping full attention to their evolutionary adaptations, behavioral needs, and welfare issues (nutrition, shelter, breeding.etc).
- 5- **Soil and Water Conservation :**Run off which erodes the soil can be prevented by contour cultivation , contour bunding, terracing ,grassing and grassed waterways etc, In-situ conservation techniques like broad bed and furrow system ridge and furrow system, inter row water harvesting, scooping , etc. can be adopted in drylands areas.

Selection of crop is very important in farming to serve many purposes like pigeon pea and moth bean are drought legumes, forage and cover crops. These can be grown in arid and semi-arid regions to earn maximum benefits. They can be used for combating soil erosion problems and recycling the nutrients.

Environmental Benefits of organic Agriculture

Sustainability over the long term: Many changes observed in the environment are long term, occurring slowly over time. Organic agriculture considers the medium- and long-term effect of agricultural interventions on the agro-ecosystem. It aims to produce food while establishing an ecological balance to prevent soil fertility or pest problems. Organic agriculture takes a proactive approach as opposed to treating problems after they emerge.

Soil: Soil building practices such as crop rotations, inter-cropping, symbiotic associations, cover crops, organic fertilizers and minimum tillage are central to organic practices. These encourage soil fauna and flora, improving soil formation and structure and creating more stable systems. In turn, nutrient and energy cycling is increased and the retentive abilities of the soil for nutrients and water are enhanced, compensating for the non-use of mineral fertilizers. Such management techniques also play an important role in soil erosion control. The length of time that the soil is exposed to erosive forces is decreased, soil biodiversity is increased, and nutrient losses are reduced, helping to maintain and enhance soil productivity. Crop export of nutrients is usually compensated by farm-derived renewable resources but it is sometimes necessary to supplement organic soils with potassium, phosphate, calcium, magnesium and trace elements from external sources.

Water: In many agriculture areas, pollution of groundwater courses with synthetic fertilizers and pesticides is a major problem. As the use of these is prohibited in organic agriculture, they are replaced by organic fertilizers (e.g. compost, animal manure, green manure) and through the use of greater biodiversity (in terms of species cultivated and permanent vegetation), enhancing soil structure and water infiltration. Well managed organic systems with better nutrient retentive abilities, greatly reduce the risk of groundwater pollution. In some areas where pollution is a real problem, conversion to organic agriculture is highly encouraged as a restorative measure (e.g. by the Governments of France and Germany).

Air and climate change: Organic agriculture reduces non-renewable energy use by decreasing agrochemical needs (these require high quantities of fossil fuel to be produced). Organic agriculture contributes to mitigating the greenhouse effect and global warming through its ability to sequester carbon in the soil. Many management practices used by organic agriculture (e.g. minimum tillage, returning crop residues to the soil, the use of cover crops and rotations, and the greater integration of nitrogen-fixing legumes), increase the return of carbon to the soil, raising productivity and favouring carbon storage. A number of studies revealed that soil organic carbon contents under organic farming are considerably higher. The more organic carbon is retained in the soil, the more the mitigation potential of agriculture against climate change is higher. However, there is much research needed in this field, yet. There is a lack of data on soil organic carbon for developing countries, with no farm system comparison data from Africa and Latin America, and only limited data on soil organic carbon stocks, which is crucial for determining carbon sequestration rates for farming practices.

Biodiversity: Organic farmers are both custodians and users of biodiversity at all levels. At the gene level, traditional and adapted seeds and breeds are preferred for their greater resistance to diseases and their resilience to climatic stress. At the species level, diverse combinations of plants and animals optimize nutrient and energy cycling for agricultural production. At the ecosystem level, the maintenance of natural areas within and around organic fields and absence of chemical inputs create suitable habitats for wildlife. The frequent use of under-utilized species (often as rotation crops to build soil fertility) reduces erosion of agro-biodiversity, creating a healthier gene pool - the basis for future adaptation. The provision of structures providing food and shelter, and the lack of pesticide use, attract new or re-colonizing species to the organic area (both permanent and migratory), including wild flora and fauna (e.g. birds) and organisms beneficial to the

organic system such as pollinators and pest predators. The number of studies on organic farming and biodiversity increased significantly within the last years. A Recent Study Reporting On A meta-Analysis Of 766 Scientific Papers concluded that organic farming produces more biodiversity than other farming systems.

Genetically modified organisms: The use of GMOs within organic systems is not permitted during any stage of organic food production, processing or handling. As the potential impact of GMOs to both the environment and health is not entirely understood, organic agriculture is taking the precautionary approach and choosing to encourage natural biodiversity. The organic label therefore provides an assurance that GMOs have not been used intentionally in the production and processing of the organic products. This is something which cannot be guaranteed in conventional products as labelling the presence of GMOs in food products has not yet come into force in most countries. However, with increasing GMO use in conventional agriculture and due to the method of transmission of GMOs in the environment (e.g. through pollen), organic agriculture will not be able to ensure that organic products are completely GMO free in the future. A detailed discussion on GMOs can be found in the FAO publication "Genetically Modified Organisms, Consumers, Food Safety and the Environment".

Ecological services: The impact of organic agriculture on natural resources favours interactions within the agro-ecosystem those are vital for both agricultural production and nature conservation. Ecological services derived include soil forming and conditioning, soil stabilization, waste recycling, carbon sequestration, nutrients cycling, predation, pollination and habitats. By opting for organic products, the consumer through his/her purchasing power promotes a less polluting agricultural system. The hidden costs of agriculture to the environment in terms of natural resource degradation are reduced.

A critical review of the relationships between organic agriculture and the environment as well as other aspects is provided by IFOAM and is presented under the shape of a list of Criticisms and Frequent Misconceptions about Organic Agriculture with Corresponding Counter-Arguments.

Organic Farming Need for Better Agriculture Practices

Adverse effects of chemical pesticide have been reported on both the abiotic and biotic component of environment. The former are exemplified by residues in soil, air, water, food etc and the latter by phyto-toxicity, residue, vegetation changes etc. in plants and physiological changes, genetic

disorders etc. in mammals, avian, insect and other organisms. Entry of pesticides into the food chain coupled with their bioaccumulation and biomagnifications trigger effects of unforeseen consequences. Chemicals like methyl bromide; chlorofluorocarbons etc. are established culprits for depletion of the ozone layer.

There are several reports of adverse effects of chemical pesticides on human beings from Punjab, Andhra Pradesh, Kerala and other parts of the country where excessive use in certain pockets of these states has led to higher incidence of cancer and other diseases. Recent examples of pesticide toxicity are of Endosulphon in Kerala and Karnataka, where the Hon'ble Supreme Court has to intervene to stop its sale.

Simultaneously, indiscriminate use of fertilizer, particularly the nitrogenous, has led to substantial pollution of soil, air and water. Fertilizer contamination of ground waters has led to eutrophication of lake and river waters causing depletion of oxygen and even death of aquatic life, nitrate pollution, increased emissions of gaseous N and mental toxicities. The presence of nitrates in potable water has been blamed for health hazards such as birth defects, impaired nervous system, cancer and methaemoglobinemia (The blue baby syndrome).

Conclusions in the organic farming:

Organification is the need of the hour to resolve the challenges of agriculture. Low economic return in the initial stages restrains farmers to adopt organic farming of practice. But this indicates the lack of knowledge about the merits of organic farming among farmers. Government agencies and schemes should try to fill this gap by giving demonstrations of the techniques of organic farming to make the farming community expert in the alternative methods of the conventional farming. The systems require good managerial skills to handle all the components in the right way to harness maximum benefits of organic farming. Therefore, the managers of farms also need trainings to enhance the sustainable utilization of resources. More research should be conducted for validation of organic methods in the field, as India has huge potential for organic crop production.

- The common perception that organic food is by default better, or is an ideal way to reduce environmental impact is a clear misconception. Across several metrics, organic agriculture actually proves to be more harmful for the world's environment than conventional agriculture.
- The debate between organic and intensive agriculture advocates is often needlessly polarized. There are scenarios where one system proves better than the other, and vice versa. If I were to advise on where and

when to choose one or the other, I'd advise trying to choose organic pulses and fruits, but sticking with non-organic for all other food products (cereals, vegetables, dairy and eggs, and meat).

The organic-conventional debate often detracts from other aspects of dietary choices which have greater impact. If looking to reduce the environmental impact of your diet, *what* you eat can be much more influential than *how* it is produced.

Greenhouse gas impacts between organic and conventional systems are typically less than a multiple of two. Compare this to the relative differences in impacts between food types where, as shown in the charts below, the difference in land use and greenhouse gas emissions per unit protein between high-impact meats and low-impact crop types can be more than 100-fold. If your primary concern is whether the potato accompanying your steak is conventionally or organically produced, then your focus is arguably misplaced from the decisions which could have the greatest impact.

References

- ❖ Gautam H.R, Bhardwaj M.L. (2011) Better practices for sustainable agricultural production and The relative difference in land use and better environment. A journal on Rural Development Kurukshetra: Pp. 3-7.
- ❖ Kumar S, (2018) Principles of organic farming : Pp1-27
- ❖ Sarkar D., Ganguly S., and Shikha (2018) organic farming for sustainable environment. A Journal on Rural Development Kurukshetra : Pp 27-30

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Chapter 14

Synthesis Of Cu:TiO₂ Nanocomposites And Its Photocatalytic Degradation of Acetic Acid In Waste Water

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Abstract

In the present study, to prepare the nanocomposites of titania by solution impregnation method and photocatalytic degradation of some target materials such as acids, dyes, and glucose in the presence of nanocomposites of titania which was prepared by the solution impregnation method, was done. The resulting powders were copper titanium dioxide. The alcohol route of synthesis, adopted here, yielded dark black homogeneous powder of copper titanium dioxide. The obtained yield of the product was more than 90% of the expected theoretical yield. In which the material has the nanodimension. The prepared material was subjected to XRD analysis which gives the information about the presence of phase rutile and anatase both phases were present in the prepared sample. It is found that, in samples sintered at 400 °C both anatase and rutile phases were presented and rutile phase was more dominant, while in samples without sintered the exclusive formation of polycrystalline anatase and rutile phase separately was occurred. Applying the Scherrer's calculations through which particle size was found 16 and 72 nm in case of copper titania and pure titania respectively. The prepared sample of titania and copper titania were subjected to photocatalytic degradation of acids e.g. oxalic acid, tartaric acid, citric acid and acetic acid was done. The degradation of acetic acid occurs efficiently. The prominent degradation was found in case of oxalic acid in the presence of nanocomposites Cu-TiO₂.

1. Introduction

Photocatalytic degradation is a rapidly expanding technology for the treatment of wastewater contaminated with organic pollutants such as acids, dyes, pesticides and non-biodegradable materials. Photocatalytic degradation is the advanced oxidation process to degrade the water contaminants such as acids, dyes, pesticides and non-biodegradable materials, which exhibit chemical stability and resistance to biodegradation. In recent years interest has been focused

on the use of semiconductor materials as photocatalysts for the removal of organic and inorganic species from aqueous or gas phase. This method has been suggested in environmental protection due to its ability to oxidise the organic and inorganic substrates.

Several catalysts have been studied as photocatalysts for the degradation purpose. These include: TiO_2 [26-28], ZnO [22,25], ZrO_2 , SnO_2 and WO_3 [29-32], ZnS [22], CdS [20,21], $\alpha\text{-Fe}_2\text{O}_3$, $\text{g-Fe}_2\text{O}_3$, [23,24], Cr_2O_7 [34], $\text{AgCl/Al}_2\text{O}_3$ [35], niobium oxides [36], lanthanide tantalates (LnTaO_4 where Ln can be La, Ce, Pr, Nd and/or Sm) [37], ZnO/TiO_2 [38], $\text{TiO}_2/\text{SiO}_2$ and $\text{TiO}_2/\text{Al}_2\text{O}_3$ [39]. Titanium dioxide (TiO_2), commonly known as Titania, is one of the most commonly used photocatalysts. Because of its high oxidative power, stability, and non-toxicity, it promises a broad range of uses as a photocatalysts. Advantage of using TiO_2 as photo-catalyst are: (a) using TiO_2 , the process occurs under ambient conditions. (b) using TiO_2 , the oxidation of the substrate to CO_2 is complete in most cases and (c) it is comparatively inexpensive and remains quite stable in contact with different substrate. TiO_2 has also played a leading role in the active research for the utilization of solar energy. The TiO_2 based, dye sensitized, photo-electrochemical cells are receiving a great deal of attention as a possible candidate for converting solar energy into electricity on a large scale.

Extensive investigations have been reported on the photocatalytic degradation of organic compounds such as chlorinated compounds, chloro- and nitrophenols, dyes, pesticides and aromatic compounds. However, the possibility of using photocatalytic reactions for the degradation of trace acids dyes and pesticides in water have been receiving much attention in recent years. Semiconductor- mediated photocatalytic oxidation is becoming one of the possible environment- friendly techniques for the removal of trace organic pollutants, including pesticides in water. Titanium dioxide is a well-known photocatalyst for water and air treatment as well as for catalytic production of gases. The general scheme for the photocatalytic destruction of organics begins with its excitation by supra band gap photons, and continues through redox reactions where OH radicals, formed on the photocatalyst surface, play a major role.

2. Experimental

2.1 Synthesis of TiO₂.

Titanium dioxide (TiO₂) nanoparticles were synthesized by the modified sol-gel method [30,31]. Titanium tetraisopropoxide (Ti[OCH(CH₃)₂]₄ (TTIP), Aldrich, England), absolute ethanol (C₂H₅OH, Merck, Germany), and ammonia (NH₃, Merck, Germany) were used as the starting materials for synthesizing TiO₂ nanoparticles. Titanium tetraisopropoxide (20 mL) was dissolved in 250 mL absolute ethanol and mixed until a homogeneous solution was obtained. The mixture of TTIP and absolute ethanol was loaded into a cellophane membrane and suspended for 1 h in a clear solution containing 1 : 1 ratio of ethanol (95%) and deionized water and 7 mL of ammonia solution (25%) as shown in Figure 1. After the completion of the dialysis process, the suspension was centrifuged at 7500 rpm for 10 min, washed with deionized water, and then dried in an oven at 60°C for 24 h. The white powders were then calcined in a furnace at a temperature of 400°C for 3 h.

2.2 Synthesis of Cu:TiO₂ nanocomposites

In this study, Cu:TiO₂ nanocomposites were prepared by solution impregnation method. In this method suitable quantity of prepared TiO₂ was dispersed in alcoholic solution of copper acetate. The dispersion is agitated continuously for 4 hour at temperature which is just below of boiling point of alcohol. After the treatment the residue will removed through filtration and will sintered for 1 hour in presence of air at 400 °C by kipping it in a silica boat inside muffle furnace. After sintering and slow anilling to room temperature. Content was taken out from furnace and was stored in closed and air tight bottles and was used as photocatalyst.

2.3: Photo-degradation studies

Photo-catalysed oxidative degradation reaction of organic substrates is holds lot of potential in pollution abatement as well as in synthetic Organic Chemistry. Although in literature several photocatalyst have been cited for this purpose many of then suffer from one or more disadvantage, particularly with regard to either then being highly expensive and chemically unstable. TiO₂ is well known semiconductor that has also been widely used as photocatalyst. In this study, to investigate the photo-degradation behavior of a

prepared TiO_2 vis-à-vis synthesized Cu-TiO_2 nanocomposites towards photo-degradation of acetic acid

3. Result

3.1. X-ray diffraction analysis

Phase identification in the samples was attempted by analyzing them using X-Ray Diffractometer (Bruker AXS D8 Advance System, Germany). The obtained X-Ray diffraction patterns of few representative samples are shown in Figures 4.1 and 4.2. The observed pattern of peaks, when compared with the standard JCPDS database, suggested that, in commercially obtained TiO_2 samples, major peaks at 2θ angles 25.5° , 37.2° , 48.3° and 55.4° correspond to anatase phase, whereas major peaks at 2θ angles 26.9° , 28.2° , 42.6° and 54.2° indicate the presence of rutile phase. In case of Cu-TiO_2 sample, the observed XRD pattern indicates not only a decrease in the peak intensity, compared to TiO_2 , but even the absence of some originally observed TiO_2 peaks. This is, probably, due to the decrease in the crystallinity, grain fragmentation and partial amorphization, when the samples were wet impregnated by Nickel acetate.

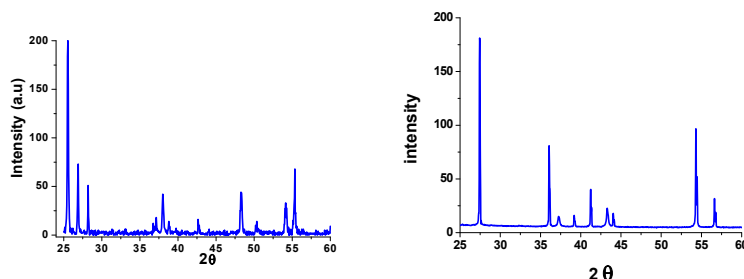


Fig-.2: Observed XRD pattern of TiO_2 & Cu-TiO_2

3.2.2: Determination of Average size of Particles/ Grains in samples

Utilizing the observed X-ray diffraction data of samples, Scherrer's calculations were attempted to know the average size of articles/grains in the samples. Although, Scherrer's calculations are only approximate in nature, but definitely provide a first-hand idea of the average size of the particles/ grains in the samples, which may be quite accurate, provided the size of particles/ grains is below 100 nm. The results of Scherrer's calculations are presented in Table 1.

The results suggest average size of the particles/ grains in the samples lying in nm range.

TABLE -1: Average size of particles/grains in the samples of TiO₂ and Cu-TiO₂

sample	Particle size from Scherrer's calculation *(nm)
Cu-TiO ₂	80
TiO ₂	35

3.2.3. SEM (Scanning Electron Microscopy)

The morphology of the samples was investigated by scanning electron microscopy and it resumes the most interesting outcomes. Fig 3 A and 3B clearly show that both the prepared samples are obtained agglomerate in nanometric dimension. The doping of copper is indicating that the particle size reduce due the penetration of copper in the lattice of titanium dioxide.

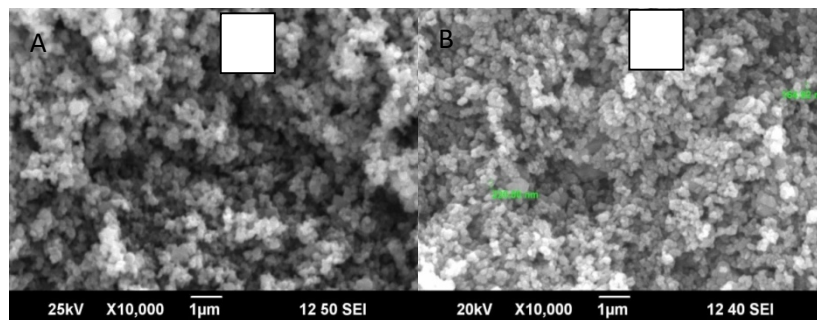


Fig. 3: Observed SEM image of (A) TiO₂ (B) Cu-TiO₂

3.2.4. Surface area analysis (B.E.T)

The specific surface area, pore volume and average pore size of the TiO₂ and Cu-TiO₂ as-prepared photocatalyst were characterized by using the N₂ adsorption technique *BET*. Table -2 summarizes their physical properties. The TiO₂ modified by Nickel are fragmented to some extent during thermal treatment, leading to a marked increase of the *BET* surface areas and the average pore radius size and decreasing of the pore volume.

Table-2: Phase surface areas, pore volume, average particle sizes of TiO₂ and Cu-TiO₂

Sample	Phase	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore radius (nm)
TiO ₂	R+A	6.4	0.018	11
Cu-TiO ₂	R+A	13.2	0.031	6

3.3: Photo-degradation of acetic acid

TABLE -9: Observed variation in Acetic acid concentration with time in the reaction mixture

Reaction Time (min)	Amount of Photocatalyst: 20 g/ L					
	Reaction Temperature 30 °C					
	TiO ₂			Cu-TiO ₂		
	10.6×10 ⁻³ M	5.3×10 ⁻³ M	2.65×10 ⁻³ M	10.6×10 ⁻³ M	5.3×10 ⁻³ M	2.65×10 ⁻³ M
0	10.6	5.3	2.65	10.6	5.3	2.65
60	8.8	4.5	2.20	8.0	4.2	2.0
120	7.6	4.0	1.8	6.6	3.5	1.4
180	6.8	3.4	1.4	4.2	3.0	1.0
240	5.8	3.0	1.0	3.2	2.2	0.5

TABLE -10: Observed variation in Acetic acid concentration with time in the reaction mixture

Reaction Time (min)	Initial concentration of Acetic acid: 10.6×10 ⁻³ M			
	Reaction Temperature 30 °C			
	TiO ₂		Cu-TiO ₂	
	Amount of TiO ₂ 20 g/ L	Amount of TiO ₂ 40 g/ L	Amount of Cu-TiO ₂ 20 g/ L	Amount of Cu-TiO ₂ 40 g/ L
0	10.6	10.6	10.6	10.6
60	8.8	8.4	8.0	6.4
120	7.6	7.2	6.6	6.2
180	6.8	6.2	4.2	4.0
240	5.8	5.4	3.2	3.0

TABLE -11: Observed variation in Acetic acid concentration with time in the reaction mixture

Reaction Time (min)	Initial concentration of Acetic acid: 10.6×10^{-3} M					
	Amount of Photocatalyst: 20 g/ L					
	WPC		TiO ₂		Cu-TiO ₂	
	RT 30 °C	RT 40 °C	RT 30 °C	RT 40 °C	RT 30 °C	RT 40 °C
0	10.6	10.6	10.6	10.6	10.6	10.6
60	10.6	10.6	8.8	7.4	8.0	6.4
120	10.6	10.6	7.6	6.5	6.6	5.2
180	10.6	10.4	6.8	5.2	4.2	3.8
240	10.6	10.2	5.8	4.0	3.2	2.4

3.5. Effect of Temperature

The effect of system temperature on photocatalysis has not attracted enough attention. But In present research, it is found that the temperature has a great effect on the photodegradation of methyl Red. The photocatalytic efficiency can be increased about 2-3 times if the temperature increased from 30 °C to 40 °C. Because the solar energy include UV light, which can be used to activate the photocatalytic course, which is increase the temperature of photocatalytic system. The experiments showed that Methyl Red cannot be photodegraded if TiO₂ or UV light was not used, indicating that Methyl Red cannot be pyrolyzed by heating with the heating temperature which was less than 40 °C and self degraded by absorbing irradiation. Only when TiO₂ and UV light were both used, the Methyl Red was efficiently degraded shown in table 3.2-3.3. The obvious decrease of concentration of dye shows that the TiO₂ and Cu-TiO₂ can serve as an effective photocatalyst.

3.6 Effect of concentration

Effect of dye concentration Keeping the catalyst loading concentration constant at 25 g/liter of the dye solution, the effect of varying amounts of the acid was studied on its rate of its degradation (from 50×10^{-4} to 25×10^{-4} M) as given in Table 3.2 and 3.3. With increasing concentration of MB the rate of degradation was found to decrease. This is because as the number of dye molecules increase, the amount of light (quantum of photons) penetrating the dye solution to reach the catalyst surface is reduced owing to the hindrance in the path of light. Thereby the formation of the reactive hydroxyl and superoxide radicals is also simultaneously reduced. Thus there

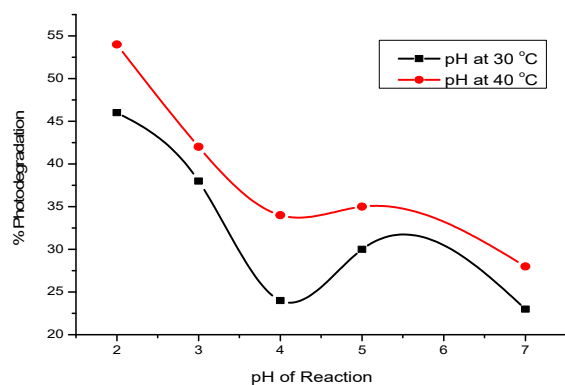
should be an optimum value maintained for the catalyst and the dye concentration, wherein maximum efficiency of degradation can be achieved.

3.7. Effect of pH

The photodegradation reaction was also carried out under varying pH conditions from (2 to 7), by adjusting with NaOH, with TiO_2 kept at constant amounts of 25 g/ L of citric acid solutions. The reaction was found to have low rates at neutral ranges of pH. While at lower cases it was found to increase at 2 to 3 pH. The photodegradation is maximum at 2-3 pH but at 4 pH the photodegradation is rapidly decrease and after increasing pH the photodegradation slightly increase. This implies that acidic conditions are favourable towards the formation of the reactive intermediates that is hydroxyl radicals is significantly enhanced, which further help in enhancing the reaction rate. On the other hand in neutral medium conditions the formation of reactive intermediates is relatively less favourable and hence less spontaneous.

Table-12: Effect of pH on photodegradation of acids with temperature.

pH	Degradation % at 30 °C	Degradation % at 40 °C
2	46	54
3	38	42
4	24	34
5	30	35
7	23	28



3.8. Effect of photocatalyst

It is clear from the results shown in table 3.2 - 3.23 and fig.3.4 - 3.5 that both TiO_2 and Cu-TiO_2 are proving as an effective photo-catalyst for the degradation of Acids. However Cu-TiO_2 seems to be more effective as photo-catalyst for the degradation of acids. The prominent degradation of acids was found in 3 hour study in the presence of Cu-TiO_2 in comparison to the prepared TiO_2 .

3.9. Effect of photocatalyst amount

It is clear from the results shown in table 3.2 that both TiO_2 and Cu-TiO_2 are proving as an effective photo-catalyst for the degradation of Acids. But when the amount of photocatalyst increases the photodegradation of acids also increase. It is observed that Cu-TiO_2 is the more effective photocatalyst than TiO_2 .

3.9. Kinetic study

The pseudo-first-order rate constant (k , min^{-1}) for the photodegradation reaction of Acids were determined through the following relation where, k can be calculated from the plot of $\ln(C_0/C_t)$ against time (t), C_0 and C denote the initial concentration and reaction concentration, respectively.

$$\ln C_0/C_t = k_1 t \dots\dots\dots(1)$$

In addition, the linear feature of plots of $\ln(C_0/C_t)$ versus time. indicates that this photocatalytic degradation reactions follow the pseudo-first-order rate law. The rate constant of the photocatalysis at 30°C is min^{-1} .

5. CONCLUSION AND DISCUSSION

Photocatalysis deals with reactions which are initiated by electronically excited molecules generated by absorption of suitable radiation in the visible or near ultraviolet region. Photocatalytic reactions are occurring in the presence of semiconductor and light. Researchers are using photocatalysts for oxidative degradation of various non-biodegradable wastes.

Titanium dioxide (TiO_2), commonly known as titania, is one of the most commonly used photocatalysts. Because of its high oxidative power, stability, and non-toxicity, it promises a broad range of uses as a photocatalysts. Advantage of using TiO_2 as photo-catalyst are (a) using TiO_2 , the process occurs under ambient conditions (b) using TiO_2 , the oxidation of the substrate to CO_2 is complete in most cases and (c) it is comparatively inexpensive and remains quite stable

in contact with different substrate. TiO_2 has also played a leading role in the active research for the utilization of solar energy.

Titanium dioxide's photocatalytic characteristics are greatly enhanced due to the advent of nanotechnology. Nanoparticles or nanocrystals of titanium dioxide are of interest for their electrical, optical and chemical properties. At nano-scale, not only the surface area of titanium dioxide particle increases dramatically but also it exhibits other effects on optical properties and size quantization. An increased rate in photocatalytic reaction is observed as the redox potential increases and the size decreases.

In the present study, to prepare the nanocomposites of titania by solution impregnation method and photocatalytic degradation of some target materials such as acids, dyes, and glucose in the presence of nanocomposites of titania which was prepared by the solution impregnation method, was done. The resulting powders were copper titanium dioxide. The alcohol route of synthesis, adopted here, yielded dark black homogeneous powder of copper titanium dioxide. The obtained yield of the product was more than 90% of the expected theoretical yield. In which the material has the nanodiamonds. The prepared material was subjected to XRD analysis which gives the rutile and anatase both phases were present in the prepared sample. It is found that, in samples sintered at 400°C both anatase and rutile phases were presented and rutile phase was more dominant, while in samples without sintered the exclusive formation of polycrystalline anatase and rutile phase separately was occurred.

Applying the Scherrer's calculations through which particle size was found 16 and 72 nm in case of copper titania and pure titania respectively.

The prepared sample of titania and copper titania were subjected to photocatalytic degradation of acids e.g. oxalic acid, tartaric acid, citric acid and acetic acid was done.

The degradation of carboxylic acids such as acetic acid, oxalic acid, citric acid, and tartaric acid occur efficiently. The prominent degradation was found in case of oxalic acid in the presence of nanocomposites Cu-TiO_2 .

References

- [1] W.A. Jacoby, P.C. Maness, E.J. Wolfrum, D.M. Blake, J.A. Fennell, *Environ. Sci., Technol.*, **32**(1998) 2650.
- [2] M.R. Hoffmann, S.T. Martin, W.Y. Choi, D.W. Bahnemann, *Chem. Rev.*, **95**(1995) 69.
- [3] Fujishima, K. Hashimoto, T. Watanabe, *TiO₂ Photocatalysis: Fundamentals and Applications*, BKC, Tokyo, 1999.
- [4] R.L. Zioli, W.F. Jardim, *J. Photochem. Photobiol. A Chem.* **147** (2002) 205.

- [5] T. Berger, M. Sterrer, O. Diwald, E. Knozinger, D. Panayotov, T.L. Thompson, J.T. Yates, Jr., *Phys., Chem.*, B 109 (2005) 6061.
- [6] S.H. Szczepankiewicz, J.A. Moss, M.R. Hoffmann, Jr., *Phys., Chem.*, B 106 (2002) 2922.
- [7] I.M. Arabatzis, T. Stergiopoulos, M.C. Bernard, D. Labou, S.G. Neophytides, P. Falaras, *Appl. Catal. B Environ.* 42 (2003) 187.
- [8] I.M. Arabatzis, T. Stergiopoulos, D. Andreeva, S. Kitova, S.G. Neophytides, P. Falaras, Jr., *Catal.* 220 (2003) 127.
- [9] C. Hu, Y.H. Tang, Z. Jiang, Z.P. Hao, H.X. Tang, P.K. Wong, *Appl. Catal. A Gen.* 253 (2003) 389.
- [10] J. Keleher, J. Bashant, N. Heldt, L. Johnson, Y.Z. Li, *World J., Microbiol. Biotechnol.* 18 (2002) 133.
- [11] C. Wang, T.M. Wang, S.K. Zheng, *Physica E* 14 (2002) 242.
- [12] B. Sun, A.V. Vorontsov, P.G. Smirniotis, *Langmuir* 19 (2003) 3151.
- [13] F.B. Li, X.Z. Li, *Chemosphere* 48 (2002) 1103.
- [14] V. Vamathevan, R. Amal, D. Beydoun, G. Low, S. McEvoy, J. Photochem. Photobiol. A Chem. 148 (2002) 233.
- [15] T. Paunesku, T. Rajh, G. Wiederrecht, J. Maser, S. Vogt, N. Stojicevic, M. Protic, B. Lai, J. Oryhon, M. Thurnauer, G. Woloschak, *Nat. Mater.* 2 (2003) 343.
- [16] T. Rajh, J.M. Nedeljkovic, L.X. Chen, O. Poluektov, M.C. Thurnauer, Jr., *Phys., Chem.* B 103 (1999) 3515.
- [17] M. Gratzel, *Nature* 414 (2001) 338.
- [18] Brune, G. Jeong, P.A. Liddell, T. Sotomura, T.A. Moore, A.L. Moore, D. Gust, *Langmuir* 20 (2004) 8366.
- [19] V. Krishna, S. Pumprueg, S.H. Lee, J. Zhao, W. Sigmund, B. Koopman, B.M. Moudgil, *Process Saf., Environ. Prot.* 83 (2005) 393.
- [20] S.H. Lee, S. Pumprueg, B. Moudgil, W. Sigmund, *Colloids Surf. B Biointerfaces* 40 (2005) 93.
- [21] Vijay Krishna, Naoki Noguchi, Ben Koopman, Brij Moudgil, Jr., *of Colloid and Interface Science* 304 (2006) 166-171
- [22] Zhang, L., Kanki, T., Sano, N., Toyoda, A., Jr., *Solar Energy* 70 (4) (2001): 331-337.
- [23] Song, K.H., Park, M.K., Kwon, V.T., Lee, K.W., Chang, W.J., Lee, W.I., *Chem. Mater.* 13, (2001) 2349.
- [24] Ameta, S.C., Punjabi, P.B., Rao, P., and Singh, B., *J. Indian Chem. Soc.*, 77, (2000) 157-160.
- [25] Ollis, D.E. and Al. Ekabi, H., *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam (1993)
- [26] Gratzel, M., *Research opportunities in Photochemical science, Dept. of Energy*, 34 (6), (1996), 1221-1230.
- [27] Ohtani, B., Ogawa, Y., and Nishimoto, S., *J. Phys. Chem. B*, 101, (1997) 3746
- [28] Cao, F., Oskam, G.J., Meyer, S., and Searson, P.C., *J. Phys. Chem. B*, 100, (1996) 17021.
- [29] Armelao, L., Barreca, D., Bertapelle, M., Balittaro, G., Sada, C., and Tondello, E., *Thin Solid Films*, 442, (2003), 48.
- [30] Balamurugan, B., Mehta, B.R., *Thin Solid Films*, 396, (2001), 90.
- [31] Fujishima, A. (2002), "Nanotechnology and Photocatalysis: Important Science and Technology for Comfortable Atmosphere," presented at the *Shanghai International Nanotechnology Cooperation Symposium (SINCS 2002)*, Shanghai, China, 2002.
- [32] Beydoun D. and Amal R, Novel Photocatalyst: Titania-Coated Magnetite. Activity and Photodissolution *J. Phys. Chem. B*, 104 (18), . (2000) 4387-4396

- [33] Kaneko, M. and Okura, I. (2002), *Photocatalysis: Science and Technology* (Springer, Berlin, 2002).
- [34] Mills A., Jishun W. Photomineralisation of 4-chlorophenol sensitised by TiO₂ thin films. *J. of Photochemistry and Photobiology A: Chem.* **118**, (1998) 53-63
- [35] Draper R. B. and Fox Marye Anne, *Langmuir*, **6**, (1990)1396-1402
- [36] Jaeger. C. D.: Bard. A. J. J., *Am., Chem., Soc.* **102**, (1980)5435.
- [37] Bickley, R. I., Munuera, G., and Stone, F. S., *J. Catal*, **31**, (1973) 398
- [38] Shiraishi, F. and Kawanishi, C., *J. Phys. Chem., A* **108**, (2004)10491
- [39] Richard C., Bosquet F, PilichowskiJ, *J. of Photochemistry and Photobiology A: Chem.* **108** (1997) 45 – 49
- [40] Rupa A V, Divakar D, Sivakumar T. *Catal Lett*, **132**: (2009), 259-267
- [41] N. Wetchakun, B. Incessungvorn, K. Wetchakun, and S. Phanichphant *Materials Letters*, vol. 82, pp. 195-198, 2012.
- [42] N. Wetchakun and S. Phanichphant, *Current Applied Physics*, vol. 8, no. 3-4, pp. 343-346, 2008.

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Chapter 15

The impact of micro and nano plastics on the environment

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Abstract-

Plastic is marine debris found in our ocean and lakes it is most prevalent type of debris. It occurs in all shapes and sizes but when it has shown less than five millimeter in length occurs in sesame seed like size known as micro plastics. The plastic fragments with dimensions less than a millimeter invading all terrestrial and marine environments is called nano plastics. Generally micro plastic has 0.1 micron to five millimeter and nano plastic has 0.001-0.1 micron in size. The micro plastic and nano plastic also being contributors of marine and fresh water pollution, the study indicates that micro plastic debris distributed with different concentration in aquatic system around the world. It has shown effect on development, behavior, growth, mortality and reproduction of animals. In around the world people discard tons of plastic every year, these plastic bits break down into pieces no bigger than sesame seeds. The plastic found throughout the oceans and locked in Arctic ice and end in food chain so animals occur big and small in size. The vast majority 82 million tons of macro plastics and 40 million tons of micro plastics is washed up, buried or resurfaced along the world's shorelines.

The scientist also finds plastic bits in all kinds of animals from crustaceans to birds and whales. The small animals concentration is low on food chain eats them. When larger animals feed on the small animals, they can end up also consuming large amounts of plastic. In the world plastic use also increased day by day 368 million tons plastic production occur in 2019 year. The plastic produced not disposed in correct way it break down into smaller particles and also shows impact on human body and environment in global. The increase of micro and nano plastic waste in food chain creates a risk of animal and human deaths. The wide bioavailability and ubiquity in aquatic and terrestrial areas it is more probable that plastic are present in many food products. The majority of plastic debris land is

littered or thrown into landfill without adequate safeguards shows its way into ocean. The dumping of plastic in environment is impossible to picture in even single day. The plastic bottle caps make up about one- third of all plastic trash because of in the time take you read this or in just few minutes about fifty thousand plastic bottles thrown away in environment.

Keywords- Degradation, Plastic, Pollution, Debris and Environment etc.

Introduction-

In old days many natural substances like rubber and silk used like plastic, before the innovation of plastic those substances that molded were metal, clay and glass it has rigid and heavy after formed. The rubber has shown many plastic related characters and properties but after bending or stretching it loses its ability and comes its original shape. The natural plastic like material made by long molecular chain known as polymers it formed by simple repeating units. The detail study of chemistry of this polymer chains than the innovation of plastic comes in light. In modern world the plastic made rigid or bendable and formed in any shape and size for making different appliances and toys. Today the production and use of plastic is very high so average person in modern society breaths and drinks many tiny partials of plastics in every day.

Today plastic pollution occur not only oceans it occurs everywhere on earth surface. The plastic goes on Himalayan region in Antarctica region also on Mars by left of curiosity rover. The plastic releases many types of toxic substance in environment. This released chemicals are now occur in blood of person. It also causes health problems including birth defects and brain damage. It is not possible virtually to make modern electronic appliances and devices without plastic. The uses of plastic reduce product weight, transportation costs and use of fossil fuel. Plastic also used for design of medical equipments. There is many examples of use of plastic in current days thousands of patients in world are victim of COVID-19 pandemic incubated with ventilators in desperate attempt to keep alive them. This all process is impossible without plastics. The plastic called acrylic can be made so clear that light can travel through a one-meter thick piece and still retain 80% of its strength. Plastics can be much stronger than steel for some purposes while weighing much less. Some plastics can even be bulletproof. Polycarbonate can be made practically unbreakable. It is hard to imagine how many modern devices such as solid-state electronics and medical instruments could

exist without plastic. Recent advances in chemistry continue to make plastics ever more useful. The plastic fragments smaller than few millimeters in size known as micro plastics. The plastic particles less than few micrometers in size called nano plastic. Generally, micro plastics are plastic fragments of 0.1 μm to 5 mm in size, whereas, the dimension of nano plastics is 0.001–0.1 μm . These fragments are so minute that they are not visible to the naked eye or even under a simple optical microscope.

The global plastic pollution problem arises last many years on micro and nano plastic has gained attention from researchers of all worlds. The micro and nano plastic able exit toxicology and interact with potentially toxic elements in environment and causes soil toxicity. The effect of micro and nano plastic so influence on soil system plant crops it also accumulate by plants roots system. It creates impacts on terrestrial environments. The consumption of micro and nano plastic contaminated plants and fruits by human and animals leads to health deterioration. The identification and measurements of micro and nano plastic in various soil sample of challenging making understanding of fate in environment and ecological system.

The plastic pollution encompassing all ranges and sizes like macro to nano plastic emerging threats and create one greatest environmental challenges in future time. The micro plastic attracts attention of researches, public and governments worldwide. The documents show the in world all parts contaminated by plastics it occurs on highest mountains and also in deepest oceans part. The interaction between aquatic and terrestrial species focuses the laboratory and field research. The scientist's reports real potential hazards of plastic are in their fragmented forms like micro and nano plastic. This minute fragments results of degeneration of large plastic materials. The micro plastics, one of the main potential risks is it being stuck in the guts of living organisms. However, for nano plastics, it can easily penetrate the tissues and organs of an organism. In a recent study, nano plastics have been reported to be present in the tissues of terrestrial plants, harming the ecosystem.

Objectives-

- To study the micro and nano plastic pollution
- To study the effect of micro and nano plastic in environment
- To focus on plastic pollution and its effect in society
- To aware young generation about micro and nano plastic pollution

Analysis and Result-

In fact, the main feature of these materials is reflected in their etymology: the word plastic originates from the Greek words *plastikos* meaning “capable of being shaped”, and *plastos*, meaning “moulded”. Typically synthetic, plastics are most commonly derived from petrochemicals and exhibit high molecular mass and plasticity. Thus, plastics are polymers, long chains comprised of linked repeated units, named “monomers”. One way to visualize this is to picture a polymer as akin to a pearl necklace in which the monomers are the individual pearls. The process through which these monomers are linked is called polymerization and, therefore, plastics can be classified according to the chemical process used in their manufacture, namely, condensation, poly-addition, or cross-linking, or according to the chemical structure of the polymer’s backbone and side chains. Among these, the most important groups are silicones, acrylics, polyesters, polyurethanes and halogenated plastics. However, quite frequently plastics are also categorized according to key characteristics that are of relevance to manufacture, product design and end-use. The micro plastics are also found in rivers and lakes, in agricultural soils, sediments and even in the atmosphere, both in indoor and outdoor environments. Once in the environment, plastics can undergo degradation through biotic and/or abiotic processes. The former is an essential first step that precedes the latter. In other words, biodegradation mechanisms require an initial abiotic degradation process. “Plastic” is an umbrella term that encompasses a wide range of materials made of semi-synthetic or synthetic organic compounds.

In water plastics show the densities vary by composition and span. In water surface or on shoreline macro debris of plastic mostly floated. The low density polymers used in single use container like polyethylene and polypropylene. The polymer like polycarbonate, polyvinyl chloride is denser than water and has expected to sink. In aquatic system polystyrene foam comes in fishing floats but after sink with air space it becomes waterlogged. The world production synthetic organic polymer or plastic has 1.7 million tons in 1950 it becomes 299 million tons in 2013. The effect of plastic are chiefly mechanical and toxicological in nature. The pieces of plastic when undergo leaching it releases different chemicals which are carcinogenic in nature. It produced chemicals like monomers, polymers, polymer associated chemicals and plastic additives which affect the endocrine system. The fishes consume tiny plastic particles resin pellets used in plastics manufacturing and its aftermath. The

study revealed that the biological functions of these fishes that include their metabolism, neurological behavior, intestinal micro biome diversity, and intestinal permeability are greatly affected. The effects of micro and nano plastics on health of human, animal and environment studied by scientists, they focused on impacts of these materials and providing possible solution in reducing these potential environmental threats. The removal of micro and nano plastics from waste and drinking are found to be highly effective. The technology reduced up to 90% micro and nano plastics. The another measure to bring about reeducation in plastic pollution minimal use of single use of plastic material example plastic bags, bottles, straws, cups, fork like materials. The changes in life style also bring great changes in environment pollution. The world produces more than 380 million tons plastic in every year it lastly enters in our nature as pollutants. Some plastics enter into ocean and most deposited on landfills. In ocean around 3% share of global plastic waste enters. In 2010 it is estimates about eight million tones. The most of micro and nano plastics come from larger plastic debris and degrades into small pieces. The micro beads also a type of micro plastic it is very tiny pieces manufactured polyethylene plastic that added as exfoliants for health, toothpaste and beauty products, it is easily carried out from water filter system and enters into aquatic system and posing potential threats to aquatic life system. The less dense plastics than water float at surface of ocean and lakes.

The ecologist found micro and nano plastics make their way into drinking water as well as foods like salt, sugar and honey. The consume of micro and nano plastics enters into body by eat, drink and inhale. In inhaling very fine particles enters and causes respiratory irritation. A lot of new plant-based, biodegradable products are similar to the natural polymers are found in trees, leaves, and grass. It is need to know they exist and demand them in our products for avoiding such problems. The single used applications like food and beverages containers, home and office furnishing, electrical and electronic devices, thermal insulation, fabrics, toys, medical devices like incubators, intravenous, fluid bags and many drug delivery devices. These are also produces the more environmental pollution and show affect on human and animal health. In 2010 the global plastic production having 270 million tons and the plastic waste generated in coastal regions is 50 kilometer of coastline amounted 99.5 million tons. The mismanaged plastic waste its leakage also produce environmental risk it occurs 31.9 million tons in that year.

The plastic occur on earth surface shows chemical oxidation of polymer as result of exposure to sunlight has most impactful. On the beaches and water surfaces photo oxidation process occurs. Interestingly, reported that incorporation of brominated flame retardant additives into polystyrene film increased UV absorption and subsequent photo oxidation of the polymer. They observed that byproducts were generated from the flame retardants themselves and from the reaction of the polystyrene with bromine radicals. The amount of degradation products leached into water constituted up 14% of the weight of the original polymeric film. Weathering of plastics by UV oxidation may also increase vulnerability to later biodegradation. The global plastic production from 1950 to 2015 has cumulative production of polymer, synthetic fiber and additives has 8300 million tons, 2500 million 30% of primary plastic use in up to 2015. In landfill 4600 million tones that are 55% went into landfill. The eight percentage was incinerated it is 700 million tons. Only 500 million tones only six percentage plastic recycled 100 million tones recycled plastic still in use, later 100 million tones incinerated and 300 million tones later sent into landfill. The no longer used primary plastic has 5800 million tons no long used only nine percent has recycled since 1950.

Some polymers are composed of monomers derived from renewable, nonpetroleum sources, for example, rayon and cellulose acetate, additionally, polyhydroxy alkanoate from bacterial precursors and polyactic acid from plant starch have recently been produced to be more inherently biodegradable. The goal is to allow complete degradation to CO₂ after the end of product service life, as partial breakdown may generate intermediates of unknown properties, as well as micro plastics.

Much of the macro plastics in our shorelines are from the past 15 years, but still a significant amount is older suggesting it can persist for several decades without breaking down. In coastal regions most macro plastics (79%) are recent less than 5 years old. In offshore environments, older micro plastics have had longer to accumulate than in coastal regions. There macro plastics from several decades ago even as far back as the 1950s and 1960s persist. Most micro plastics three-quarters in offshore environments are from the 1990s and earlier, suggesting it can take several decades for plastics to break down. According to report daily eight million pieces of plastic enters into ocean and yearly it reaches 4.8- 12.7 million tones. This amount is equal to a garbage truck full by plastic and

dumped into ocean in every minute. The out of total amount of landfill plastics 79% is transported into ocean, less than 10% is recycled and 12% is incinerated. The twenty five trillion macro and 51 trillion micro plastics litter the ocean and 269,000 tons float on the surface of water. This is equal to 1345 blue whales and 500 times number of stars in the Milky Way. The plastic is expected to increase tenfold in next five years.

A report states that average 80% plastic in ocean washed from land on 10 rivers two from Africa and other from Asia. China produces highest world's plastic pollution the next polluter is Indonesia. The rest ocean plastic comes from various ships in the form abandoned fishing nets, gear and debris lost or tossed overboard. The plastic bags, food wrappers, food related items, drinking containers, cups, glass, straws, plates and utensils share pollution. The miniaturization is sometimes done purposefully, as with micro plastics added to cosmetics and toothpaste. Though intended to be washed into waste water, these added particles still find their way into the drinking water supply all around the world. A study in *Frontiers in Chemistry* found that 93% of bottled water contains on average 325 particles of plastic per liter.

In the study tap water from 159 global sources tested then 81% found as contaminated by micro plastic particles which is less than five millimeter in size. The test conducted on 259 individual bottle of water of 11 brands and 27 different batches it also shows 93% contained with micro plastic. The average levels of micro plastic pollution in food occurs as like seafood has 1.48 particles /g, sugar 0.44 particles/g, honey 0.10 particles/g, salt 0.11 particles/g, alcohol 32.27 particles/L, bottled water 94.37 particles/L, tap water 4.23 particles /L, and air 9.80 particles /m³. The all food data continued micro plastic by this account it is possible to extrapolate that the average human is consuming around 39,000 to 52,000 micro plastic particles per year, with age and gender impacting the total amount. If inhalation of plastic particles is included in the figures, then the amounts rise to between 74,000 and 121,000 particles per year. Further, an individual who only ingest bottled water is potentially consuming an extra 90,000 particles in comparison to people who only drink tap water, who will ingest only 4000 extra particles. These results indicate that the human food chain is, indeed, a major source of micro plastic consumption by humans.

Plastics are made of natural materials that have undergone several chemical processes and physical reactions. The main processes used are polymerization and poly condensation, during which the core elements are fundamentally transformed into polymer chains. This process is rarely reversible; the plastics must go through more chemical processes in order to be recycled into new types of plastics. The use of industrial additives, such as pigments, plasticizers and stabilizers, allows plastics to be engineered to various application requirements. Due to the chemical stability of the conventional plastics, environmental accumulation is on the rise. The inherent economic impact due to plastic waste is also vast. Studies suggest an economic damage to the global marine ecosystems surpassing € 11 billion. In Europe, € 630 million are spent every year to clean plastic waste from coasts and beaches while the failure to recycle costs the European economy € 105 billion. Plastic pollution represents one of the major perceived threats to biodiversity. Due to its abundance, durability and persistence in the environment, it is a cause of special concern. By comparing the listed encounters with the International Union for Conservation of Nature (IUCN) Red List, at least 17% of species affected by entanglement and ingestion were listed as threatened or near threatened. The interaction of organisms with plastic debris results in a wide range of consequences, both direct and indirect, includes the potential occurrence of sub lethal effects, which, owing to their uncertainty, may be of considerable concern.

Conclusion-

The plastic is modern marvel it benefited to society in all sectors like food and health. The production plastic increases from 1950. However, the same characteristics that render plastics highly desirable are also those that render them ubiquitous in the environment, especially as a large fraction of plastics is designed to be discarded almost immediately following their use. Society's ability to cope with the sheer amounts of plastic produced and discarded is vastly overwhelmed, and only 9% of all the plastic ever manufactured has been recycled. Most of the plastic waste ends up in landfills and, ultimately, in the environment. Most plastics do not degrade. Instead, they slowly fragment into smaller particles, referred to as micro plastics, and, probably, nano plastics. These particles, whether in the form of larger or smaller plastics, have profound detrimental consequences for ecosystems, biota, and the environment, but also for the economy and human health. Plastics have been found in the stomach contents of numerous organisms,

including earthworms, birds, turtles, dolphins and whales. Smaller particles may be even more pervasive, as these may be ingested by organisms that are at the basis of different food webs. It is more dangerous to environment so a variety of regulatory and legislative tools exists, aimed at controlling, reducing and managing the use of plastics, with a particular emphasis on single-use plastics. Existing legislation consists mainly of levies, bans, and voluntary efforts through the 3R rule: reduce, reuse and recycle controls the plastic pollution and makes awareness in society.

References-

- ❖ Arora Mohan P. (1990) 'Ecology' Mumbai Himalaya publishing house Publication.
- ❖ Botkin D.B. and Kler E.A. (2005) 'Environmental Science: Earth as a Living Planet' Johan Wiley and Sons, INC Publication.
- ❖ Baskar S. and Baskar R. (2007) First edition 'Environmental Studies for Undergraduate' New Delhi Unicorn publishers Publication.
- ❖ Carl J Sindermann (1996) 'Ocean Pollution' USA CRC Press Publication.
- ❖ Carl J Sindermann (2005) 'Coastal Pollution: Effects on Living Resources and Humans' USA CRC Press Publication.
- ❖ EIRI (2009) 'Plastic Waste Recycling Technology' Engineers India Research Institute Publication.
- ❖ Frank R. Spellm (1999) 'The Science of Environmental Pollution' USA CRC Press Publication.
- ❖ Joshi P.C. and Namita Joshi (2009) 'A Text book of Environmental Science' New Delhi A.P.H.Publishing Corporation Publication.
- ❖ Nobel B.J. and Wright R.T. (2000) 'Environmental Science' New Delhi Prentice Hall INC Upper Saddle River Publication.
- ❖ R M Harrison (2018) 'Plastics and the Environment' Royal Society of Chemistry Publication.
- ❖ Russell (2021) 'An Earth-Bot's Solution to Plastic Pollution' Ayto Kids Can Press Publication.
- ❖ Rana SVS (2005) 'Essentials of Ecology and Environmental Science' New Delhi Prentice Hall INC of India Publication.
- ❖ Sharma P.D. (2004) 'Ecology and Environment' Meerut Rastogi publication
- ❖ Shukla R.S. and P. S. Chandel (2008) 'A Text book of Plant Ecology' New Delhi S Chand publishing Company publication.
- ❖ Vannessa Goodship (2007) 'Introduction to Plastics Recycling' Rapra Technology Limited Publication.

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Chapter 16

Synthesis of Iron-based Metal-Organic Framework for heavy metal adsorption from water

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Abstract

The most current crisis that the world is facing is water contamination. It is estimated that if the rate of water depletion continues, the drinking water shortage is the problem that the world will face in the near future. The two elements that are majorly responsible for water contamination are arsenic and chromium. As such work needs to be done in the area of removing these contaminants from the water bodies which are done by synthesizing Iron-based Metal-Organic Framework (MOF) materials. MOF was synthesized by taking two precursors viz oxalic acid and ethylene glycol. The synthesized iron-based-MOF was characterized by using various characterization techniques and was subsequently tested by adsorption route for decontaminating the water containing chromium impurities.

Keywords-Metal-organic framework, adsorption, chromium and water

Introduction

1.1 Water Contamination:

Water contamination is a global problem as water is the basic need of life. It is found in a more or less pure state in nature, forming rivers, lakes, and seas, which occupy three-quarters of the world. It is composed of chemical elements and gases (H₂O). [1] It is used almost by every single form residing on Earth. It is indeed one of the most precious natural resources. It has been said that three-fourths of the Earth's surface is covered with water. [2] It provides a habitat for many animals and plants. It is a vital body fluid that regulates life

processes such as digestion of food, transportation of nutrients, and excretion of body wastes. It also plays an important role in seed germination. It is an important reactant in photosynthesis. [3] We use water for our domestic purposes, like drinking, cooking, bathing, washing, etc. Water from rivers and lakes is used for irrigation, thereby helping agriculture. When water falls from height, as in waterfalls or dams, it can be harnessed to generate hydroelectricity. Mother Earth is like a terrarium. The terrarium is an artificial enclosure kept for small plants. About 97% of the earth's water is in oceans and seas. Another 2% of water is in the form of ice caps and glaciers which cannot be used by us. This only 1% of the earth's water is easily available and fit for human use. [3][4] The water which exists today was presented even centuries ago. The water used to irrigate a field in Punjab may have flowed down the Brahmaputra River a century ago. [3][5] Water is present on Earth in all its forms. The oceans, seas, lakes, rivers, and ponds constitute surface water. Water that is found in the pores of rocks under the surface of the earth is called groundwater. Water is also found in form of ice sheets or water vapors. Rain is the main source of underground water which is available to us from wells or springs. When it rains, part of the rainwater gets absorbed in the soil. It keeps flowing through various layers of soil and reaches the rock bed from where it is unable to go further. At this level, it forms a water reservoir. It does not go below the Rocky bed. When wells are dug deep, water reservoirs are found above impervious rocks. [4] At different places, water beds are formed at different depths. Water from these reservoirs is drawn as well as water. The level of underground water is called the water table. [3] Excessive pumping can cause a fall in the water level. Rainwater harvesting can improve the quality of groundwater by diluting the dissolved salts and other substances found in groundwater. In this method, water is collected in percolation pits and recharge wells to recharge groundwater. Water acts as a support system for life. Water is as important as the air of our existence. When your body feels dehydrated, then we need fresh water to drink. One cannot stay thirsty for long. Plants too cannot live long without water. [4] Water is also needed for cooking, bathing, working, and construction work. So, we need to drink pure water, otherwise, we will be prey to various diseases. It is generally said that that rainwater is the safest to drink. But rainwater can dissolve substances from the air, collect dirt, certain living and dead things, and other impurities. As we can see, over time everyone needs fresh water. This water should be made pure and drinkable. But there reside various sorts

of impurities in water that we see around. The water of wells and rivers is polluted by impractical impurities which can be seen; soluble impurities that cannot be detected and germs that cause diseases. Since the arrival of the industrial revolution, human activities posing a deeply negative impact on our environment. The continuing increasing population along with increasing energy and commodity consumption threatens sustainable development. Increasing demands cause more production leading to more amount of non-disposable waste. The results of these unprecedented activities can be evident in our water table. Now almost half of the world's population residing in the area under water-stressed region and the situation is expected to get worse in following decades. [6] Global warming acts as a prominent reason as it causes an increase in global temperature. The main goal of the sustainable development program is to provide clean drinking to each individual. The biggest solutions to mitigate the water crisis that is practically possible as well are freshwater harvesting from groundwater and desalination of seawater. However, the advancement required to perform the tasks efficiently is not affordable all over the world. [6] Overexploitation of aquifers ultimately results in saltwater intrusion and desalinized plants can become a source of contamination of coastal waters. It is a need of the hour to generate specialized technologies for the removal of contaminants from water which allow reusing water, again and again, eventually helps in the re-establishment of the planet's ecological balance. The contaminant may be defined as any physical, chemical, biological, or radiological substance or matter in water as per the Safe Drinking Water Act (SDWA). [3] This term has been referred to as any kind of polluting or poisonous substance present in water due to unethical activities performed by humans. Their presence in water proves to be hazardous for the natural development of living beings. These can be commonly categorized into inorganic and organic ones, as per chemical composition. As per the concern for inorganic pollutants, oxyanions/cations and metal ions, especially the heavy or radioactive ones, marks the main environmental stress. These are highly soluble as well as mobile in nature due to their charged nature and are extremely bioavailable. Also, these ions are easily accumulated in the human body and food chain, along with sets a narrow range between deficiency and toxicity and imposes a lethal impact on living beings at both ppm and sometimes even at ppb level concentrations, inorganic contaminants act as a primary point to ponder for water remediation. But organic pollutants have a way bigger family to explore than inorganic ones.

Dyes, oils, various polyaromatic hydrocarbons, detergents, pesticides/insecticides/herbicides and pharmaceuticals, and personal care products (PPCPs) are some commonly found organic contaminants found in water streams. They are pseudo-persistent in the ecosystem. Hence, their removal from water streams must be carefully considered for maintaining a sustainable ecosystem.

Freshwater resources have been contaminated because of the proliferate development in the industry which led to lethal consequences to the environment and health. [8] The water found in the different regions contains different organic and inorganic impurities. [7] Inorganic impurities such as heavy metals, Arsenic, Cadmium, mercury, and chromium can pollute the water which leads to creating health even fatal diseases. Recent research of Tezpur University Assam of "Dr. Robin Kumar Dutta" worked on the removal of arsenic and fluorides from waste [9]. Arsenic is a metalloid that is harmful to the body. Arsenic in the drinking water creates different allergic reactions or diseases. It is the cause of cancer disease. Arsenic can cause spots to stain on the body and the face. Organic impurities such as hydrocarbon, pesticides, fertilizers, phenols, greases, and oil are toxic substances that can pollute the water; the main sources of these toxic substances are hospital water, industry, and household. [10] There are so many reported processes and methods of removal of inorganic impurities such as. [2] Solvent extraction, filtration, membrane distillation, adsorption, electrochemical treatment, chemical precipitation, and ion exchange method. Adsorption of pollutants with porous materials is the perfect alternative to removing contaminants from our ecosystem in an efficient manner. [6]

1.2 Chromium:

It is a heavy metal found in water and the cause of many health diseases, Chromium (VI) is carcinogenic. It can be found in human blood in the form of trivalent chromium (Cr^{3+}) in trace amounts. Trivalent chromium is significantly less toxic and stable. Water contamination with hexavalent chromium (Cr^{6+}) is a serious and big environmental problem. Environmental contamination of (Cr^{6+}) due to high levels in water and human activities including industries. A recent report shows that the researcher is trying to remove the hexavalent chromium by the reduction process using different iron nanomaterials like metal-organic framework (MOF).

1.3 Arsenic:-

It is commonly found in the water in the form of arsenate ($H_xAsO_3^{3-x}$) and arsenite ($H_xAsO_4^{3-x}$) species. Arsenic can be found in arsenate [As(III)] and arsenate [As(V)] oxidizing state, here arsenate [As(III)] is more toxic than arsenate [As(V)]. Arsenate [As (III)] is more difficult to remove from water as compared to arsenate [As (V)] because of the low affinity of H_3AsO_3 to the surface of the sorbent and due to uncharged from pH values. Thus, its two variants have attracted the attention of research groups and, as a result, our attention is drawn. Although it can be found as organoarsenic compounds.

The US Environmental Protection Agency (EPA) reported that the arsenic standard for drinking water at 9-10 ppb to protect consumers against the effects of long-time chronic exposure to arsenic in drinking water. (Marton Mon, 2018) The Iron-based nanomaterials, such as Fe - granular activated carbon (GAC), Fe -zeolite, and Fe_2O_3 nanoparticles, iron-contaminants MOFs are too be best promising candidate sorbents for arsenic removal from drinking water and wastewater. The ultimate technique of arsenic removal is recently reported by Huo. et al. [6] [11] Removal of As (III) from water, by using magnetic responsive Fe_3O_4 - ZIF - 8 core-shell composite. The above substance is capable of adsorbing 100 mg of As (III) per gram of MOF, which has been allocated to strong surface complex interactions. The adsorption process is the most promising technology that used in the removal of arsenic from water, [12] due to its low cost, simple operation, and high efficiency, and mainly to use adsorbents materials from many types of origin. [10] [6] Overall, the economic and technical feasibility of adsorption processes depends on several factors including the adsorbent type, fluid properties, and pollutants to be removed, operating conditions, process configuration, regeneration, and waste disposal. The continuous adsorption system can be utilized for water purification or water treatment, and they offer several capabilities. Many reports showed the description of adsorption rate maximum adsorption capacities and adsorbate - adsorbent interaction. [13] On another way, packed-bed columns are appropriate for water treatment or purification in a large-scale application where the treatment of consequential volumes of fluids is produced in small operating times. Therefore, the removal effectiveness of the continuous adsorption technique is usually lower than obtained for batch processes. One million deaths in 25 years: [14]

Arsenic contamination raises cancer risk in 200 Indian cities. [14] [15] Recent studies show that the first 10 million people in India have been exposed to arsenic in groundwater. In a 2004 file photo (Fig.1.1).

A West Bengal woman shows her hands in her wrinkles after drinking arsenic-contaminated water. Priya Brath Sharma, 70, of Munger district in Bihar, who has been bedridden for many years, is one of the one million cases of arsenic poisoning in India. "I have stopped walking for many years because my lower body does not move, I also went to AIIMS for treatment a few years ago and they said it was an arsenic-related disease," he said.

Known to people as the biggest poison in history, arsenic contamination has become a major concern for people living in northern India. Studies show [5] that about 10 million people in India are exposed to groundwater contamination and at least 1 million people have clinical manifestations. Arsenic is found naturally in groundwater in many South Asian countries such as India, Nepal, and Bangladesh. Sharma, who lives near Ganga, said doctors advised him not to drink water from wells or hand pumps. "There are more than 100 people in my village Khaira Basti who are battling cancer and other diseases due to contaminated water. Others have spots and colors on their skin," said Sharma. Chairman of Bihar State Pollution Control Board and Head of Research at Mahavir Cancer Institute and Research Center, Patna, A study by Dr. Ashok Ghosh found that "arsenic contamination has been reported in 17 of India's 28 states." [14] [15] Arsenic contamination was first identified in Punjab, Haryana, Himachal Pradesh, and Uttar Pradesh. It was later identified in the lower Ganga plains in West Bengal, Bangladesh, Nepal, Bihar, Uttar Pradesh, Jharkhand, and lower parts of Assam." Currently, there is a risk of arsenic-contaminated drinking water in India in about 200 districts in the northern part of the country in the Ganga plain," said the coordinator of the Invincible Voice Foundation, a civil society group working on the issue said. The organization said that in the last 25 years, about one million people have died due to arsenic exposure.

In Bihar, the village of Samaria Ojapati in the Bhojpur district was the first to detect high levels of groundwater and related health problems in the state. [15] Ghosh's study showed that Bhojpur, Bhagalpur, Buxar, Patna, Vaishali, Khagaria, and Samastipur were among the worst affected districts of Bihar. The study showed that 22 out of 38 districts in the state had arsenic above the compliance limits (10 ppb) as per the criteria set by the World Health Organization.



Fig.1.1: File photo from 2004, a woman from West Bengal shows her wrinkled hands, a condition caused by drinking arsenic-contaminated water. (18, 2021)

Recent studies show that groundwater pollution is not the only source of exposure for the Indian population. In many cases, contamination is often associated with food intake, putting large populations at risk. According to a recent study by Ashok Ghosh, the consumption of food, rice, wheat, and potatoes was equivalent to drinking water. The rice that contributed the most to the food was cooked. His study indicates that arsenic is more prevalent in drinking water in common areas of Bihar. [15]

Another study on water contamination also indicated that the spread of prostate cancer was linked to arsenic hotspot areas in the Ganga-zone of Bihar. [14] There has been a significant increase in the number of cancer patients in the breath therapy department of the Mahavir Cancer Institute. According to hospital figures, it rose to 631 in 2014 from 508 in 2009. In 2004, it was lower than just 345 cases. [14] [15]

1.4 Metal-Organic frameworks(MOFs):-

These are the class of compounds consist of the metal ions or clusters coordinated to organic ligands (Fig.1.2) to form one, two, three - dimensional structures. [16]

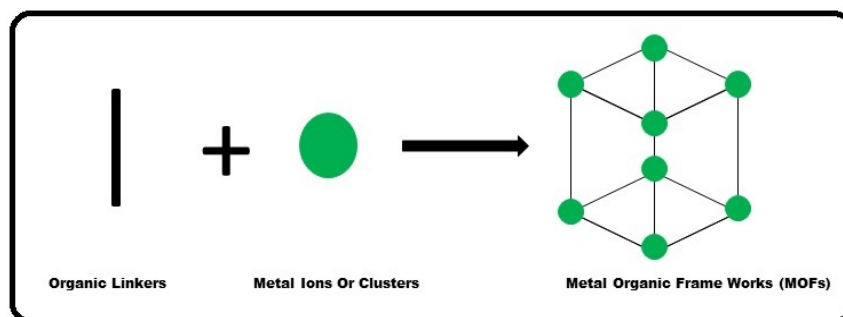


Fig: 1.2 Metal-Organic Frameworks (MOFs). [16]

These are a subclass of the coordination polymers. One possible application of MOFs based on recent research is purification, in gas separation. The recent report showed that water-stable MOFs can be synthesized and used for heavy metal decontamination such as arsenic. [17] This report focuses on the synthesis of iron base MOF materials and their application in the adsorption of heavy metals such as Ar and Cr from water.

The organic-inorganic hybrid crystalline porous materials that contain a regular array of positively charged metal ions surrounded by organic linker molecules are known to be Metal-organic frameworks (MOFs). The metal ions from a hollow structure by binding the arms of linkers of nodes thereby resulting in forming a repeating, cage-like structure, having an extraordinarily large internal surface area.

There are various already synthesized MOFs having more than 7800 square meters per gram of surface area.

MOFs have a vast diversified feature making it more unique than any other porous material as it acquires uniform pore structure, uniform atomic structure, tunability in porosity, flexible network, geometry, dimension, and chemical functionality. Researchers can easily create selectively absorbable materials for specific gases by making MOF from different metal atoms and organic linkers. Therefore, they offer a huge potential for effective integration and exploration in various applications.

MOFs can be integrated arbitrarily like Lego bricks and outperform in terms of flexibility.

Here, we can enlist numerous applications of MOFs in various fields that exploit MOFs' cage-like structure, such as in gas storage and separation, liquid separation and purification, electrochemical energy storage, catalysis, and sensing. Here, not only applications are

studied but MOFs are also used as unique precursors for forming inorganic functional materials with unparalleled designs like carons, metal-based compounds, and their isomers.

In recent times, materials using carbon as a constituent act as a center of attraction due to their applications in adsorption, catalysis, batteries, fuel cells, supercapacitors, drug delivery, and imaging. Carbonaceous materials also have a marvelous application in some sensors as they are directly related to human health.

There can be various methods for their preparation but directly carbonizing from organic precursors is the most prevalent method to produce nanoporous carbons due to its simplicity and flexibility. These materials also have revealed some drawbacks like low surface areas, disordered structures, and non-uniform sizes, and it limits their applications.

MOF Gas Sensors

These are the instruments that can detect traces of a specific gas in the air. Generally, gas sensors are much expensive and energy-intensive machines but MOFs gas sensors are not much expensive and they are energy efficient too. By using different metal atoms and organic linkers, a material that selectively absorbs specific gases into tailor-made sockets within the structure can be created. One such example is a thin film of tailor-made MOF, coated onto an electrode, which forms an electronic sensor that could detect traces of sulphur dioxide gas. Scientists also found that MOF, MFM-300(Al), not precisely filters harmful nitrogen dioxide gas, but also is the best for ammonia storage. One of the MOF materials shows a remarkable cooperative mechanism for carbon dioxide capture and release with little shifts in temperature. MOF structure absorbing CO₂ looks like RuBisCO enzyme, which converts atmospheric CO₂ into essential nutrients. In various researches, M-MOF-74, an open metal site MOF, has been seen as the best alternative for capturing and storing greenhouse gases. MOFs can hold a large number of refrigerant gases and help in lower energy consumption for air conditioning. MOF derivatives that absorb water vapor lead to cooling. The smaller nanostructure of MOF and its higher sorption rate make it a more efficient and pocket-friendly product. Researchers have found that MOF known as Fe-BTC, with dopamine, which gets polymerized to polydopamine (PDA) sticking the polymer inside the MOF. The final product can selectively remove higher amounts of heavy metal deposits like Pb, Hg derivatives from water samples quickly. At nuclear power plants and legacy waste sites, the most lethal problem to resolve is radioactive organic iodides (compounds made of hydrocarbons and

iodine). MOF traps have been created by scientists by chemically modifying MOFs with binding sites having reactive nitrogen that can easily bind to organic iodides, exhibiting higher methyl iodide capacity. Furthermore, these MOFs are advantageous as can be recycled multiple times without losing capacity and act as good absorbents even at lower temperatures. Vaccines can also be made using MOFs that freeze proteins inside vaccines due to their biocompatible polymer framework (their porous structure acting as semi-permeable membrane and transports proteins or antigens in vaccines). These proteins further dissolve when injected into human skin. This innovative approach can help various health care providers and make vaccines viable in remote areas. These can perform better at room temperature. By properly using MOFs, electrochemical detection of nutrients without using enzymes can be done. These can also help better understand various life processes as can be easily implanted due to their versatile stability and proper monitoring of biomolecules can be performed at different locations simultaneously.

2.2 Synthesis:-

Required Materials:- Ferric chloride, ferric nitrate, Oxalic Acid or terephthalic acid, ethanol, baking soda, (5%) potassium permanganate, DMF (N-dimethylformamide), trimesic acid, deionized water.

a) Synthesis of Iron-based metal-organic framework using Oxalic acid and FeCl_3 as a nanomaterial for water purification: Iron-based MOF was synthesis by terephthalic acid and trimesic acid. (Marton Mon, 2018) They report the synthesis of Iron-based nanomaterial by modifying the reported method in the literature. We follow the procedure of synthesis by modifying as given.

In this synthesis as follows: oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) (0.5 molar) and FeCl_3 (1 molar) were crushed and mixed with mortar. Add baking soda (0.5g) and 5% sol. Of KMnO_4 (2ml) in the reaction mixture as shown in (Fig 1.3), then the whole mixture of the substance in 250 ml beaker and centrifuge for 1–2 hours and the mixture were placed in different volume of the ethanol and stirred for 4–5 hours at atmospheric temperature.

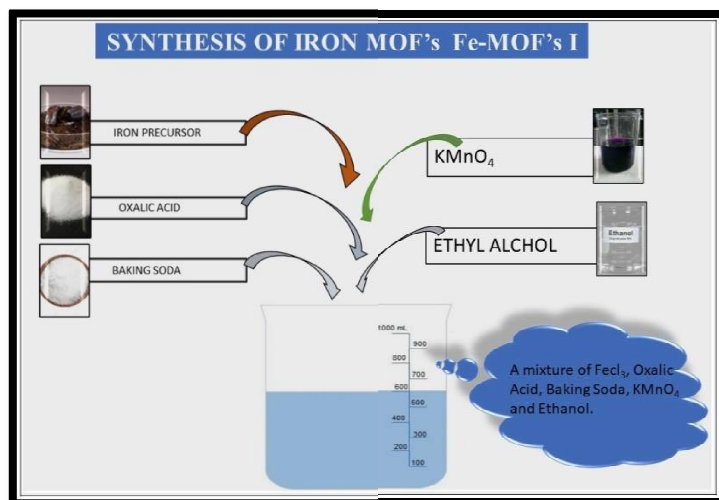


Fig: 1.3: Synthesis of IRON MOF's (Fe-MOF's I). [6]

Now, after the completion centrifugation process collect the product and immediately washed with the help of DMF for the prevention of unreacted oxalic acid. The products were washed with the help of ethanol 2-4 times. At last, the final product was left to dry under vacuum at 75-85 °C for 1 day. This final product was known as activated Iron nanomaterials.

b) Synthesis of Iron-based metal-organic framework using Oxalic acid and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as a nanomaterial for water purification: -

In this synthesis as follows: oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) (0.5 molar) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1 molar) were crushed and mixed with mortar. Add baking soda (0.5g) and 5% sol. Of KMnO_4 (2ml) in the reaction mixture, then the whole mixture of the substance in 250 ml beaker and centrifuge for 1-2 hours and the mixture were placed in different volumes of the ethanol and stirred for 4-5 hours at atmospheric temperature. Now, after the completion centrifugation process collect the product and immediately washed with the help of DMF for the prevention of unreacted oxalic acid. The products were washed with the help of ethanol 2-4 times. At last, the final product was left to dry under vacuum at 75-85 °C for 1 day. This final product was known as activated Iron nanomaterials.

c) Synthesis of Iron-based metal-organic framework using Ethylene glycol and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as a nanomaterial for water purification:

In this synthesis as follows: Ethylene glycol (0.5 M) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1 M) were crushed and mixed with mortar. Add baking soda (0.5g) and 5% sol. of KMnO_4 (2ml) in the reaction mixture, then the whole mixture of the substance in 250 ml beaker and centrifuge for 1 – 2 hours and the mixture were placed in different volume of the ethanol and stirred for 4–5 hours at atmospheric temperature. Now, after the completion centrifugation process collect the product and immediately wash with the help of DMF for the prevention of unreacted oxalic acid. The products were washed with the help of ethanol 2-4 times. At last, the final product was left to dry under vacuum at 75-85 °C for 1 day. This final product was known as activated Iron nanomaterials.

2.4 Spectrophotometric Analysis of the Chromium Ion:-

This experiment is demonstrating the principles playing a significant role in the spectrophotometric determination of colored ions. Firstly, the absorption spectrum of chromium(III) ion will be allocated in the range between 350 nm and 650 nm. Secondly, the amount of light absorbed by a sample and the concentration of species is noted and their quantitative relationship has been established and this relationship has been clearly illustrated through Beer's Law. Then, the absorbance pattern of standard chromium(III) solutions has been studied till their specific absorption spectrum. A series of tabular representations have been made to find out the concentration of unknown samples using the known concentrations and the absorbances. Similarly, it can be found out using graph paper.

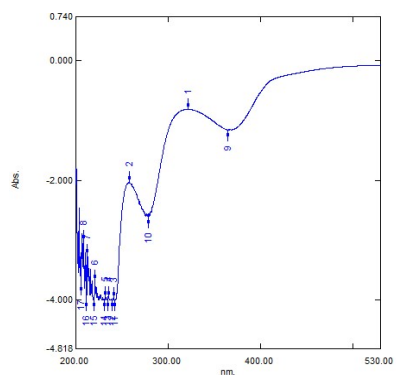


Figure 1.4:UV spectra of Cr^{3+}

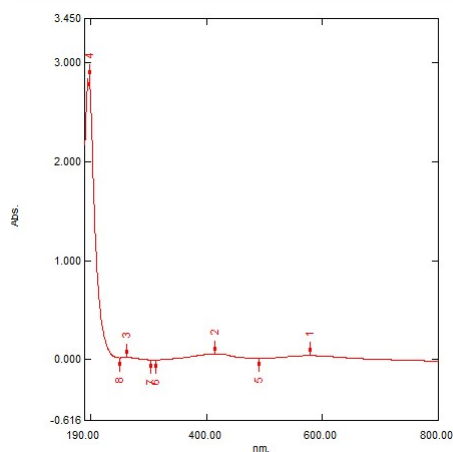


Figure 1.5: UV spectra of Standardized Cr^{3+}

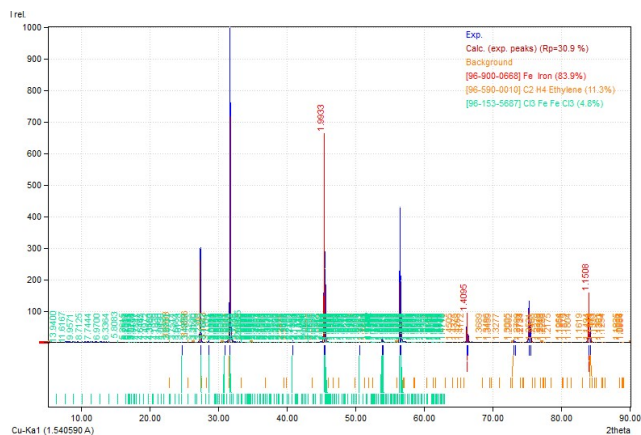


Figure 1.6: XRD graph of the synthesized MOF

The above Figure represents the XRD patterns of the synthesized MOF. The prominent peaks are visible in the XRD graphs corresponding to the presence of C, H, Cl and Fe in the synthesized crystal lattice. The Spectrum was measured at (500-4000 cm^{-1}) in which fingerprint region from (600-1200 cm^{-1}) and functional group region (1200-3600) was recorded in addition, the Fe-O and $\text{Fe}_3(\mu_3\text{-O})$ vibrations at 540 and 614 cm^{-1} existed in both spectra before and after Chromium adsorption.

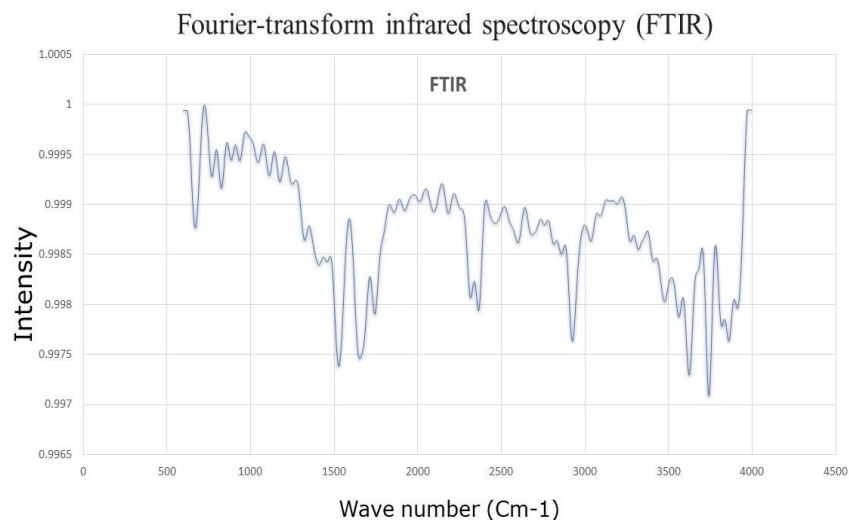


Figure 1.7: FTIR graph of synthesized MOF

3.1 Conclusion:-

We worked on iron-based organic metal frameworks (MOFs) using the precipitation method in this master thesis. These MOFs play a crucial role in the removal from drinking and groundwater of heavy metals such as chromium. We synthesized Fe-MOF I and Fe-MOF II in this novel work and characterized them by various analytical techniques such as TLC and U.V spectroscopy, followed by an adsorption

References

- [1] E. G. a. B. A. Nour Sh., "Green Synthesis of Nanoparticles for Water Treatment," *Scrivener*, Vols. 205-264, pp. 205, 207, 208(2019).
- [2] P. s. K. K. Pooja Devi, "Inorganic Pollutant in water" *Science Direct*, ,p.444,2020.
- [3] D.J.S.NeetuTewari, *Science In- Depth*, 2012ed., 2008.
- [4] I.c.L.m.Manjulakhuller, *LivingScience*, thirdrevised2011ed., 2009.
- [5] S. Dhyani, "Arsenic: Lurking in the shadows across Ganga, Brahmaputra basins," *Down to Earth*, 1501, 2020.
- [6] R. B. j. f.-S. D. A. a. E. P. Marton Mon, "Metal-Organic framework technologies for waterremediation: towards a sustainable ecosystem.," *Materials Chemistry A*, vol. 6, no. 12, p. 36, 132018.
- [7] A.Dwivedi, "RESEARCHESINWATERPOLLUTION:AREVIEW," *ResearchGate*, 2017.
- [8] S. L. S. E. R.-B. E. Z. L. Rafael Castañeda Olvera, "Review of nanotechnology value chain for watertreatmentapplications," *ScienceDirect*, p.11, 2017.

- [9] J. C. V. Z. Z. M. S. W. Huifeng Qian. Lori A. Pretzer, "Gold nanoparticles for cleaning contaminated water." *Chemical Technology and Biotechnology SCI*, vol.88, p.735, 11 February 2013.
- [10] L.X.J.-C. E.Y. H.-J.C. B.Y.a.M.-L. F.J.-B.Huo, "Colloids Surfaces," vol.539, pp.59-68, 2018.
- [11] T. A. S. P.V. Nidheesh, "Arsenic removal by electrocoagulation process: Recent trends and removal mechanism," *ELSEVIER*, vol.181, pp.418-432, 2017.
- [12] a. M.-C. D. a. R. H. Bonilla-Petriciolet, "Adsorption Processes for Water Treatment and Purification," 07 2017.
- [13] N.18, "News report 2021," *News 18*, 1012021.
- [14] D.A.Ghosh, D.a. kumar, R.kumar, M.Ali and R.Md, "High Arsenic Concentration in Blood Samples of People of Village Gyaspur Mahaji, Patna, Bihar Drinking Arsenic-Contaminated Water," *Journal of Toxicology and Environmental Health*, vol.12, 16 2020.
- [15] M.Berger, "What is a MOF (metal organic framework)" *Royal Society of chemistry*, 2019.
- [16] Y. L. j. Y. G. Y. R. X. X. kai Li, "Alpha-ferrous oxalate dihydrate: an Fe-based one-dimensional metal organic framework with extraordinary photocatalytic and fenton activities," *Catalysis technology*, 211 2019.
- [17] S. C. G. F. L. L. Y. L. Y. Jour, "Preparation of Fe(II)/MOF-5 Catalyst for Highly Selective Catalytic Hydroxylation of Phenol by Equivalent Loading at Room Temperature," *Journal of chemistry*, 07 11 2019.

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Chapter- 17

Increase in Levels of Concentration of Air Pollutants on Onset of Autumn Season in Srinagar City

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Abstract

Air pollution is growing rapidly due to modernization. On the one hand, air pollution is an environmental problem and on other hand, it is a social problem. Air pollution leads away to unfavorable effects on human well-being, the ecosystem, and the climate. As air pollution is increasing day by day the human well-being is decreasing. Many hearts and lung diseases are increasing due to air pollution and decreasing the life of humans. Therefore air quality monitoring stations are the basic necessity of a digital city to have an overview of present levels of pollution. The project looks into the levels of pollutants sulphur dioxide, nitrogen oxides, particulate matter (PM₁₀), from numerous sources over ambient air quality of Srinagar city. My research is conducted in Srinagar city. The samples of PM were collected in the main office Jammu and Kashmir pollution control board Rajbagh as a monitoring station was installed on the campus of Jammu and Kashmir Pollution Control Board (JKPCB). Sox and NOx was the first time conducted in the valley. Every sample is weekly taken and the average is taken monthly according to regulations of the central pollution control board. The main cause of pollution in Srinagar city is increased the number of vehicles, use of old engine vehicle and no norms have been set for them to combat such problem. From the observation, the data while lockdown was data analyzed was much less than permissible value which is due to vehicular movements.

Keywords: *Air Quality Index (AQI), Pollution Control Board (PCB), Particulate Matter (PM), Air Quality, Air Quality Monitoring.*

1. Introduction

The air around us in which we respire is a mixture of gases, strong debris, and liquid debris. Our priority is air quality as we have to live in the air. Those living beings who reside in industrial areas are concerned as they have to deal with a greater number of pollutants which are coming from industries, automobile traffic, and commercial. Some of the pollutions are caused due to natural catastrophes like a volcanic eruption, dust from the Sahara desert, forest fires other are Anthropogenic such as motor vehicle use, household activities, industries, and businesses. Human activities have an unfavorable result on the environment by way of polluting the water we tend to drink, the air we tend to respire, and additionally the soil inside which vegetation grows. Although the industrial revolution was a fulfillment in phrases of technology, society, and additionally the supply of multiple offerings, it conjointly introduced the meeting of massive quantities of pollutants emitted into the air that rectangular degree dangerous to human fitness. with absolute confidence, the sector environmental pollutants are taken into consideration global public health trouble with more than one aspects. Social, financial, and legislative considerations and mode conduct square measure related to this important drawback. Urbanization and industrial business enterprise square degree accomplishing unparalleled and displeasing proportions worldwide in our era. Phylogenesis pollution is considered one of the largest public fitness dangers international, as long as it debts for regarding 9 million deaths every 12 months [1]

As Kashmir sees a harsh iciness and there's no strength supply to provide the human beings of Kashmiri with not unusual fireplaces referred to as kangri (in the Kashmiri language) to preserve them heat internally and out. This conventional method of wintry weather warming is customary by using all lessons of humans. This leads to a higher level of biofuel emissions from the surroundings in a chilly dry environment and contributes to winter air pollutants

From the modern-day take a look at, specifically vehicles, big population, dry climate, and existing industries produce a huge amount of pollution. Consequently, the air quality of the city of Srinagar desires to be studied in element as its miles the main challenge for the fitness care of the human beings living in Srinagar resulting from air pollution. The vicinity I may be concerned approximately might be the Rajbagh location. As safety stations are set up inner Srinagar.

2. Sampling of Air

The term air sampling determines the procedure how to collect air pollutants to identify and measure the amount of pollution. Air sampling assemblage of impurities of air to find the pollutant and to determine the amount of pollutant present. Air sampling involves every process that is related to finding the particular type of pollutant in a particular area and the quantity of pollutant present. Initially, the air sample is taken on-site and then the whole process of sampling is done in a laboratory. The samples are taken very precisely from the site as the concentration is wholly dependent on the precision on which they are taken from the site. It is very important for Air sampling to have a person on-site to check the regular flow and manometer readings continuously. On-site it is necessary to have a regular power supply so that the respirable dust sampler has interpreted sampling data. Before taking the filter paper on site it is important to remove moisture by keeping it in a desiccator and should be pre-weighted before use. The vital sources of pollution may be known with the installation of close air quality of observation station. The sampling with observation station will give the current standing of air quality of that exact space[2]. Concentration is numerically calculated in ppm or PBM or it can either be calculated mass per unit $\mu\text{g}/\text{m}^3$

3. Sequence of Air sampling

The sequence of air sampling means the systematic manner in which the air contaminants all the intermediate steps are taken to measure the total amount of concentration present in the air. It is also called the workflow of air sampling. It involves all the steps taken to calculate a particular type of pollutants in the atmosphere. Every step in the workflow process is done with precision and accuracy. The workflow process involves three-step that are;

- Collection of sample:- Sample is collected on-site either on filter paper or Sorbent tubes
- Extraction of sample:- The filter paper or sorbent tubes is taken to the laboratory to analyze the contaminants
- Analysis:- Analysis of sample is done to determine the concentration of a particular pollutant and to check the concerned air is good for health or not.

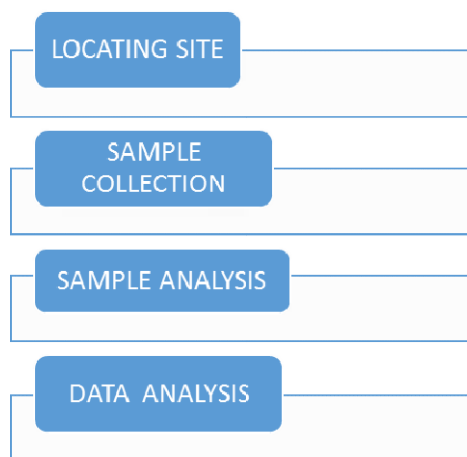


FIGURE 1: Sequence of Air sampling

4. Air quality monitoring

Air fine monitoring is the preparation technique of checking the degrees of contamination in assessment to standards. Air quality monitoring is a prolonged evaluation of pollutant levels in the atmosphere. Air monitoring is the measure of the number of pollutants as well as the kind of pollutant in the atmosphere. Air quality monitoring helps to find the severity of a particular type of pollutant and its adverse effect on society. The main aim of air quality monitoring is to attain clean air. It also targeted measures that lead to a pollution-free environment. Positive norms are set by using the principal pollutants to manipulate the board to reduce the level by putting a permissible restriction. The permissible limit is standards that are set by regulatory bodies to reduce pollution and ultimately get cleaner air. Ambient air quality observance is that the organized, end-of-the-day analysis of contamination levels by estimating the number and types of specific toxins within the encompassing outside air. The contaminations like residue, smoke, gases, and exhaust could be either from regular or artificial sources. The assets of air pollution encompass cars, industries, domestic assets, and natural assets. as a result of the presence of high stay of air pollutants in the around the air, the well-being, and assets of the human beings in obtaining unfavorably encourage[3]. Air quality monitoring is operated by the state government that works on the principle of the central government. The sample of air is taken from the site and analysis is done in the laboratory. The air quality monitoring indicates the exposure of various pollutants in a particular area. It also determines that how

much concentration of pollutant we are exposed to whether the particular area is under the permissible limit or not so that necessary steps should be taken by various governmental agencies to reduce the influence of pollutants. Clean Air is a basic need to society to have a check on clean air. Air quality monitoring is essential.

4.1. Air Quality Monitoring Process

The air nice tracking technique involves all of the organized steps from tracking to information analysis. The sequential procedure that ends in an analysis of facts is referred to as the manner of air pleasant monitoring. The first process involves the selection of an area for the installation of the instrument. Site selection is basically to locate the particular area that fulfills all the requirements of monitoring. The second process involves the collection of air samples and that air sample is taken to the laboratory for analysis and the data is obtained from the analysis

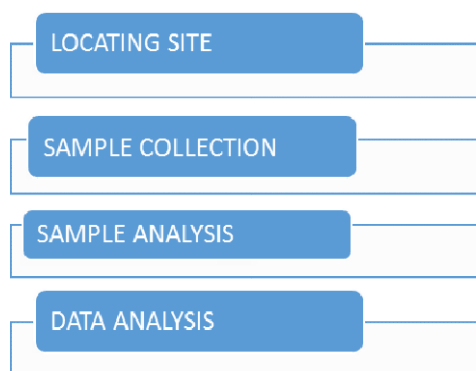


FIGURE 2: AIR QUALITY MONITORING PROCESS

4.2. Air quality index

An air satisfaction index (AQI) is a range utilised by government agencies to speak to the public approximately how tons of air is polluted. Air quality index (AQI) is awareness about the quality of present air and evaluation of limits and their impact on health. The air high-quality index is broadly categorized into six classes namely desirable, first-rate, fairly polluted, bad, Very terrible, and extreme. These categories of air quality index are obtained by ambient concentration of pollutants and their health issues these are called health breakpoints. Air high-quality index is evolved for 8 pollution PM_{10} , $PM_{2.5}$, NO_2 , SO_2 , CO , O_3 , NH_3 and Pb for twenty-four hours the use of as countrywide Ambient Air fine trendy are intently associated with a health problem as lots as Air quality index is growing the air is not appropriate for health. The air exceptional index value is from 0-50 to

301-500. The influence of human fitness is mentioned in those ranges. Air satisfactory index (AQI) or pollution index (API) is normally aware of record the amount of severity of pollutants to the general public. style of ways was developed inside the beyond via various researchers/environmental agencies for determination of AQI or API but there may be no universally established methodology that exists, that is proper for all matters. Exceptional absolutely unique} method uses one-of-a-kind aggregation performs in conniving AQI or API and considers differing kinds and numbers of pollutants. The meant makes use of AQI or API place unit to spot the bad air first-class zones and public reportage for the severity of exposure of terrible air great. most of the AQI or API indices can be widely classified as single waste remember index or multi-pollutant index with completely distinct aggregation methodologies. every categorization methodology has its characteristic strengths and weaknesses that affect its suitability for particular packages. This paper decide to gift an evaluation of all the foremost air fine indices advanced global[4]



FIGURE 3: Air quality index standards
TABLE 1: Air Quality Index table

Air quality standard	AQI category	Colour
0 to 50	Good	Green
51 to 100	Satisfactory	Yellow
101 to 200	Moderately polluted	Orange
201 to 300	Poor	Red
301 to 400	Very Poor	Purple
401 to 500	Severe	Maroon

4.3. AQI REPORT

The population of the Metropolitan Statistical Area is more than 350,000 have to represent the air quality index to the general public. The report has to be represented daily. The report must be taken at a maximum of 5 days a week. Two days in a week are left in case of non-functioning of the instrument or non-availability of manpower. AQI report takes 24 hours to be made. Air quality index requires systematic processes:



Figure 4: layout of aqi report

5. Air pollutants

Any substance which causes pollution is referred to as a pollutant. The air pollutants may be classified as primary or secondary pollutants. The World Health Organization (WHO) reviews six major air pollution, mainly particle pollution, floor-level gasoline, CO, sulphur oxides, detail oxides, and lead. Pollutants could have an unfortunate effect on all factors of the putting, in addition to groundwater, soil, and air. as well, it poses an extensive chance to residing organisms at some point in this vein, our interest is mainly to concentrate on these pollutants, as they're related to several extensive and excessive problems in human fitness and environmental effect. Acid rain, warming, the atmospheric phenomenon, and climate changes have a crucial ecological impact on pollution [5]

➤ **Primary Pollutant:** - The number one air pollution is detrimental chemical compounds that without delay input the air because of natural events of human activities.

Ex Hydrocarbons (HC, VOCs), Carbon monoxide (CO), NO_x, SO_x, Particulate matter, etc

➤ **Secondary Pollutant:** - now not without delay emitted as such but bureaucracy when other pollution seats inside the environment. A secondary air pollutant is a damaging chemical produced within the air because of a chemical reaction between or extra components this is the main pollutants that work with sure elements of the surroundings to create secondary pollution.

Ex Tropospheric ozone (O₃), PAN (Peroxy acetyl) nitrate, Acidrain, Photochemical smog

The maximum not unusual and toxic air pollutants are sulphur dioxide (SO₂), formed whilst fossils along with coal, gasoline, and oil are used to generate energy, other assets including man-made and natural supply commercial dust, volcanic eruptions, diesel-powered motors; fixed particle remember (SPM), solid and liquid debris emitted by way of many man-made and herbal assets consisting of industrial dirt, volcanic eruptions, diesel-powered automobiles emitting fixed substances (SPM) into the air these are the pollutants that continue in my study

(i) Sulphur dioxide

(ii) Nitrogen oxides

(iii) TSP

(iv) PM10

(1) **Sulphur dioxide:** - Sulphur dioxide (SO₂) is a non-painted fuel emitted as a final result of the mineral strength that contains sulphur. It has a burnt matches smell. fitness results as a result of

subordination to excessive degrees of SO_2 encompass respiration issues, respiratory ailments, adjustments in lung immunity, and the severity of heart sickness. Even slight exposure to SO_2 can result in a collapse of lung asthmatics interest. Acid rain is also an essential source of care because it may damage something in contact with it, along with buildings, lakes, and timber. Acid rain can be termed as rain with a lower pH than every day (pH at 7). Sulphur dioxide might be a harmful fuel it is emitted principally from fuel intake or business sports. The yearly common for SO_2 is 0.03 ppm[6]. It impacts humans, animals, and plants. willing people as people with breathing organ unwellness, old humans, and children, international fitness company gift a better chance of injury. the key fitness problems related to dioxide emissions in business area gadgets are metastasis infection, bronchitis, secretion production, and spasm due to the fact it can be a sensory thorn and penetrate deep into the respiratory organ regenerate into bisulphite, and interact with sensory receptors, causing bronchoconstriction. furthermore, pores and skin redness, damage to the eyes (lacrimation and membrane opacity) and mucose membranes, and worsening of the pre-existing ailment are ascertained [7].

(2) **Nitrogen oxides(NO_x):**- the main supply of nitrogen oxides (NO_x) is to do away with the auto as its miles shaped as a result of high-temperature combustion techniques in the engine most of the NO_x emitted from automobiles is within the shape of NO , which is oxidized in air to NO_2 . NO_x gases are considered indirect greenhouse gases and are one of the foremost contributors to acid deposits. The fitness consequences of NO_2 publicity may be bronchial asthma or persistent allergies. Nitrogen oxide can be a visitors-related waste due to the fact it's far emitted from car motor engines [7, 8]. It's far pronounced that long-time period publicity to excessive tiers of nitrogen dioxide can be responsible for a persistent lung disorder. Lengthy-term publicity to NO_2 can impair the feel of scent. However, structures other than respiration ones can be involved, as signs which include eye, throat, and nose inflammation had been registered. Excessive ranges of nitrogen dioxide are deleterious to crops and flowers, as they were observed to reduce crop yield and plant boom efficiency. Furthermore, NO_2 can reduce visibility and discolor fabrics [9].

(3) **Total particle size (TSP):** Particulate matter (PM) is occasionally long-established in the environment because of chemical reactions between the diverse pollutants. The penetration of particles is closely enthusiastic about their length. Particulate matter (PM) turned into

outlined as a term for debris with the aid of the American Environmental protection organization. material (PM) pollutants consist of debris with diameters of ten micrometers (μm) or smaller, known as PM_{10} , and really fine particles with diameters which can be typically 2.5 micrometers (μm) and smaller. total particle size, PM_{10} and $\text{PM}_{2.5}$ overall fixed particles (TSP) discuss with a small institution of strong or liquid debris suspended from an electric or liquid less than a hundred micrometers and might stay suspended within the air for some seconds a few to 3 months. Particulate emissions occur due to coal burning in electricity vegetation, various industrial procedures, mining operations, and disputes, municipal boilers/heaters, and gasoline burning. TSP consists of additives of PM_{10} and $\text{PM}_{2.5}$.

The PM_{10} is a fundamental particle with a diameter of less than or identical to 10 microns. large particles do now not breathe and are eliminated from the air by way of the earth's formation manner. the main supply of the PM_{10} 's air problem is road emissions, mainly from diesel automobiles. PM_{10} ends in fitness troubles as it has a barrier to the chest region of the human respiratory gadget in which it could reason infection and deterioration in humans with heart and lung disorder Particulate be counted carries little liquid or solid droplets that may be indrawn and cause extreme health effects [10]

$\text{PM}_{2.5}$ refers to the debris of 2.5 micrometers or even less. $\text{PM}_{2.5}$ resources include gas-burning from vehicles, electricity stations, wooden burning, business strategies, and diesel-powered motors which include buses and vehicles. $\text{PM}_{2.5}$ is also produced in the atmosphere when gases which include SO_2 , NO_x , and VOCs are transformed into the air through chemical reactions. $\text{PM}_{2.5}$ can motive critical health troubles due to the fact $\text{PM}_{2.5}$ can enter the breathing tract into the bloodstream. a couple of epidemiological research has been finished on the fitness effects of PM. An advantageous relation became proven between each brief-time period and lengthy-term exposures of $\text{PM}_{2.5}$ and acute nasopharyngitis. Further, lengthy-term publicity to PM for years was determined to be related to cardiovascular diseases and infant mortality [11].

Month	Rajbagh (910)
April 2019	72.41 $\mu\text{g}/\text{m}^3$
May 2019	58.13 $\mu\text{g}/\text{m}^3$
June 2019	75.47 $\mu\text{g}/\text{m}^3$
July 2019	88.44 $\mu\text{g}/\text{m}^3$
August 2019	Curfew
September 2019	58.97 $\mu\text{g}/\text{m}^3$
October 2019	54.08 $\mu\text{g}/\text{m}^3$
November 2019	61.16 $\mu\text{g}/\text{m}^3$
December 2019	134.25 $\mu\text{g}/\text{m}^3$
January 2020	68.29 $\mu\text{g}/\text{m}^3$
February 2020	70.05 $\mu\text{g}/\text{m}^3$
March 2020	71.49 $\mu\text{g}/\text{m}^3$
YEARLY AVERAGE	73.88 $\mu\text{g}/\text{m}^3$

Results

TABLE 1: Air Quality Monitoring data of PM₁₀ for the year 2019-2020

NOTE:

- 1) All mentioned data is taken for the financial year 2019-2020
- 2) The monitoring data is restricted to the samples collected only.
- 3) The permissible limit of PM_{2.5} for 24 hours=100 $\mu\text{g}/\text{m}^3$ and year =60 $\mu\text{g}/\text{m}^3$

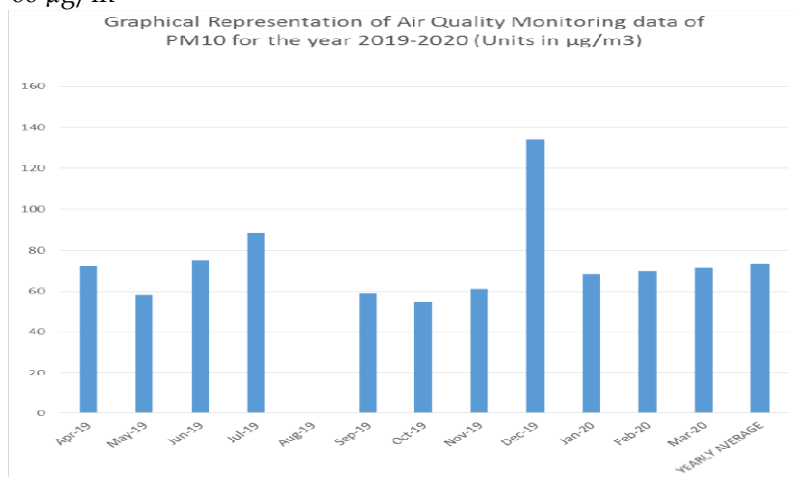


Figure 5: Air Quality Monitoring data of PM₁₀ for the year 2019-20

TABLE 2: Air Quality Monitoring data of PM10 for the year 2020

Month	Srinagar
January 2020	68.29 $\mu\text{g}/\text{m}^3$
February 2020	70.05 $\mu\text{g}/\text{m}^3$
March 2020	71.49 $\mu\text{g}/\text{m}^3$
April 2020	Sampling not done due to covid-19
May 2020	38.96 $\mu\text{g}/\text{m}^3$
June 2020	42.6 $\mu\text{g}/\text{m}^3$
July 2020	53.62 $\mu\text{g}/\text{m}^3$
August 2020	57.05 $\mu\text{g}/\text{m}^3$
September 2020	81.45 $\mu\text{g}/\text{m}^3$
October 2020	99.28 $\mu\text{g}/\text{m}^3$
November 2020	95.89 $\mu\text{g}/\text{m}^3$
January 2021	92.34 $\mu\text{g}/\text{m}^3$
February 2021	160.15 $\mu\text{g}/\text{m}^3$
March 2021	174.69 $\mu\text{g}/\text{m}^3$

NOTE:

- 1) All mentioned data is taken for the financial year 2019-2020
- 2) The monitoring data is restricted to the samples collected only.
- 3) The permissible limit of PM_{2.5} for 24 hours=100 $\mu\text{g}/\text{m}^3$ and year =60 $\mu\text{g}/\text{m}^3$

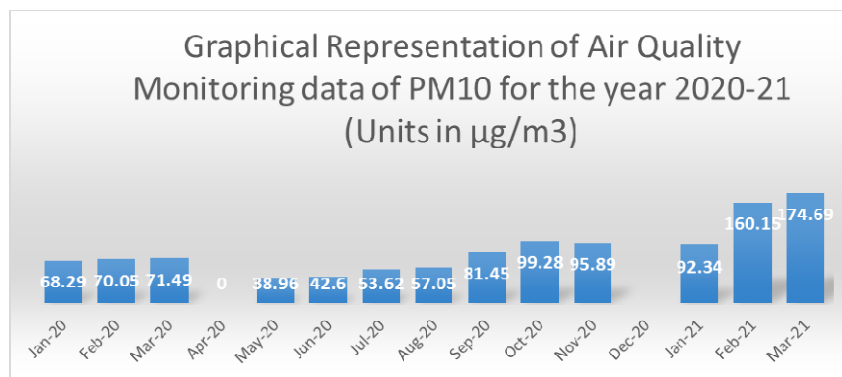


Figure 6: Air Quality Monitoring data of PM10 for the year 2020

TABLE 3: Air Quality Monitoring data for NO_x for January 2021

S. N o.	Place	Date of sampling	Absorbance of blank	Absorbance of sample	Time duration	Result (NO _x)
1.	Srinagar	12-01-2021	0.0071	0.1440	08 hours	41.68 µg/m ³
2.	Srinagar	15-01-2021	0.0070	0.0784	08 hours	21.73 µg/m ³
3.	Srinagar	22-01-2021	0.0125	0.1442	08 hours	40.09 µg/m ³
					Average	34.5 µg/m³

NOTE:

- 1) All mentioned data is taken for the financial year 2020
- 2) The monitoring data is restricted to the samples collected only.
- 3) The permissible limit of NO_x for 24 hours=80 µg/m³ and the year=60 µg/m³

TABLE 4: Air Quality Monitoring data for SO_x for April 2021

S. N o.	Place	Date of sampling	Absorbance of blank	Absorbance of sample	Time duration	Result (SO _x)
1.	Srinagar	01-04-2021	0.0067	0.0090	08 hours	1.04 µg/m ³

NOTE: -

- 1) All mentioned data is taken for the financial year 2020
- 2) The monitoring data is restricted to the samples collected only.
- 3) The permitted limit of SO_x for 24 hours=80 µg/m³ and the year=60 µg/m³

7. CONCLUSION

Ambient air quality was assessed in the Rajbagh area of Srinagar city the studies have revealed the levels of air pollutants for PM₁₀, NO_x, and SO_x. The trend of a pollution-free environment is decreasing on the arrival of winter in Kashmir (by the end of Oct). The increase in

AQI on the site is likely to be due to an increase in transport and government offices near the raj bagh area are also responsible for this. As in winter the locals of Srinagar switch to biofuels i.e burning coal and wood for various domestic works. The main contributor to Rajbagh station (910) the surrounding area has chinara trees and during autumn (i.e mid-September and mid-October) the falling of chinara takes place and the leaves are burnt, with the ash combined with charcoal for winter. Instead of burning the leaves must be buried in soil and the soil could be enriched in nutrients naturally and dry chinara leaves work as manure for the soil. This leads to an eco-friendly environment. Many unmacadamized roads are also contributing to air pollution.

As my concerned area of study is the Rajbagh area there are many state offices due to their vehicular exhaust the Air quality is declining. Therefore the government must encourage mass transportation for offices. The main concern of my study is increasing levels of pollution in the winter season due to the storage of electricity the people of Kashmir are solely dependent on biofuels i.e burning of traditional kangri, burning of traditional Hamam to keep themselves warm in freezing temperature. This leads to an increase in pollution levels in the ambient and also leads to the destruction of natural resources e.g coal, wood, fuels, etc. This is due to the storage of electricity as most of the reservoirs lack water supply due to freezing temperatures. So there must be made a provision of renewable source of energy i.e Sun. Sunlight can be stored in summers and then can be later on used in winter for central heating systems like hamams

Declaration of competing interest

The author announces that they have no economic interests or peculiar relationships that could appear to influence the work reported in this paper.

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References

1. WHO. *Air Pollution*. WHO. Available online at: <http://www.who.int/airpollution/en/> (accessed October 5, 2019). Google Scholar
2. Krishna, R. & SM, Shiva Nagendra & Saraswati, & Diya, M..(2020). Air Quality Monitoring and Techniques. 10.1007/978-981-15-5511-4_2.
3. Sharma, Arvind & Pandey, Neeraj. (2021). Monitoring of ambient air quality.
4. Kanchan, Kanchan & Gorai, Amit & Goyal, Pramila. (2015). A Review on Air Quality Indexing System. Asian Journal of Atmospheric Environment. 9. 101-113. 105572/ajae.2015.9.2.101.
5. Wilson WE, Suh HH. Fine particles and coarse particles: concentration relationships relevant to epidemiologic studies. *J Air Waste Manag Assoc.* (1997) 47:1238-49. doi: 10.1080/10473289.1997.10464074
6. US EPA. *Table of Historical SO₂ NAAQS, Sulfur US EPA*. Available online at: https://www3.epa.gov/ttn/naaqs/standards/so2/s_so2_history.html (accessed October 5, 2019).
7. Chen T-M, Gokhale J, Shofer S, Kuschner WG. Outdoor air pollution: nitrogen dioxide, sulfur dioxide, and carbon monoxide health effects. *Am J Med Sci.* (2007) 333:249-56. doi: 10.1097/MAJ.0b013e31803b900f
8. Richmond-Bryant J, Owen RC, Graham S, Snyder M, McDow S, Oakes M, et al. Estimation of on-road NO₂ concentrations, NO₂/NO_x ratios, and related roadway gradients from near-road monitoring data. *Air Qual Atm Health.* (2017) 10:611-25. doi: 10.1007/s11869-016-0455-7
9. Hesterberg TW, Bunn WB, McClellan RO, Hamade AK, Long CM, Valberg PA. Critical review of the human data on short-term nitrogen dioxide (NO₂) exposures: evidence for NO₂ no-effect levels. *Crit Rev Toxicol.* (2009) 39:743-81. doi: 10.3109/10408440903294945
10. Zhang L, Yang Y, Li Y, Qian ZM, Xiao W, Wang X, et al. Short-term and long-term effects of PM_{2.5} on acute nasopharyngitis in 10 communities of Guangdong, China. *Sci Total Env.* (2019) 688:136-42. doi: 10.
11. Kloog I, Ridgway B, Koutrakis P, Coull BA, Schwartz JD. Long- and short-term exposure to PM_{2.5} and mortality using novel exposure models. *Epidemiology.* (2013) 24:555-61. doi: 10.1097/EDE.0b013e318294beaa

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Chapter:18

Flood Management of Jhelum Basin

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ABSTRACT

Because of its geological structure and position, the Kashmir valley is particularly prone to flooding. Flooding has been a frequent occurrence in the valley since it took on its current shape after draining out of the ancient karewa lake. Flood mitigation measures were implemented beginning in 1950, with the construction of a number of dams and barrages. Floods remain a threat, though, owing to the massive amount of sediment transported by rivers coming from the Himalayas.

Key Words: *Flood, Rainfall, Dredging, Tributaries, Historical Floods, Flood Management.*

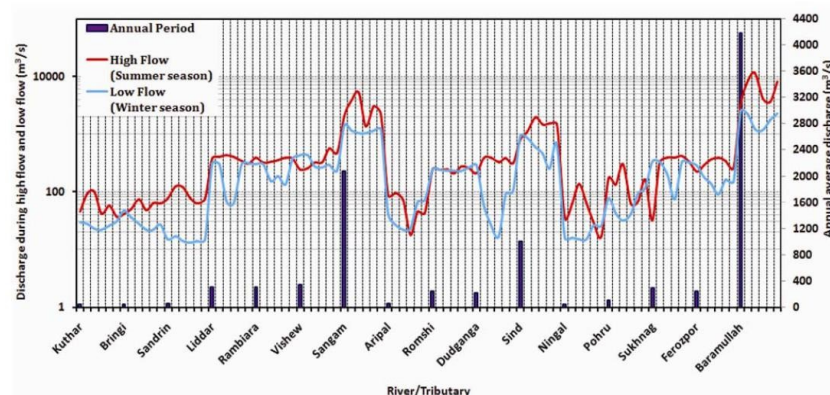
INTRODUCTION

The state of Jammu and Kashmir encompasses an area of approximately 222236 square kilometres, ranging from 32° 17' N to 36° 05' N and from 73° 02' E to 80° 30' E. The state rises in many stages from plains in the south to higher altitude valleys and peaks in the north, encompassing some of the world's highest mountain peaks. The state of Jammu and Kashmir is split into four areas based on their meteorological conditions: Temperate Kashmir valley, Tropical Jammu province, Alpine Ladakh, and Kargil regions. The Kashmir valley is bordered by the Himalayas, which range in height from 1000 feet to 1800 feet above mean sea level and span between 33° 22' N to 34° 43' N and 73° 52' E to 75° 42' E, encompassing an area of approximately 15948 square kilometres.

KASHMIR, recognized across the globe for its lush green beauty and river flows, has been severely impacted by floods in its rivers, particularly the JHELM and its tributaries. These floods have wreaked devastation on cultivable areas and villages. JHELM is renowned as Kashmir's lifeblood since all of the main towns and cities with large populations are located on its banks. However, with the

2014 floods, this lifeline turned into a lethal torrent. The floods of 2014 are not new in Kashmir's history; previous floods have also occurred; nevertheless, our current analysis will be mostly focused on data obtained during the 2014 floods. The major cause of recent floods has been the inadequate carrying capacity of Jhelum, Kashmir's only drainage route. The current analysis makes an attempt to show 2014 rainfall statistics as well as its influence on the river. Furthermore, an attempt has been made to examine the encroachments on the river Jhelum, particularly the river wetlands.

Let us proceed with this research by first looking at the Jhelum River and its tributaries. Then we'll look at rainfall statistics, and then we'll look at decreasing wetlands.



Reasons for Floods:

- Deforestation.
- Reduction in Velocity.
- Reduction in slope.
- Obstruction due to new bridges.
- Sewerage and waste from urban areas.
- Reduction in area of Wular Lake.
- Uncontrolled and random mining of river / nallah bed material.
- Climatic change and rise in average water temperature.

Problem Formulation

The particular research is related to flood problem in river Jhelum. The 2014 floods created havoc in Kashmir and entire Srinagar city

along with the peripheral areas got submerged under flood water. The thesis has collected high discharge data of 40 years for four sites from irrigation and flood control department Srinagar. The four sites are Sangam, Asham, Rammunshi Bagh, and Baramulla. At all the four sites using gumbell distribution method and log pearson (THIRD) method (using Microsoft excel), I have calculated the return of a particular flood and also the estimated discharge. Using the data of calculated discharge the problem of flood and its effects can somehow be mitigated by using both structural and non-structural measures.

Objectives of Research

- The flood discharge calculated can be used in designing the flood channels to by-pass floods.
- The flood discharge can also be used to design spill channels at various locations.
- The government can also focus on designing and construction of parallel channel to river Jhelum so that the excess water can be transported through it.
- My research has also identified three dam sites in district Anantnag, so that flood waters can be harnessed into the electrical energy.
- The study also showcases the encroachments near Jhelum so an encroachments free drive is also important to make Jhelum healthy.
- Various important sites of designing can also be identified which will let Jhelum maintain its capacity of flowing hassle free.

Methodology

The flood control of the Jhelum basin was first separated into two phases.

- Analysis of Flood Frequency
- Flood Control

Analysis of Flood Frequency

The frequency of occurrence of extreme hydrologic events such as floods, droughts, and severe storms is critical in water resource planning and management. There is a clear relationship between frequency of occurrence and magnitude; ordinary events occur more frequently than catastrophic storms. The frequency and probability distributions aid in relating the size of these extreme events to their number of occurrences, allowing their likelihood of occurrence over time to be effectively anticipated. To fit any theoretical distribution to

the collected historical records, the data must first be examined in order to gain statistical information. The observed frequent distribution, also known as the empirical frequency distribution, is supposed to correspond to any of the theoretical distributions. This provides the required probability of the event occurring. To do this, the hydrological data used should be carefully chosen such that the homogeneity, independence assumption, and minimum length of sample record are fulfilled to match the fitted distribution. Theoretical distribution equations are less commonly employed in hydrology because the probability distribution function for the vast majority of distributions is not easily invertible. There are two simple approaches for fitting theoretical distributions to empirical distributions. These are the methods:

I. Chow's frequency factor technique.

II. Graphical approach based on probability paper.

Before delving into frequency factor techniques, it is necessary to understand the broad idea of recurrence interval, return period, or frequency (T). The recurrence interval is defined as the average time (T) interval during which a flood (or other severe event) of a certain size will be equaled or exceeded at least once. As an example, suppose the probability of an event P is 0.25. This indicates that the event has a 25% chance of occurring every year. Thus, during the course of the project's 100-year lifespan, a flood of this scale will last for more than 25 years. As a result, the average flood return period is $100/25=4$ years.

If p is the probability in percentage then,

Return period $T = 1/p$ if p is the probability in percentage (5.1)

The probability of an event not occurring is $(1-p) = 1 - 1/T$. (5.2)

Probability of non-occurrence over n years $(1 - 1/T)^n$ (5.3)

The likelihood of occurrence is $1 - (1 - 1/T)^n$. (5.4).

This possibility of occurrence is referred to as risk. If an engineer is permitted to incur 5% risk during a life span of, say, 40 years, the return period of the event should be computed as

$$0.05 = 1 - (1 - 1/T)^{40} \text{ or}$$

$$(1 - 1/T)^{40} = 1 - 0.05 = 0.95 \text{ or}$$

$$1 - 1/T = 0.9987184 \text{ or } T = 780 \text{ years.}$$

The average time interval of an occurrence of a particular size being equaled or exceeded, rather than the actual time interval, is the return period. When hydrologic values are sorted in some order (ascending or descending), it is clear that every variate may be written as:

$$X_T = x_{av} + D_x.$$

1.1.1.1 Flood Management

1.1.1.2 Once we established the Stage-Discharge rating curve at four main sites using stage data obtained from the desired sites' gauging stations, we performed flood frequency analysis at the various sites using distributions such as Gumbel's, Pearson Type III, Log-Pearson Type III, and Normal Distribution, and we obtained the desired design flood discharges at these sites over a five-year, twenty-year period. Now that we've evaluated everything and gathered all of the necessary info. At the sites, we might consider flood mitigation and control strategies.

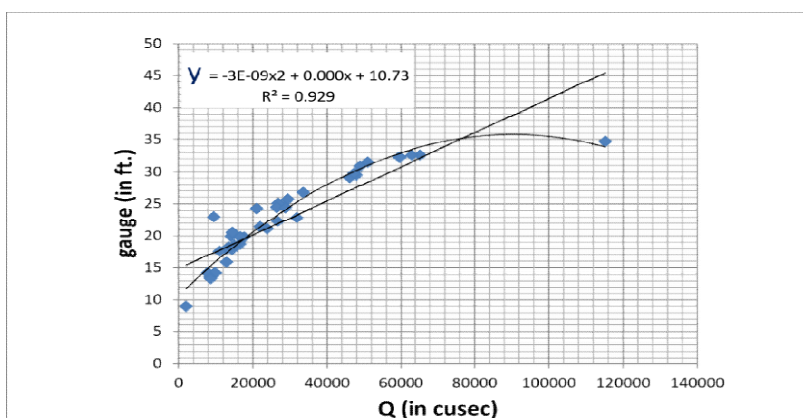
1.1.1.2.1 Measures for flood management

Various methods have been implemented to prevent flood/erosion losses and preserve flood plains. Flood protection and flood management measures can be roughly categorised as follows, depending on how they work:

- Engineering/Structural Measures.
- Non-Structural Metrics.
- Treatment of Catchment Areas.

Results

FIG.: SANGAM-GD CURVE



SITE: Sangam gumbel distribution (with chi square test):

TABLE 1

YEAR	DISCHARGE	RANK	Discharge INTERVAL	RECURANCE	Q	Q-Ō REDUCED
1975	47900	1	115218	41	115218	87559.483.701251
1976	50958	2	65305	20.5	65305	37646.482.995524
1977	9075	3	62876	13.66666667	62876	35217.482.577207
1978	16528	4	59700	10.25	59700	32041.482.27639
1979	14400	5	59400	8.2	59400	31741.482.039812
1980	7900	6	50958	6.833333333	50958	23299.481.843743
1981	26778	7	48900	5.857142857	48900	21241.481.675516
1982	13505	8	47900	5.125	47900	20241.481.527561
1983	14125	9	47300	4.555555556	47300	19641.481.394987
1984	12885	10	46110	4.1	46110	18451.481.274449
1985	33600	11	33600	3.727272727	33600	5941.4751.163552
1986	26435	12	31831	3.416666667	31831	4172.4751.060518
1987	29390	13	29390	3.153846154	29390	1731.4750.963992
1988	48900	14	28812	2.928571429	28812	1153.4750.872908
1989	15150	15	26778	2.733333333	26778	-880.525 0.786413
1990	9520	16	26717	2.5625	26717	-941.525 0.703811
1991	17660	17	26435	2.411764706	26435	-1223.53 0.62452
1992	65305	18	23850	2.277777778	23850	-3808.53 0.548047
1993	46110	19	21952	2.157894737	21952	-5706.53 0.473964
1994	23850	20	21065	2.05	21065	-6593.53 0.401897
1995	59400	21	17660	1.952380952	17660	-9998.53 0.331509
1996	59700	22	16593	1.863636364	16593	-11065.5 0.262491
1997	62876	23	16528	1.782608696	16528	-11130.5 0.194556
1998	12950	24	15150	1.708333333	15150	-12508.5 0.127426
1999	8742	25	14500	1.64	14500	-13158.5 0.06083
2000	9865	26	14400	1.576923077	14400	-13258.5 -0.00551
2001	2031	27	14125	1.518518519	14125	-13533.5 -0.07187
2002	8676	28	13505	1.464285714	13505	-14153.5 -0.13856
2003	21065	29	12950	1.413793103	12950	-14708.5 -0.20593

2004	14500	30	12885	1.366666667	12885	-14773.5	-0.27435
2005	16593	31	10989	1.322580645	10989	-16669.5	-0.34429
2006	47300	32	9865	1.28125	9865	-17793.5	-0.4163
2007	21952	33	9520	1.242424242	9520	-18138.5	-0.49111
2008	8540	34	9075	1.205882353	9075	-18583.5	-0.56966
2009	8610	35	8742	1.171428571	8742	-18916.5	-0.65327
2010	28812	36	8676	1.138888889	8676	-18982.5	-0.7439
2011	26717	37	8610	1.108108108	8610	-19048.5	-0.8447
2012	10989	38	8540	1.078947368	8540	-19118.5	-0.96125
2013	31831	39	7900	1.051282051	7900	-19758.5	-1.1054
2014	115218	40	2031	1.025	2031	-25627.5	-1.31199

Jump Test For Sangam Station :

YEAR	Q (average)	Average of Average
1975	7513	6088.766
1976	11635	
1977	3140	
1978	4186	
1979	6715	
1980	4070	
1981	6911.8	
1982	4539.33	
1983	5935	4470.879
1984	3822	
1985	2769	
1986	5728.79	
1987	5727	
1988	5649	
1989	3123	

1990	3013.24	
1991	5332.76	6236.676
1992	8247	
1993	8358	
1994	8821	
1995	7449	
1996	8632	
1997	6569	
1998	4724	
1999	2158	
2000	2076	
2001	1198	4901.942
2002	2237	
2003	3175	
2004	2522	
2005	5182.87	
2006	3370.264	
2007	3141.89	
2008	2550.31	
2009	2504	
2010	3012	
2011	3281	
2012	3545	
2013	3048	
2014	29859.86	

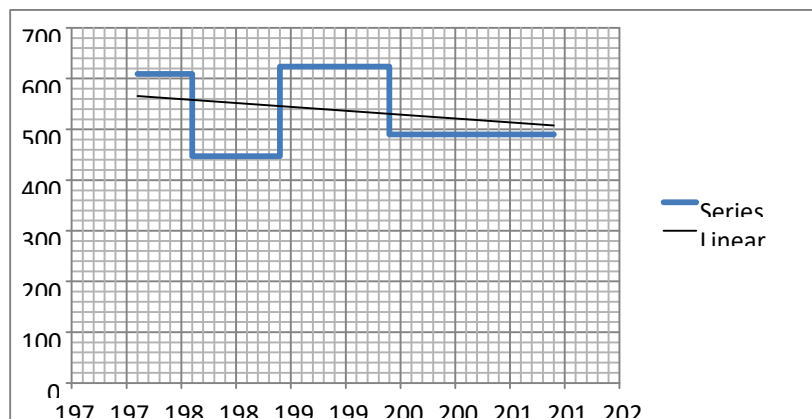


FIG.: JUMP TEST OF SANGAM

1.1.2 Kandle's Trend Test

YEAR	DISCHARGE	Discharge	p
1975	47900	115218	32
1976	50958	65305	34
1977	9075	62876	6
1978	16528	59700	17
1979	14400	59400	14
1980	7900	50958	1
1981	26778	48900	25
1982	13505	47900	12
1983	14125	47300	13

1984	12885	46110	10
1985	33600	33600	29
1986	26435	31831	23
1987	29390	29390	27
1988	48900	28812	33
1989	15150	26778	16
1990	9520	26717	7
1991	17660	26435	19
1992	65305	23850	38
1993	46110	21952	30

1994	23850	21065	22
1995	59400	17660	35
1996	59700	16593	36
1997	62876	16528	37
1998	12950	15150	11
1999	8742	14500	5
2000	9865	14400	8
2001	2031	14125	0
2002	8676	13505	4
2003	21065	12950	20
2004	14500	12885	15
2005	16593	10989	18
2006	47300	9865	31
2007	21952	9520	21
2008	8540	9075	2
2009	8610	8742	3
2010	28812	8676	26
2011	26717	8610	24
2012	10989	8540	9
2013	31831	7900	28
2014	115218	2031	39

CONCLUSION

Flood management in the Jhelum Basin is a complicated subject due to its unique terrain. It has a flashy character for its greatest length, thus floods come with little warning and also dissipate within one to two days. The devastation inflicted by these floods is likewise significant. In the current study, four of its key sites were analyzed for flood estimate, and different measures based on the site circumstances were recommended. The four research locations are as follows:

- Sangam Site,
- Munshibagh Site,
- Asham Site,
- Baramulla Site.

The common weakness discovered at the aforementioned four locations was in terms of the carrying capacity of the river at these places, which is practically true for the whole length of the river. As a

result, carrying capacity must be enhanced, and the solutions proposed differ per site. The numerous solutions proposed for improving carrying capacity mostly involve raising embankments, dredging the bed to remove silt and other unwanted boulders, and so on. Furthermore, measures such as retention basins and additional spill routes, among others, have been proposed in various locations to reduce flood effects. It was also discovered that the Flood Spill Channel upstream of Srinagar City, which was built very early to bypass heavy flood discharges, is not carrying its full capacity and requires prompt attention for repair as well as steps to increase its original capacity. Dredging, provision of a cunnette throughout the whole length, weed eradication, reducing the roughness of the channel border, and other solutions has been proposed.

REFERENCES

- ❖ Umar, Sheikh & Lone, Mohammad & Goel, N & Zakwan, Mohammad. (2021). Trend Analysis of Hydro-meteorological Parameters in the Jhelum River Basin, North Western Himalayas. 10.21203/rs.3.rs-791405/v1.
- ❖ Alam, A., Bhat, M.S., Hakeem, F., Ahmad, B., Ahmad, S., Sheikh, A.H., 2018. Flood risk assessment of Srinagar city in Jammu and Kashmir, India. *Int. J. Disaster Resilience Built Environ.* 2, 9. <https://doi.org/10.1108/IJDRBE-02-2017-0012>.
- ❖ Alam, A., Rashid, S.M., Bhat, M.S., Sheikh, A.H., 2011. Impact of land use/land cover dynamics on himalayan wetland ecosystem. *J. Exp. Sci.* 2 (3), 60–64.
- ❖ Alexander, T.W., Wilson, G.L., 1995. Technique for Estimating the 2- to 500-year Flood Discharges on Unregulated Streams in Rural Missouri. U.S. Geological Survey WaterResources Investigations Report 95-4231. .
- ❖ AL-Mashidani, G., Lal Pande, B.B., Fattah, Mujda M., 1978. A simple version of Gumbel's method for flood estimation/Version simplifiée de la method de Gumbel pour l'estimation des crues. *Hydrol. Sci. Bull.* 23 (3), 373–380. <https://doi.org/10.1080/02626667809491810>.
- ❖ Bailey, J.F., Thomas Jr., W.O., Wetzel, K.L., Ross, T.J., 1989. Estimation of Flood-frequency Characteristics and the Effects of Urbanization for Streams in the Philadelphia, Pennsylvania Area. U. S. Geological Survey Water-Resources Investigations Report 87-4194. .
- ❖ Bilham, R., Bali, B., 2014. A ninth century earthquake-induced landslide and flood in the Kashmir Valley, and earthquake damage to Kashmir's Medieval temples. *Bull. Earthq. Eng.* 12 (1), 79–109.
- ❖ Bhatt, C.M., Rao, G.S., Farooq, M., Manjusree, P., Shukla, A., Sharma, S.V.S.P., et al., 2017. Satellite-based assessment of the catastrophic Jhelum floods of September 2014, Jammu & Kashmir, India. *Geomatics, Nat. Hazards Risk* 8 (2), 309–327.
- ❖ Benito, G., Lang, M., Barriendos, M., Llasat, M., Frances, F., Ouarda, T., Thorndycraft, V., Enzel, Y., Bardossy, A., Couer, D., Bobbe, B., 2004. Use of systematic, paleoflood and historical data for the improvement of flood risk estimation: review of scientific methods. *Nat. Hazards* 31, 623–643.
- ❖ Black, A.R., Fadipe, D., 2009. Use of historic water level records for re-assessing flood frequency: case study of the Spey catchment. *Water Environ. J.* 23, 23–31. <https://doi.org/10.1111/j.1747-6593.2007.00105.x>.

- ❖ Blainey, J.B., Webb, R.H., Moss, M.E., Baker, V.R., 2002. Bias and information content of paleoflood data in flood frequency analysis. In: House, P.K., Webb, R.H., Baker, V.R., Levish, D.R. (Eds.), *Ancient Floods, Modern Hazards: Principles and Applications of Paleoflood Hydrology*. American Geophysical Union, Washington, DC.
- ❖ Bobee, B.B., Robitaille, R., 1997. The use of the Pearson type 3 and log Pearson type 3 distributions revisited. *Water Resour. Res.* 13 (2), 427–443. <https://doi.org/10.1029/WR013i002p00427>.
- ❖ Bobee, B., Cavidas, G., Ashkar, F., Bernier, J., Rasmussen, P., 1993. Towards a systematic approach to comparing distributions used in flood frequency analysis. *J. Hydrol.* 142, 121–136.
- ❖ Chow, V.T., Maidment, D.R., Mays, L.W., 1988. *Applied Hydrology*. McGraw-Hill, International.
- ❖ Cohn, T.A., Lane, W.L., Baier, W.G., 1997. An algorithm for computing moments-based flood quantile estimates when historical flood information is available. *Water Resour. Res.* 33 (9), 2089–2096.
- ❖ Dirceu, S., Reis Jr., , Jerry, R., Stedinger, 2005. Bayesian MCMC flood frequency analysis with historical information. *J. Hydrol.* 313, 97–116.

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Chapter : 19

Synthesis of Nanomaterials: Green methods & Technology

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Abstract

The global movement toward more environmentally friendly "green" techniques has expressed itself in the chemistry of green nanomaterials. Green chemistry emphasizes the importance of avoiding the usage, or at the very least reducing the consumption, of organic solvents during a chemical process. Traditional methods are time-consuming, and the waste generated from the process may be detrimental to human health. Currently, nanomaterials are synthesized using both top-down and bottom-up approaches. Both processes are highly effective and often involve the use of toxic reagents. In contrast, green synthesis requires very little energy and can be easily recycled. The green synthesis of nanomaterials has many advantages over conventional methods. It is environmentally friendly, cost-effective, and can be used to make other substances, like nanoparticles. One of the most prominent benefits of green synthesis is the fact that it does not produce toxic byproducts. In addition to this, it is highly recyclable and does not require any harmful chemicals. Additionally, green synthesis of nanomaterials reduces the risks of contamination. Nanomaterials have been widely used for fluorescent cell imaging, drug delivery, and cancer diagnostics. As a result, the green synthesis process can also be extended to semiconductor nanoparticles. These materials have less growth, which makes them suitable for solar cells, fuel cells, and load carriers. The emphasis of this chapter will be on green synthesis or biosynthesis of nanomaterials using various approaches.

Key words: Nanotechnology, Nanomaterials, Green Synthesis

1. Introduction

The term "nanotechnology" was first used in the 1990s by Norio Taniguchi and Eric Drexler, and it is now commonly used[1,2]. It refers to manufacturing technologies based on molecular machine systems. Nanomaterials have emerged as an attractive class of materials, covering a wide variety of examples with at least one dimension between 1 and 100 nm. Nanomaterials have the potential to be used in a variety of applications. The sensible design of nanomaterials can result in the creation of surfaces with large surface areas. Nanomaterials can be fabricated with magnetic [3], electrical [4], optical [5], mechanical [6], and catalytic [7] properties that differ significantly from their bulk materials. Nanomaterials can also be used to develop novel materials with distinct properties. Fine controls of size, shape, synthesis conditions, and appropriate functionalization can all be utilised to adapt the properties of nanomaterials to specific needs. Nanomaterials have unique properties that allow them to be used in a variety of applications in various fields like industrial catalysis[8], food packaging[9], biosensing [10], battery [11], superconductor systems [12], agriculture[13] and medicine[14]. These nanomaterials can be synthesized using chemical, physical, and biological processes. The top-down and bottom-up techniques are the most widely adopted methods for the synthesis of nanomaterials. Traditional chemical and physical methods need enormous amounts of energy and produce hazardous byproducts, among other things. In green, low-cost, and ecofriendly synthesis, biomass or organisms act as reducing and stabilising agents. These eco-friendly strategies have a positive impact on the environment. Nowadays, various microorganisms and organisms such as viruses, bacteria, yeast, algae, fungus, and plants are used to synthesize various nanomaterials. These resources, when used in conjunction with other resources, enable precise control over the form, size, and composition of nanomaterials generated. Microorganisms, plants, and their extracts have recently received increased attention for their potential to be employed in the biosynthesis of nanomaterials [15].

2. Classification of Nanomaterials

One way to categorise nanomaterials is by the number of dimensions they have, as illustrated in Fig. 1. Nanostructured materials are classified into four types: zero-dimensional, one-dimensional, two-dimensional, and three-dimensions.

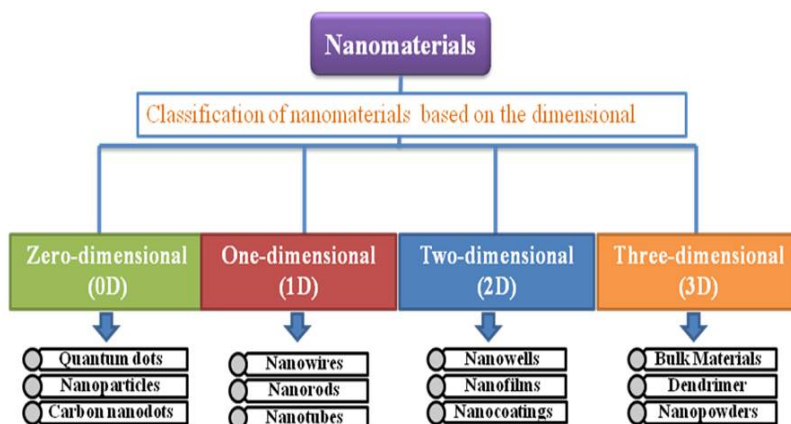


Fig.1: Dimension-based classification of nanomaterials

Nanomaterials can be divided into four types: (1) inorganic nanomaterials; (2) carbon nanomaterials; (3) organic nanomaterials; and (4) composite nanomaterials. Carbon-based nanomaterials are found in hollow tubes, ellipsoids, and spheres and contain carbon. Fullerenes, graphene, carbon black, carbon nanotubes, Carbon nanodots, carbon nanofibers and carbon onions are all included in this group. Nanomaterials derived from organic components, such as dendrimers, cyclodextrin, liposomes, and micelles, are used to create organic-based nanomaterials. Metals and metal oxide nanoparticles are types of inorganic-based nanomaterials. Silver, gold, platinum, aluminium, cadmium, copper, iron, and zinc nanoparticles are examples of inorganic nanomaterials, whereas metal oxide-based inorganic nanomaterials include zinc oxide, copper oxide, titanium dioxide (TiO_2), and cerium oxide (CeO_2). Any combination of metal nanoparticles, metal oxide nanoparticles, carbon or organic-based

nanoparticles with complicated structures, such as a metal-organic framework, is considered a composite nanomaterial.

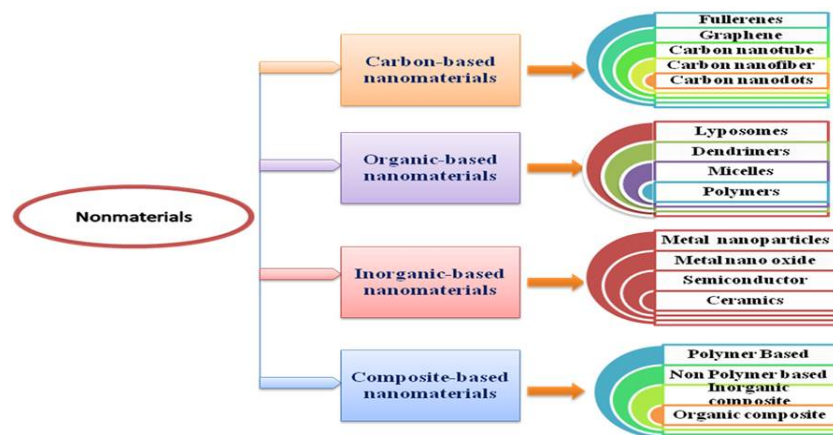


Fig.2:Diagrammatic representation of composition of nanomaterials

3. Synthetic strategies and techniques of nanomaterials

There are numerous approaches for synthesizing nanoparticles from a wide range of materials. In the synthesis and fabrication of nanostructures, materials from the gas, liquid and solid phases are used. They use either chemical reactivity or physical compaction to generate nanostructures. There are two general approaches to manufacturing: "bottom-up" and "top-down." Bottom-up construction refers to the process of building up a material from the bottom up, i.e. atom-by-atom, molecule-by-molecule, or cluster-by-cluster. The bottom-up approach of nanolithography and nanomanipulation is also applicable. Structural composite nanomaterials have been widely produced using these approaches. A top-down technique begins with a block of bulk material and is designed or milled into the desired shape. This method is analogous to the semiconductor industry's usage of pattern formation to create devices (such as electron beam lithography). Modern industry and nanotechnology are expected to benefit greatly from both approaches. Both systems have their merits and disadvantages. For the top-down technique, the key issue is to create progressively smaller structures with sufficient accuracy, whereas the main challenge for the bottom-up approach is to

generate structures large enough and of sufficient quality so that they may be used as materials[16-18].

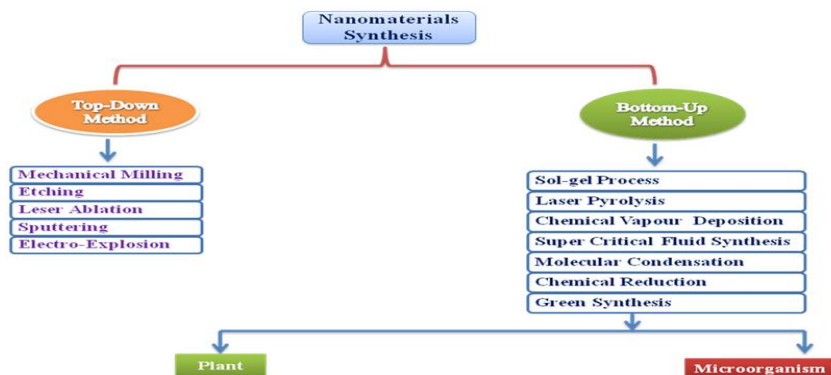


Fig.3: Synthesis approaches available for the preparation nanomaterials

Nanostructures with fewer flaws, a more uniform chemical composition, and superior short- and long-range ordering can be achieved via a bottom-up strategy. As a result, the bottom-up strategy is primarily driven by the lowering of Gibbs free energy, resulting in nanostructures and materials that are closer to a thermodynamic equilibrium. When a top-down technique is used, internal stress and surface flaws are likely to be introduced. Numerous techniques for the synthesis of metallic nanoparticles have been reported in recent years, including sol-gel synthesis [19], electrochemical synthesis [20]; microwave assisted synthesis [21], biosynthesis [22], ultrasonication method[23], precipitation method[24], physical vapour deposition method [25] and chemical vapour deposition method [26].

Conventional chemical and physical techniques, on the other hand, damage the environment and biological systems due to the harmful reducing agents utilised in the synthetic methods. Green synthesis has received a lot of attention in order to address the growing need for environmentally friendly metal nanoparticle production techniques. One of the most significant aspects to consider when designing a green synthesis strategy is the use of environmentally

friendly, benign reducing agents and solvents, as well as renewable and non-toxic materials[27,28].

4. Green nanosynthesis

The technique of synthesizing nanomaterials using naturally occurring reducing and stabilising agents is referred to as "Green nanosynthesis." Green synthesis strategies are required to avoid the formation of undesired or hazardous by-products by developing dependable, long-lasting, and environmentally friendly synthesis technologies. As a result, a more environmentally benign way of synthesizing nanomaterials is necessary. At the moment, the main focus of research is on the green synthesis of nanomaterials via biological routes such as microbial enzymes, microbes (bacteria, algae, yeast, and fungi), plants, polysaccharides, and degradable polymers. Green synthesis techniques are more favourable than traditional physical and chemical procedures since they are easy, cost-effective, and clean of harmful and environmentally unfriendly ingredients[29,30]. As a result, green synthesis approaches have received a lot of attention in the last few years.

4.1. Nanomaterials synthesis by Bacteria

Bacteria have a remarkable ability to decrease heavy metal ions and are regarded as one of the most promising nanoparticle production options. Microorganisms are important nanofactories because they may accumulate and detoxify heavy metals, especially addition to the availability of numerous reductase enzymes capable of reducing metal salt to metal nanoparticles. Bacteria such as *Bacillus methylotrophicus*, *Pseudomonas deptonis*, *Bhargavaea indica*, *Visella oriza* and *Brevibacterium frigoritolerans* have been shown in recent investigations to be capable of producing silver (Ag) and gold (Au) nanoparticles[31-33]. A number of bacteria, including *Lactobacillus*, *Bacillus*, *Pseudomonas*, *Streptomyces*, *Klebsiella*, *Enterobacter*, *Escherichia*, *Aeromonas*, *Corynebacterium*, *Weissella*, *Rhodobacter*, *Rhodococcus*, *Brevibacterium*, *Desulfovibrio*, *Sargassum*, and *Shewanella*, have synthesised nanoparticles. Silver nanoparticles can be produced by the bacteria *Staphylococcus aureus*, *Escherichia coli*, *Bacillus licheniformis*, and *Corynebacterium glutamicum* [34-37].

4.2. Nanomaterials synthesis by Yeast

As a result of their better tolerance to harmful metals, yeasts, which are eukaryotic microorganisms, have been shown to be suitable for the production of metallic nanoparticles in a number of studies [38]. The synthesis of AgNPs has been widely investigated using the yeast strains MKY3, *Saccharomyces cerevisiae* and *Yarrowia lipolytica*. Yeast species *Hansenula anomala*, *Yarrowia lipolytica* NCIM3589 was used in the biosynthesis of AuNPs, and the results have been published [39-41]. The marine yeast *Rhodospiridium diobovatum* has been shown to create stable lead sulphide nanoparticles intracellularly in a few studies [42].

4.3. Nanomaterials synthesis by Fungi

Fungi have several distinct benefits over bacterial systems, including toxin tolerance, convenience of processing and scaling up the process, large surface areas that enable for greater production rates, easy and simple downstream processing, economic feasibility, and a larger spectrum of nanomaterials [43]. The fungal system has been reported to be a flexible biological system capable of synthesising metal nanoparticles both intracellularly and extracellularly. Furthermore, because of their widespread distribution in nature, they are chosen over other biological systems, and as a result, several fungi have been investigated for the synthesis of diverse metal nanoparticles of varying shapes and sizes. Among the various fungal families employed for nanoparticle synthesis, the genus *Fusarium* has been chosen by numerous researchers [44]. Various fungal strains, including *Trichoderma harzianum*, *Fusarium oxysporum*, *Colletotrichum* sp. ALF2-6, *Aspergillus oryzae* (MTCC no. 1846), *Rhizopus stolonifer*, and *Aspergillus fumigatus* BTCB10, have been used to successfully synthesise silver nanoparticles [45-50]. Silver has been the most mass produced metal among others by using diverse fungal strains. Nanoparticles Furthermore, Au, Ti, and Zn have been reported as the next major metal ions used in the biosynthesis of nanoparticles by fungi [51-53].

4.4. Nanomaterials synthesis by algae:

Recently, algae (eukaryotic aquatic photoautotrophs) are being used in the synthesis of nanoparticles with a range of various features for a variety of purposes. Silver nanoparticles are formed by algae such as *Chlorella vulgaris*, which are found in abundance in the ocean. Algae species such as *Padina gymnospora*, *Sargassum wightii* and *Chaetomorpha linum* have been shown to be capable of generating Silver nanoparticles in the laboratory[54-57]. Green algae such as *Klebsormidium flaccidum* and *Chlorella vulgaris* were shown to be capable of producing colloidal gold nanoparticles and gold nanoplates[58,59]. Similarly, described a quick, green synthesis method for obtaining ZnO utilizing extracts of the brown marine macroalga *Sargassum muticum* [60].

4.5. Nanomaterials synthesis by Plant Extracts

Plant-based materials appear to be the greatest choices, as they can be used to produce nanoparticles on a massive scale while also being environmentally benign alternatives to physical and chemical techniques. Gold nanoparticles can be synthesized using banana peel extracts[61]. Similarly, extracts of *Mentha piperita* and *Coriandrum sativum* were employed to create gold nanoparticles[62,63]. Several plant extracts, such as *Abutilon indicum*, *Acalypha indica*, *Avena sativa*, *Calotropis procera*, and *Cassia fistula*, have been used for the synthesis of silver nanoparticles. At normal temperature, *sorghum Bran* aqueous extract produces Fe (iron) and silver nanoparticles[64].

5. References:

2. Taniguchi, N. (1974) On the Basic Concept of Nanotechnology. Proceedings of the International Conference on Production Engineering, Tokyo, 18-23.
3. Drexler, E.K. (1986). Engines of Creation: The Coming Era of Nanotechnology. NY, USA, Anchor Press: Garden City, 8.
4. Asfaram, A., Ghaedi, M., Hajati, S. &Goudarzi A. (2016).Synthesis of magnetic γ - Fe_2O_3 -based nanomaterial for ultrasonic assisted dyes adsorption: Modeling and optimization, *Ultrasonics Sonochemistry*, 32, 418-431.
5. Datta, A., Panda, S.K. &Chaudhuri, S.(2007). Synthesis and Optical and Electrical Properties of CdS/ZnS Core/Shell Nanorods, *The Journal of Physical Chemistry C*, 111(46), 17260-17264.

6. Chin, K.C., Gohel, A., Elim, H.I., Chen, W., Ji, W., Chong, G. L., Sow, C.H. & Wee, A.T.S.(2006). Modified carbon nanotubes as broadband optical limiting nanomaterials, *Journal of Materials Research*, 21(11), 2758–2766.
7. Li, J.H., Hong, R.Y., Li, M. Y., Li, H. Z., Zheng, Y. & Ding, J. (2009). Effects of ZnO nanoparticles on the mechanical and antibacterial properties of polyurethane coatings. *Progress in Organic Coatings*, 64(4), 504–509.
8. Zhou, K., Wang, R., Xu, B., & Li, Y. (2006). Synthesis characterization and catalytic properties of CuO nanocrystals with various shapes. *Nanotechnology*, 17, 3939–3943.
9. Prieto, O., Feroso, J., Nunez, Y., Del Valle, J.L. & Irusta, R.(2005). Decolouration of textile dyes in wastewaters by photocatalysis with TiO₂. *Solar Energy*, 79, 376–383.
10. Hoseinnejad, M., Jafari, S.M. & Katouzian, I. (2018). Inorganic and metal nanoparticles and their antimicrobial activity in food packaging applications. *Critical Reviews in Microbiology*, 44, 161–181.
11. Liang, H., Zhang, Xiao-Bing, Lv, Y., Gong, Liang; Wang, R., Zhu, X., Yang, R. & Tan, W. (2014). Functional DNA-Containing Nanomaterials: Cellular Applications in Biosensing, Imaging, and Targeted Therapy. *Accounts of Chemical Research*, 47(6), 1891–1901.
12. Gogotsi, Y., Penner & R. M. (2018). Energy Storage in Nanomaterials – Capacitive, Pseudocapacitive, or Battery-like. *ACS Nano*, 12(3), 2081–2083.
13. Sangiao, S., Morellón L., Ibarra, M. R. & De Teresa, J. M. (2011). Ferromagnet-superconductor nanocontacts grown by focused electron/ion beam techniques for current-in-plane Andreev Reflection measurements. *Solid State Communications*, 151(1), 37–41.
14. Bratovic, A., Hikal, W., Said-Al Ahl, H., Tkachenko, K., Baeshen, R., Sabra, A. & Sany, H. (2021). Nanopesticides and Nanofertilizers and Agricultural Development: Scopes, Advances and Applications. *Open Journal of Ecology*, 11, 301–316.
15. Han, M., Gao, X., Su, J.Z. & Nie S.(2001). Quantum-dot-tagged microbeads for multiplexed optical coding of biomolecules. *Nature Biotechnology*, 19,631-635.
16. Mohanpuria, P., Rana, N.K. & Yadav, S.K. (2008). Biosynthesis of nanoparticles: technological concepts and future applications. *Journal of Nanoparticle Research*, 10(3), 507–517.
17. Luechinger, N. A., Grass, R. N., Athanassiou, E. K. & Stark, W. J. (2010). Bottom-up fabrication of metal/metal nanocomposites from nanoparticles of immiscible metals. *Chemistry of Materials*, 22(1), 155–160.
18. Tiwari, D. K., Behari, J. & Sen, P. (2008). Time and dose-dependent antimicrobial potential of Ag nanoparticles synthesized by top-down approach, *Current Science*, 95 (5), 647– 655.
19. Bello, S.A., Agunsoye, J.O. & Hassan, S.B.(2015). Synthesis of coconut shell nanoparticles via a top down approach: Assessment of milling duration on the particle sizes and morphologies of coconut shell nanoparticles. *Materials Letters*, 159, 514–519.
20. Liu, H., Yang, W., Ma, Y., Cao, Y., Yao, J., Zhang, J. & Hu, T. (2003). Synthesis and characterization of titania prepared by using a photoassisted sol-gel method. *Langmuir*, 19(7), 3001–3005.

21. Dai, X., Compton & R. G. (2006). Direct electrodeposition of AuNPs onto indium tin oxide film coated glass: application to the detection of arsenic(III). *Analytical Sciences*, 22, 567–570.
22. Pal, A., Shah, S. & Devi, S. (2009). Microwave-assisted synthesis of silver nanoparticles using ethanol as a reducing agent. *Materials Chemistry and Physics*, 114(2-3), 530–532.
23. Zheng, D., Hu, C., Gan, T., Dang, X. & Hu, S. (2010). Preparation and application of a novel vanillin sensor based on biosynthesis of Au-Ag alloy nanoparticles, *Sensors and Actuators B: Chemical*, 148 (1), 247–252.
24. Dang, F., Kato, K., Imai, H., Wada, S., Haneda, H., Kuwabara, M. (2010). A new effect of ultrasonication on the formation of BaTiO₃ nanoparticles. *Ultrasonics Sonochemistry*, 17(2), 310–314.
25. Ghorbani, H. R., Mehr, F.P., Pazoki H. & Rahmani, B. M. (2015). Synthesis of ZnO Nanoparticles by precipitation method, *Oriental journal of chemistry*, 31(2), 1219–1221.
26. Kumar, M., Parashar, K. K., Tandi, S. K., Kumar, T., Agarwal, D. C. & Pathak, A. (2013). Fabrication of Ag:TiO₂ nanocomposite thin films by sol-gel followed by electron beam physical vapour deposition technique. *Journal of Spectroscopy*, Article ID 491716.
27. Zhang, R., Zhang, Y., Zhang, Q., Xie, H., Wang, H., Nie, J., Wen Q. & Wei, F. (2013). Optical visualization of individual ultralong carbon nanotubes by chemical vapour deposition of titanium dioxide nanoparticles. *Nature communications*, 4, 1727.
28. Devi, R.S., & Gayathri, R. (2014). Green Synthesis of zinc oxide nanoparticles by using Hibiscus rosa-sinensis. *International Journal of Current Engineering and Technology*, 4, 2444–2446.
29. Iravani, S. (2011) Green synthesis of metal nanoparticles using plants. *Green Chemistry*, 13, 2638–2650.
30. Kanchana, A., Devarajan, S. & Ayyappan, S. R. (2010). Green synthesis and characterization of palladium nanoparticles and its conjugates from Solanum trilobatum leaf extract. *Nano-Micro Letters*, 2, 169–176.
31. Duran, N., Marcato, P. D., Duran, M., Yadav, A., Gade, A. & Rai, M. (2011). Mechanistic aspects in the biogenic synthesis of extracellular metal nanoparticles by peptides, bacteria, fungi and plants. *Applied Microbiology and Biotechnology*, 90, 1609–1624.
32. Wang, C., Kim, Y. J., Singh, P., Mathiyalagan, R., Jin, Y. & Yang, D. C. (2016). Green synthesis of silver nanoparticles by Bacillus methylotrophicus, and their antimicrobial activity, Artificial Cells. *Nanomedicine, and Biotechnology*, 44(4), 1127–1132.
33. Jo, J.H., Singh, P., Kim, Y.J., Wang, C., Mathiyalagan, R. & Jin, C.-G. (2016). Pseudomonas deceptionensis DC5-mediated synthesis of extracellular silver nanoparticles. Artificial Cells. *Nanomedicine, and Biotechnology*, 44(6), 1576–81.
34. Singh, B., Garg, T., Goyal, A. K., & Rath, G. (2016). Development, optimization, and characterization of polymeric electrospun nanofiber: a new attempt in sublingual delivery of nicorandil for the management of angina pectoris. Artificial Cells. *Nanomedicine, and Biotechnology*, 44(6), 1498–507.

35. Li, W.R., Xie, X.B., Shi, Q.S., Duan, S.S., Ouyang, Y.S. & Chen, Y.B. (2011). Antibacterial effect of silver nanoparticles on *Staphylococcus aureus*. *Biomaterials*, 24(1), 135-41.
36. Li, D., Chen, S., Zhang, K., Gao, N., Zhang, M., Albasher, G., Shi, J. & Wang, C. (2021). The interaction of Ag₂O nanoparticles with *Escherichia coli*: inhibition-sterilization process. *Scientific Reports*, 11, 1703.
37. Sneha, K., Sathishkumar, M., Mao, J., Kwak, I.S., & Yun, Y.S. (2010). *Corynebacterium glutamicum*-mediated crystallization of silver ions through sorption and reduction processes. *Chemical Engineering Journal*, 162(3), 989-996.
38. Tan, L.V., Tran, T., & Thi, V.D. (2021). Biosynthesis of silver nanoparticles from *Bacillus licheniformis* TT01 isolated from quail manure collected in vietnam. *Processes*, 9, 584-596.
39. Kumar, D., Karthik, L., Kumar, G. & Roa, K.B. (2011). Biosynthesis of silver nanoparticles from marine yeast and their antimicrobial activity against multidrug resistant pathogens. *Pharmacology online*, 3, 1100-1111.
40. Kowshik, M., Ashtaputre, S., Kulkarni, S.K. & Paknikar, K.M.M. (2003). Extracellular synthesis of silver nanoparticles by a silver-tolerant yeast strain MKY3. *Nanotechnology*, 14, 95-100.
41. Gericke, M., & Pinches, A. (2006). Biological synthesis of metal nanoparticles. *Hydrometallurgy*, 83, 132-140.
42. Pimprikar, P.S., Joshi, S.S., Kumar, A.R., Zinjarde, S.S. & Kulkarni, S.K. (2009). Influence of biomass and gold salt concentration on nanoparticle synthesis by the tropical marine yeast *Yarrowia lipolytica* NCIM 3589. *Colloids Surfaces. B Biointerfaces*, 74, 309-316.
43. Seshadri, S., Saranya, K., & Kowshik, M. (2011). Green synthesis of lead sulfide nanoparticles by the lead resistant marine yeast, *Rhodospiridium diobovatum*. *Biotechnology Progress*, 27(5), 1464-9.
44. Sastry, M., Ahmad, A., Khan, M. I. & Kumar, R. (2003). Biosynthesis of metal nanoparticles using fungi and actinomycete. *Current Sciences*, 85, 162-170.
45. Li, G., He, D., Qian, Y., Guan, B., Gao, S., Cui, Y., Yokoyama, K. & Li, W. (2011). Fungus-mediated green synthesis of silver nanoparticles using *aspergillus terreus*. *International Journal of Molecular Sciences*, 13(12), 466-476.
46. Ahluwalia, V., Kumar, J., Sisodia, R., Shakil, N. A. & Suresh Walia, S. (2014). Green synthesis of silver nanoparticles by *Trichoderma harzianum* and their bio-efficacy evaluation against *Staphylococcus aureus* and *Klebsiella pneumonia*. *Industrial Crops and Products*, 55, 202-206.
47. Birla, S.S., Gaikwad, S.C., Gade, A. K., & Rai, M.K. (2013). Rapid synthesis of silver nanoparticles from *fusarium oxysporum* by optimizing physiocultural conditions, *The Scientific World Journal*, Article ID 796018.
48. Azmath, P., Baker, S., Rakshith, D., & Satish, S. (2015). Mycosynthesis of silver nanoparticles bearing antibacterial activity, *Saudi Pharmaceutical Journal*, 2(2), 1-8.
49. Phanjom, P., & Ahmed, G. (2015). Biosynthesis of silver nanoparticles by *aspergillus oryzae* (MTCC No. 1846) and its characterizations, *Nanoscience and Nanotechnology*, 5(1), 14-21.

50. Rahim, K. A., Younis, S., Mahmoud, A. M., Almaary, K. S., Abd El-Zaher, M. A. Mustafa, A. E.-Z. M. A. & Hussein, S.M. (2017). Extracellular biosynthesis of silver nanoparticles using *Rhizopus stolonifer*, *Saudi Journal of Biological Sciences*, **24**(1), 208-216.
51. Shahzad, A., Saeed, H., Iqtedar, M., Hussain, S.Z., Kaleem, A., Abdullah R., Sharif, S., Naz, S., Saleem, F., Aihetasham, A. & Chaudhary A. (2019). Size-controlled production of silver nanoparticles by *Aspergillus fumigatus* BTCB10: likely antibacterial and cytotoxic effects, *Journal of Nanomaterials*, Article ID 5168698.
52. Sawle, B.D., Salimath, B., Deshpande, R., Bedre, M.D., Prabhakar, B.K., & Venkataraman, A. (2008). Biosynthesis and stabilization of Au and Au-Ag alloy nanoparticles by fungus, *Fusarium semitectum*. *Science and Technology of Advanced Materials*, **9**, 1-6.
53. Rajakumar, G., Rahuman, A., Roopan, S.M., Khanna, V.G., Elango, G., Kamaraj, C., Zahir, A.A. & Velayutham, K. (2012). Fungus-mediated biosynthesis and characterization of TiO₂ nanoparticles and their activity against pathogenic bacteria. *Spectrochimica Acta Part A: Molecular Spectroscopy*, **91**, 23-29.
54. Velmurugan, P., Shim, J., You, Y., Choi, S., Kamala-Kannan, S., Lee, K.J., Kim, H.J. & Oh, B.T. (2010). Removal of zinc by live, dead, and dried biomass of *Fusarium* spp. isolated from the abandoned-metal mine in South Korea and its perspective of producing nanocrystals. *Journal of Hazardous Materials*, **182**, 317-324.
55. Soleimani, M., & Habibi-Pirkoohi, M., (2017). Biosynthesis of silver nanoparticles using *Chlorella vulgaris* and evaluation of the antibacterial efficacy against *Staphylococcus aureus*. *Avicenna Journal of Medical Biotechnology*, **9**(3), 120-125.
56. Johnson, M., Narayani, M., Perumal, M. S., Kalaiarasi, V. (2015). Biopotential of silver nano-peptides synthesized from protein extracts of *Padina*. *Journal of Microbiology & Experimentation*, **2** (1), 42-45.
57. Suganya, S., Dhanalakshmi, B., & Kumar, S. D. (2020). Biosynthesis and characterization of silver nanoparticles from *Sargassum wightii* and its antibacterial activity against multi-resistant human pathogens, *Indian Journal of Geo-Marine Sciences* **49**(5), 839-844.
58. Kannan, R. R. R., Arumugam, R., Ramya, D., Manivannan, K., & Anantharaman, P. (2013). Green synthesis of silver nanoparticles using marine macroalgae *Chaetomorpha linum*, *Applied Nanoscience*, **3**, 229-233.
59. Dahoumane, S.A., Djediat, C., Yepremian, C., Coute, A., Fievet, F., Coradin, T. & Brayner, R. (2012). Recycling and adaptation of *Klebsormidium flaccidum* microalgae for the sustained production of gold nanoparticles. *Biotechnology & Bioengineering*, **109**(1), 284-288.
60. Annamalai, J. & Nallamuthu, T. (2015). Characterization of biosynthesized gold nanoparticles from aqueous extract of *Chlorella vulgaris* and their anti-pathogenic properties, *Applied Nanoscience*, **5**, 603-607.
61. Brayner, R., Dahoumane, S. A., Yepremian, C., Djediat, C., Meyer, M., Coute, A. & Fievet, F. (2010). ZnO Nanoparticles: synthesis, characterization, and ecotoxicological studies. *Langmuir*, **26**(9), 6522-6528.
62. Bankar, A., Joshi, B., Kumar, A.R. & Zinjarde, S. (2010). Banana peel extract mediated synthesis of gold nanoparticles, *Colloids Surf B Biointerfaces*, **80**(1), 45-50.

63. Valencia, G.A., Vercik, L. C. D.O. Ferreira, L.G. Llanos J. H.R. & Vercik, A. (2014). Synthesis and characterisation of gold nanoparticles using Mentha piperita leaf extract: A green, non-toxic and rapid method, *International Journal of Nano and Biomaterials*, 5(2/3), 181-191.
64. Narayanan, K.B. & Sakthivel, N. (2018). Coriander leaf mediated biosynthesis of gold nanoparticles. *Materials Letters*, 62(30), 4588-4590.
65. Mittal, A. K., Chisti, Y., & Banerjee, U. C. (2013). Synthesis of metallic nanoparticles using plant extracts. *Biotechnology Advances*, 31(2), 346-356.

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