

# SELECTED TOPICS IN ENVIRONMENTAL SCIENCE

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**POST GRADUATE DEPARTMENT OF CHEMISTRY**

**KAHM Unity Women's College, Manjeri**

Narukara (PO), Malappuram (DT), Kerala-676122

[www.unitywomenscollege.in](http://www.unitywomenscollege.in)

E-mail: [chemistry@unitywomenscollege.in](mailto:chemistry@unitywomenscollege.in)

## **Editors:**

**Dr. C. Saidalavi; M. A., B. Ed., Ph. D.**

*Principal, KAHM Unity Women's College, Manjeri, Narukara (PO), PIN 676122, Malappuram (DT), Kerala, India.*

**Dr. Muhammed Basheer Ummathur; M. Sc., B. Ed., Ph. D.**

*Associate Professor & Head, PG Department of Chemistry, KAHM Unity Women's College, Manjeri, Narukara (PO), PIN 676122, Malappuram (DT), Kerala, India.*

**Dr. Deepa K; M. Sc., B. Ed., M. Phil., Ph. D.**

*Assistant Professor, PG Department of Chemistry, KAHM Unity Women's College, Manjeri, Narukara (PO), PIN 676122, Malappuram (DT), Kerala, India.*

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2. To produce scientifically literate graduates and post graduates with a broad and deep knowledge of fundamental chemical principles.

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## PHYSICOCHEMICAL ANALYSIS OF WELL WATERS IN MANJERI MUNICIPALITY

Dr. Muhammed Basheer Ummathur

Associate Professor & Head, PG Department of Chemistry, KAHM Unity Women's College,  
Manjeri, Kerala-676122, India  
E-mail: [mbummathur@gmail.com](mailto:mbummathur@gmail.com)

### **INTRODUCTION**

Water is nature's most wonderful, most abundantly available and most widely used resource, without which life cannot exist. Most of the water in this planet is stored in oceans and polar ice caps which is difficult to be recovered for our diverse needs. Most of our demand for water is fulfilled by rain water which gets deposited in surface and ground water resources. Though water is continuously purified by evaporation and precipitation, pollution of water has emerged as one of the most significant environmental problems of recent time. The gross pollution of water has its origin namely in urbanization, industrialization and increase in human population observed during the past one and half century. The impurities present in water vary greatly from one place to another. Water is regarded polluted when it changes its quality or composition either naturally or as a result of human activities.



*Ocean*



*Polar ice caps*

Water accounts for about 70% of the mass of our body. It is an essential constituent of all animal and vegetable matter and forms about 75% of matter of earth crust. Since it is one of the constituent in the reaction of photosynthesis which captures energy from sun, it is also an important substance in detecting the energy flow in the living system. In fact life in this planet is possible only because of the presence of abundant water.

All organisms use water in their metabolic process and all the biochemical reactions in the body of living beings take place in the water medium. It dissolves a number of substances without changing their chemical properties, hence carryout transportation of materials in the body. Blood is mostly water. Sperms are also mobile in water medium. Waste products are removed from the body in dissolved state with water. In higher plants the nutrients are carried from roots to other parts in water through xylem.

## **SOURCES AND QUALITY OF WATER**

Surface and ground water are the two main sources of fresh water. The quantity of water on the land surfaces formed during the hydrological cycle is the sources for all surface water which are mainly distributed in lakes, rivers, streams, irrigation canals, reservoirs and dams. In most of the places major sources of water supply are surface water. The quantity and quality of surface water depends on many factors. So, surface water has to be treated properly before its use.



*Lake*



*River*



*Stream*



*Irrigation canal*



*Reservoir*



*Dam*

Ground water is the important source of fresh water, being 99% of the total. The source of water which supplies water from below the earth's surface is called sub-surface or ground water. The movement of precipitation through the soil surface into the soil and on downwards by gravity, is known as infiltration. Water further moves downwards through the unsaturated layers of soil and voids of rocks which is called percolation. Infiltration and percolation occurs in the sub-terrain region, known as zone of aeration.

The usual method of abstracting ground water is by means of a well. Shallow wells draw water from the previous layer overlying the first impermeable layer. Deep wells are wells, dug into pervious layers below the first impermeable structure. They may be dug well, sunk well, bored well or driven well, depending on construction. Bored wells are useful for obtaining water from shallow as well as deep aquifers. Bored wells draw out a large quantity of water from one or more previous strata. Usually a metal casing is inserted in the regions of loose formations of bore hole. Besides the above methods, infiltration galleries and infiltration wells are also used to tap ground water.

The slow percolation of water through the ground results in the prolonged contact of water with minerals in soil and bed rocks. Many of these minerals are dissolved slowly as ground water passes over them and in time a quasi-chemical equilibrium can be reached between ground water and the minerals in the soil and rocks. The water gets saturated with dissolved solids which are derived from these minerals.

Silica and silicate minerals are abundant in earth crust. But it is not reflected in the concentration of ground water because of its low solubility. The concentration ranges from a few ppm to 60 ppm. Relatively high concentrations are observed in hot springs.

Iron, one of the most abundant elements in the earth crust, exists as oxide, sulphide, silicate, carbonate and hydroxide minerals. Both iron and manganese when present in excess result in the deterioration of ground water quality.

Most types of rocks – igneous, metamorphic and sedimentary- contain calcium usually as silicate and as carbonates. Sandstones and other deposits also contain calcium carbonate as cementing material. Silicates even though insoluble in water, weathering breaks them down into soluble calcium products. Because of its abundance and solubility calcium is present almost everywhere in groundwater.

Magnesium is also an important component of various rocks forms. Igneous and volcanic rocks, basalts, metamorphic rocks such as talc and sedimentary rocks such as dolomite, contribute to the magnesium content of ground water.

In ground water the calcium content generally exceeds the magnesium content even though the solubility of salts is reversed, due to its relative abundance. Magnesium carbonate is more soluble in sea water, containing large sodium salts. High magnesium content in ground water in coastal areas indicates sea water contamination. Hardness of water, which is quite known, is as a result of the combined calcium and magnesium salts present in water.

Usually chloride content of atmospheric precipitation is less than 10 ppm except in coastal areas. Chloride bearing rock minerals such as sodalite and chlorapatite are minor constituents in rocks. Therefore, the bulk of the chloride in ground water is either from atmospheric sources or by sea water contamination. Chloride salts remain stable, once they enter into solution. Most chloride in ground water is present as sodium chloride. Abnormal concentration of chloride indicates pollution by sewage waste or leaching of saline residues in the soil.

In general the relative concentrations of the common cations and anions present in most ground waters are in the order  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$  or  $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+$  and  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$  or  $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ .

### **NETWORK OF WATER QUALITY MONITORING**

The program involves the collection of information on physical, chemical and biological quality of water to provide an accurate base line data on present condition. The two main activities required to achieve this goal are sampling strategy and sampling techniques. Sampling strategy mainly comprises of location of sampling stations, sampling frequency, temporal and spatial aspects. The aim of sampling is to collect a portion of any material of interest such that their quality represents the quality of that material. The sampling should be representative and valid. Sampling techniques comprises types of sample containers, quantity, different kinds of sampling devices *etc.*

Polluted water is hardly of any use for most purpose. It cannot be used for drinking because of its inherent health risk. Saline water cannot be used for agricultural and for some industries and the quality of water affect the aquatic life. Every use of water requires a certain minimum quality of water with regard to pressure of dissolved and suspended materials of chemical, physical and biological nature.

The achievements of this minimum quality of water for diverse uses have lead to the formation of water quality criteria, water quality objectives and water quality standards. The criteria levels of drinking water source have to be based upon removability of the constituents at water treatment plants and available data on human health. The criteria for the waste water generated from industries may be based on nature of industry and effect of their constituent on water and land.

Criteria are not set of static values but are subject to modifications as the scientific data get updated and more knowledge is gathered. Water quality objective can be defined as an aim or goal with regard to the water quality which is to be achieved. The team standard applies to any definite principle or measure established by an authority by limiting concentration of constituents in water which ensures the safe use of water and guards the environment.

### **DRINKING WATER STANDARDS**

In view of the direct consumption of water by human beings, the domestic water supply is considered to be the most critical use of water in India. Agencies like the Indian Council of Medical Research (ICMR), Bureau of Indian Standards and Ministry of Work and Housing have formulated certain drinking water standards. WHO also has laid down certain drinking water standards, which are considered as international standards. A copy of Indian standard for drinking water published in 2012 by Bureau of Indian standards is given in Table 1.

### **NEED OF WATER ANALYSIS IN MANJERI MUNICIPALITY**

Manjeri is a Town and Municipality in Malappuram District in the state of Kerala, India. The Municipality has a total population of 97,104 as per the 2011 Census, with a population density of 1,878 per km<sup>2</sup> making it one of the largest towns in Kerala. Males constitute 49% of the population and females 51%. Manjeri has an average literacy rate of 95.8%, higher than the national average of 74.04%. Here, most of the people depends agriculture for their livelihood. Our college is situated in Manjeri municipality Even though Manjeri is very rich in its water resources, it faces water scarcity in summer season. Moreover most of the people depends wells for their water requirements. Water is used for industrial purpose, irrigation, drinking and domestic uses. But, to the best of our knowledge, no studies have been conducted on the quality of well water in this area. From this current situation we have decided to conduct water analysis of Manjeri municipality. Through this study we can check whether the water quality is in compliance with the standard, and hence, suitable for the designated use in order to ensure the public health.

### **Sampling**

Ten samples were collected randomly from Manjeri Municipal area; W<sub>1</sub>: Manjeri NSS College Road; W<sub>2</sub>: Thurakkal; W<sub>3</sub>: Payyanad; W<sub>4</sub>: Narukara; W<sub>5</sub>: Alukkal; W<sub>6</sub>: Patterkulam; W<sub>7</sub>: Parakkulam; W<sub>8</sub>: Manjeri town; W<sub>9</sub>: Unity College; W<sub>10</sub>: Manjeri Bus Stand.

### **DETERMINATION OF WATER QUALITY PARAMETERS**

#### **pH Analysis**

pH is measured using a pH meter which is an electronic digital volt meter sealed to read the pH directly. When a pair of electrodes, namely pH sensitive glass electrode and reference electrode, is dipped in a solution, they generate e.m.f which is proportional to the pH of the solution. The pH of the sample was measured after necessary calibration of the instrument using standard pH buffers advised by the manufactures.

#### **Electrical Conductivity**

Electrical conductivity is the measure of the ability of an aqueous solution to carry an electric current. The ability depends on the presence of ions, their total concentration, mobility and valence and on the temperature of the measurement. The measurement consists of altering the variable resistance until no current flows through detecting circuit containing the meter.



**Table 1: Indian Standard (IS 10500: 2012) Drinking Water Specification**

<i>Sl. No</i>	<i>Substance or Characteristics</i>	<i>Requirements/Desired Limit</i>	<i>Permissible Limit in the absence of alternative sources</i>
<b>ESSENTIAL CHARACTERISTICS</b>			
1	Color, Hazen unit max	5	15
2	Odour	Agreeable	Agreeable
3	Taste	Agreeable	Agreeable
4	Turbidity ,NTU	1	5
5	pH value	6.5-8.5	No relaxation
6	Total hardness (as CaCO <sub>3</sub> ) mg/L	300	600
7	Iron (as Fe)mg/L	0.3	No relaxation
8	Chloride(as Cl )mg/l	250	1000
9	Residual free chloride mg/L	0.2	1
<b>DESIRABLE CHARACTERISTICS</b>			
10	Dissolved solids mg/L	500	2000
11	Calcium (as Ca)mg/L	75	200
12	Copper (as Cu) mg/L	0.05	1.5
13	Manganese (as Mn)mg/L	0.1	0.3
14	Sulphate (as SO <sub>4</sub> ) mg/L	200	400
15	Nitrate (as NO <sub>3</sub> ) mg/L	45	No relaxation
16	Fluoride (as F) mg/L	1.0	1.5
17	Phenolic compound mg/L	0.001	0.002
18	Mercury (as Hg) mg/L	0.001	No relaxation
19	Cadmium (as Cd) mg/L	0.003	No relaxation
20	Selenium (as Se) mg/L	0.01	No relaxation
21	Arsenic (as As) mg/L	0.01	0.05
22	Cyanide( as CN) mg/L	0.05	No relaxation
23	Lead (as Pb) mg/L	0.01	No relaxation
24	Zinc (as Zn) mg/L	5	15
25	Chromium (as Cr) mg/L	0.05	No relaxation
26	Mineral oil mg/L	0.01	0.03
27	Pesticides mg/L	Absent	0.001
28	Alkalinity mg/L	200	600
29	Aluminium (as Al) mg/L	0.03	0.2

The conductivity  $K$ , of a solution contained between electrodes of surface area  $A$ , situated at a distance of  $L$  apart is given by  $K = L/AR$  where,  $R$  is the measured resistance and the value  $(L/A)$  is the cell constant.

### **Temperature**

Temperature exerts a major influence on biological activity and growth. Temperature governs the kinds of organisms that can live in rivers and lakes. Fish, insects, zooplankton, phytoplankton, and other aquatic species all have a preferred temperature range. As temperatures get too far above or below this preferred range, the number of individuals of the species decreases until finally there are none.

Temperature is also important because of its influence on water chemistry. It is related to the dissolved-oxygen concentration in water, which is very important to all aquatic life. Many lakes experience a "turning" of its water layers when the seasons change. In summer, the top of the lake becomes warmer than the lower layers.

### **Chemical Oxygen Demand**

Chemical oxygen demand (COD) test determines the oxygen required for chemical oxidation of organic matter with the help of strong chemical oxidant. The organic matter gets oxidized completely by  $K_2Cr_2O_7$  in the presence of  $H_2SO_4$  to produce  $CO_2$  and  $H_2O$ . The excess  $K_2Cr_2O_7$  remaining after the reaction is titrated against ferrous ammonium sulphate,  $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ . The volume of dichromate consumed gives the oxygen required for oxidation of the organic matter.

### **Chloride: Argentometric Method**

Chloride ion is one of the major inorganic anion in water and waste water. The estimation is based on the reaction between silver nitrate and chloride solution. A standard solution of chloride was prepared using sodium chloride. A measured volume of the standard chloride solution was titrated against silver nitrate solution using potassium chromate as indicator. From the titer value, the strength of silver nitrate solution was determined. When the chloride ions are removed as silver chloride precipitate, the excess of silver nitrate react with potassium chromate forming silver chromate which is red in colour (the end point).

### **Total Hardness**

Hardness is one of the important parameters for quality determination of portable water. Originally, the hardness of water was understood to be a measure of the capacity of the water for precipitating soap. Soap is precipitated chiefly by the calcium and magnesium ions commonly present in water, but also may be precipitated by ions of other polyvalent metals, such as aluminium, iron, manganese, strontium and zinc by hydrogen ions. Because only the first two are usually present in significant concentration in natural waters, hardness is defined as a characteristic of water that represents the total concentration of just the calcium and magnesium ions expressed as calcium carbonate.

Ethylene diamine tetra-acetic acid and its sodium salts (EDTA) form a chelated soluble complex when added to solution of certain metal cations. If small amount of a dye such Eriochrome Black-T is added to an aqueous solution containing calcium and magnesium ions at a pH of  $10 \pm 0.1$ , the solution will become wine red. If EDTA is then added as titrant, the calcium and magnesium ions will be complexed with EDTA. After sufficient EDTA has been added to complex all the magnesium and calcium ions, the solution will turn from wine red to blue. This is the end point of titration.

**Iron: Phenanthroline Method**

Iron is brought in to solution, reduced to the ferrous state by boiling solution with acid and hydroxylamine and is treated with 1,10 phenanthroline at pH 3.2 to 3.3. Three molecules of phenanthroline chelate with each atom of ferrous iron to form an orange-red complex,  $[(C_{12}H_8N_2)Fe]^{2+}$ . The coloured solution obeys Beer-Lambert's law. A pH between 2.9 and 3.5 insures rapid colour development in the presence of an excess of phenanthroline. Colour standards are stable up to six months. In presence of excessive amounts of organic constituent, the sample is first digested with  $H_2SO_4$  to destroy organic complexes and to ensure complete dilution of iron. The resulting solution is made 7 to 8 N in HCl and iron is separated from the interfering substances by extraction of ferric chloride in to isopropyl ether. After re-extraction of the iron in to water, it is reduced with hydroxylamine.

**Sulphate: Turbidimetric Method**

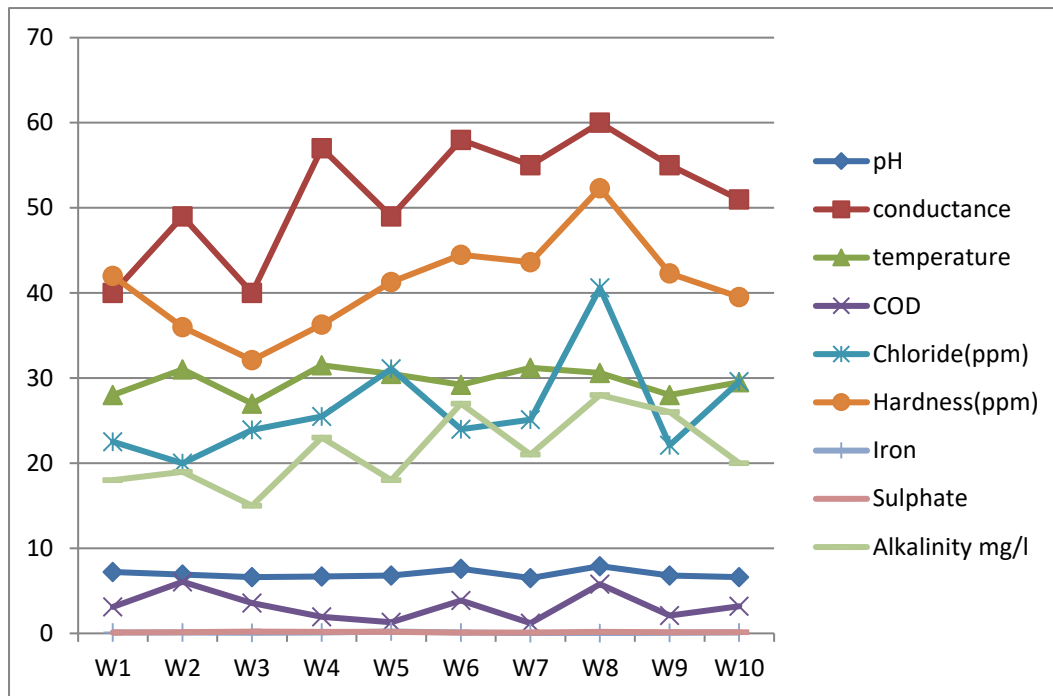
Sulphate ion is precipitated in HCl medium with  $BaCl_2$  in such a manner as to form  $BaSO_4$  crystals of uniform size. The absorbance of the  $BaSO_4$  suspension is measured by a nephalo-turbidity meter and the sulphate ion concentration is determined by comparison of the reading with a standard curve.

**Total Alkalinity**

The alkalinity of water is its quantitative capacity to neutralize a strong acid to a designated pH. Alkalinity is a measure of gross property of water and can be interpreted in terms of specific substance only when the chemical composition of the sample is known. The determination of alkalinity provides an idea of nature of the salt present and it is an important parameter involved in corrosion control. It mainly represents the concentration of carbonate, bicarbonate and hydroxide content. Alkalinity is estimated by titration against a standard acid.

**Table 2: Water Quality Parameters of Water Samples from Manjeri Municipality**

Sample No	pH	Conductivity	Temperature	COD	Chloride	Hardness	Iron	Sulphate	Alkalinity
W1	7.2	40	28	3.13	22.5	42	0.12	0.11	18
W2	6.9	49	31	1.06	19.99	36	0.11	0.13	19
W3	6.6	40	27	3.56	23.9	32.1	0.05	0.21	15
W4	6.7	57	31.5	1.96	25.5	36.3	0.12	0.18	23
W5	6.8	49	30.5	1.30	31.1	41.3	0.22	0.16	18
W6	7.6	58	29.2	3.86	24	44.5	0.10	0.09	27
W7	6.5	55	31.2	1.2	25.1	43.6	0.02	0.12	21
W8	7.9	60	30.6	5.8	40.6	52.3	0.04	0.19	28
W9	6.8	55	28	2.1	22.1	42.3	0.06	0.14	26
W10	6.6	51	29.5	3.2	29.6	39.5	0.09	0.13	20



**Fig.1:** Water Quality Parameters of Water Samples from Manjeri Municipality

From Table 2 and Fig.1 it is clear that different samples show different values for same parameters. The pH of all samples is within the desired limit (6.5-8.5). The chloride content of all samples is also within the desirable limit. The values of temperature are almost same for all samples. Most of alkalinity in natural waters is formed due to dissolution of  $\text{CO}_2$  in water. The conductivity of water is also within the desirable limit. Sample W8 is from an industrial area showing high value of hardness, conductance, chloride and COD. The value of hardness ranges from 30-55 mg/L. The values of iron contents are almost same for different samples. Sulphate content is very low in all samples.

## **CONCLUSIONS**

This work provides a comparison between well waters in Manjeri Municipality. From this study it was revealed that the different drinking water parameters of well water in the Manjeri Municipality are comparable to drinking water specification as per Indian Standard. In the present investigation, colour, odour and turbidity of the water samples were measured only qualitatively. Water samples from all the wells have ordinary taste, odour and clear appearance.

The study reveals that the various constituents are within the permissible limits, showing that water from wells of Manjeri Municipality is safe for domestic purposes. The unfavorable nature of one water sample can be attributed to the relatively high hardness, chloride and COD. It is due to soil leaching in industrial area. The parameters lie in the desirable range, indicating no contamination, hence suitable for domestic usages which ensure public health.

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## INTERACTION OF NANOPARTICLES ON THE ENVIRONMENT AND POLLUTION FROM NANO MATERIALS

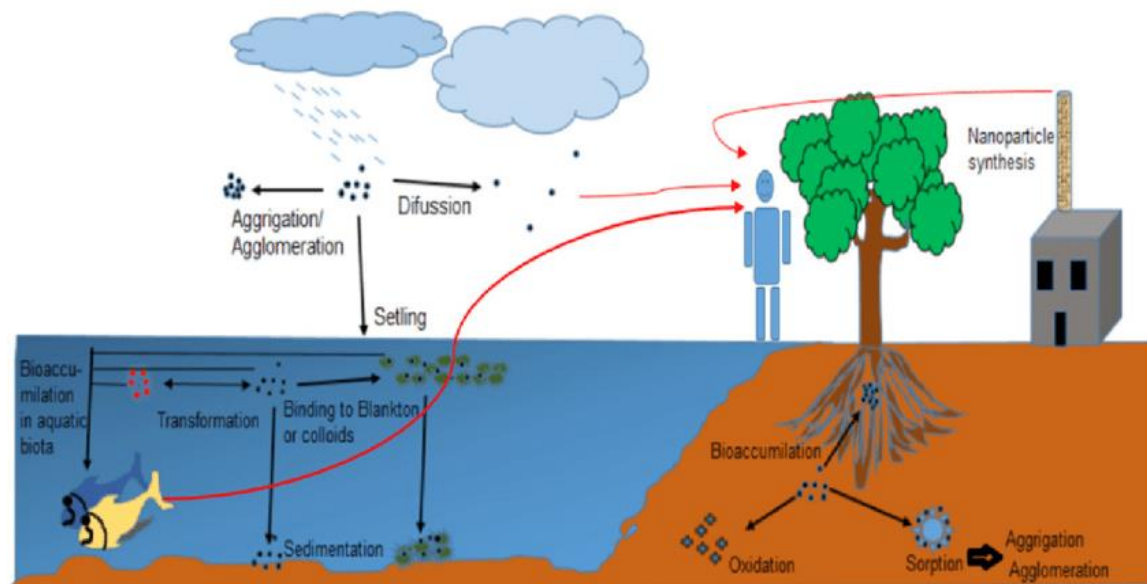
Mrs. Shabana K

Assistant Professor (Ad hoc), PG Department of Chemistry, KAHM Unity Women's College,  
Manjeri, Kerala-676122, India  
E-mail: [shabshabana@gmail.com](mailto:shabshabana@gmail.com)

### INTRODUCTION

Nanoparticles have existed for millions of years on the Earth, and they have been used by humans for thousands of years. In recent years, due to the increased human capacity to make synthetic nanoparticles, much attention has been focused on this type of material. Today, nanoparticles are used in different areas, such as the electronics industry, medical applications, pharmaceuticals, cosmetics, and environmental processes. Due to the significant potential of this technology, investments in the applications of nanotechnology are a growing trend worldwide

The available information on the current uses and the production rate of nanoparticles is inadequate. According to estimates of the production rate of nanoparticles, about 2,000 tons were produced in 2004, and it is expected that the production rate will increase to 58,000 tons by 2020. Due to the exponential increase in the production and use of nanoparticles, environmental and human exposures also will increase.



*The fate and behavior of nanoparticles in the environment. This behavior of nanoparticles in agroecosystems includes the positive and the negative effects as well as the release, transport and toxicity of engineered nanoparticles in the terrestrial environments.*

### EFFECTS OF NANOPARTICLES ON ORGANISMS

#### Absorption and toxicity

All nanoparticles, on exposure to tissues and fluids of the body, will immediately adsorb on to their surface some of the macromolecules that they encounter at their portal of entry. The

specific features of this adsorption process will depend on the surface characteristics of the particles, including surface chemistry and surface energy, and may be modulated by intentional modification or functionalization of the surfaces. This is well demonstrated through the use of specific bio molecular linkers that are anchored on the surface of nanoparticles or within vesicles and liposomes. In this way the affinity of a nanoparticle can be shaped to fit to a particular protein, and thus target a specific bio molecular assembly on a membrane, or within a specific organelle or cell surface. The specificity of such surface layers is used for analytical purposes, for optical labeling of biomolecules in molecular libraries and for drug or gene delivery to cells. Thus, both the existence of passive surface layers and surface active agents compromise the risk evaluation of nanoparticles by mere chemical composition. In agreement with bulk surface chemistry, metallic nanoparticles are of considerable chemical reactivity while ionic crystal nanoparticles have been observed to accumulate protein layers when exposed to the cytoplasm or in the lymphatic fluid. This protein layer is possibly involved in the interaction of the nanoparticle by the cellular system.

### **The Effects of Size, Shape, Surface and Bulk Composition**

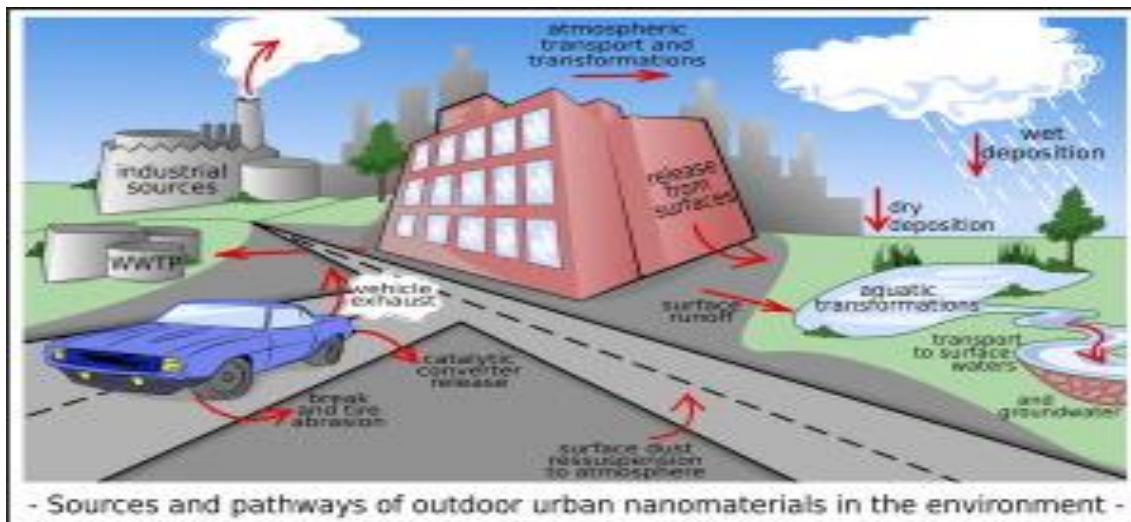
The interaction of nanoparticles with living systems is also affected by the characteristic dimensions. Nanoparticles, of a few nm in size, may reach well inside biomolecules, a situation not possible for larger particles. It has been reported that inhaled nanoparticles reach the blood and may reach other target sites such as the liver, heart or blood cells. Nanoparticles may translocate through membranes. There is little evidence for an intact cellular or sub-cellular protection mechanism. For humans, inhalation is the most frequent route of access, and therefore the process of aggregation of the nanoparticles in the inhaled air has to be taken into account.

In order to understand and categorize the mechanisms for nanoparticle toxicity, information is needed on the response of living systems to the presence of nanoparticles of varying size, shape, surface and bulk chemical composition, as well as the temporal fate of the nanoparticles that are subject to translocation and degradation processes. The typical path within the organ and / or cell, which may be the result of either diffusion or active intracellular transportation, is also of relevance. Very little information on these aspects is presently available and this implies that there is an urgent need for toxic kinetic data for nanoparticles.

### **Solubility and Persistence**

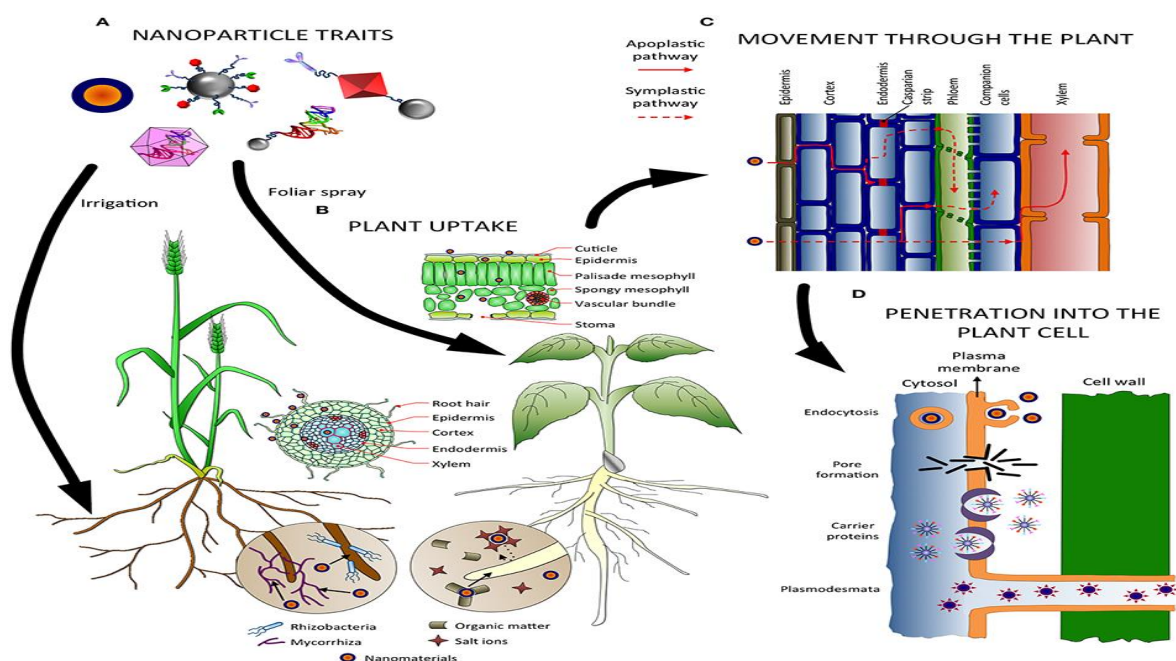
In view of the active functionalization and the possible interaction of nanoparticles with bio-molecular structures, it is important to consider the dose and dose rate of the particulate agent, its ability to spread within the body and ecosystem, the decay of number concentration and the erosion of individual particles. Many nanoparticles will have considerable solubility. For these materials the interaction with living systems remains close enough to the bulk chemical agent to justify the use of well-established toxicological testing procedures and approaches. For biodegradable particles, the particle composition and degradation products will influence their biological effects. On the other hand, materials with very low solubility or degradability could accumulate within biological systems and persist there for long durations. It is with nanoparticles of this character that the greatest concerns must arise, and attention will have to be paid to the comparison of the persistence of the particles and the time constants of the metabolic and cellular activities within the target host.

**NANOPARTICLES IN OUTDOOR SPACES**



Many natural and manmade processes lead to the release of nanoparticles in indoor and outdoor spaces. Some construction workers, gas and petroleum transmission pipeline workers, members of police forces, farmers, and workers in many other jobs spend their work time in outdoor environments. Few studies have been conducted on the effects of the exposure of such workers to nanoparticles; however, the limited research that is available suggests that such people are subject to increased risk of adverse health effects caused by their exposure to nanoparticles. In some cases, the penetration of nanoparticles from indoor places into the outdoor environment is likely. For example, the nanoparticles that pass through a filtration system can enter the outdoor spaces through ventilation ducts and affect the workers outside. Due to their special physical and chemical properties, nanoparticles readily enter indoor and outdoor workplaces and are distributed throughout these spaces. They can cause biochemical damage by creating some reactions in the cells of the human body. Today, many researchers are measuring the concentrations of various nanoparticles in indoor and outdoor workplaces in order to determine the workers' levels of exposure.

**INTERACTION OF NANOPARTICLES WITH PLANTS**





In a study of the impact of aluminum oxide nanoparticles on the growth of plants' roots, a slight reduction was seen in the growth of roots in the presence of uncoated alumina nanoparticles, but no reduction was observed when the nanoparticles were coated with phenanthrene. The surface properties of alumina have an important role in its toxicity. Several papers have shown that a positive effect on the growth of spinach occurred when the spinach seeds were smeared with titanium dioxide nanoparticles or the leaves were sprayed with these nanoparticles. Titanium dioxide nanoparticles, unlike larger samples of titanium dioxide, can enhance enzymatic activity, increase the absorption of nitrates, and accelerate the conversion of inorganic nitrogen to organic nitrogen. There is some limited information that suggests that nanoparticles of inorganic oxides can interact with plants' cells and with green algae that have cell walls similar to those of other plants.

Nanoparticles can interact with plants' roots by being absorbed from the surface of the roots, entering the cell wall, and being absorbed into the roots' cells. It also is possible that nanoparticles enter the intercellular space where they can be absorbed by the membranes. The surfaces of plants' cells have a negative charge, which allows the entry of negatively-charged species into the intercellular space of the roots' bark. Nanoparticles can find their way into the woody tissue of the plant by entering this space.

The interaction of nanoparticles with toxic materials and organic compounds can either increase or reduce their toxicity. Thus, even though nanoparticles can have harmful environmental effects, they also can be helpful for the environment. The contaminants may be absorbed by nanoparticles, thereby reducing the concentrations of the free molecules of pollutants around the cells and reducing the toxic effects of the pollutants. However, if the nanoparticle and its combination with the pollutant would not be toxic, no toxic effects may be seen.

### **ENVIRONMENTAL RISK ASSESSMENT OF NANOPARTICLES**

The environmental impacts of nanoparticles depend on how they are used in the workplace, how they are separated into different media (e.g., water and air), their mobility in each of these media, and their stability. Colvin's discussion on the potential impact of engineered materials demonstrates the lack of data on the exposure and effects of nanoparticles. To date, only a few studies have been carried out with species used for ecotoxicological testing. Oberdörster showed the 48 hours  $LC_{50}$  in *Daphnia magna* for uncoated water soluble fullerenes  $nC_{60}$  is 800 ppb. E. Oberdörster demonstrated a significant increase of lipid peroxidation in the brain and glutathione depletion in the gill of juvenile largemouth bass (*Micropterus salmoides*) after exposure for 48 hours to 0.5 ppm of fullerenes  $nC_{60}$ , but the increase was not significant at 1 ppm. In their follow-up studies, Oberdörster *et al.* report the possible molecular mechanism of these observations. The bactericidal properties of fullerenes have been reported by Yamakoshi *et al.* However, considering that a large number of the above cited human toxicology studies have examined the uptake and effects of nanoparticles at a cellular level, it can be hypothesized that these observations may also hold for species other than humans. As such the reports may be useful for the assessment of the effects on environmental species. Work to support this hypothesis is needed. Careful examination and interpretation of existing data and careful planning of new research is, however, required if we are to establish the true ecotoxicity of nanoparticles, and the differences with conventional forms of the substances.

**POLLUTION FROM NANOMATERIALS*****Air pollution by nanoparticles linked to brain cancer for first time***

Nano pollution is a generic name for waste generated by Nano devices or during the nanomaterial manufacturing process. Nano waste is mainly the group of particles that are released into the environment, or the particles that are thrown away when still on their products. The thrown away nanoparticles are usually still functioning how they are supposed to (still have their individual properties), they are just not being properly used anymore. Most of the time, they are lost due to contact with different environments. Silver nanoparticles, for example, they are used a lot in clothes to control odor; those particles are lost when washing them. The fact that they are still functioning and are so small is what makes Nano waste a concern. It can float in the air and might easily penetrate animal and plant cells causing unknown effects. Due to its small size, nanoparticles can have different properties than their own material when on a bigger size, and they are also functioning more efficiently because of its greater surface area. Most human-made nanoparticles do not appear in nature, so living organisms may not have appropriate means to deal with Nano waste. New research has linked air pollution nanoparticles to brain cancer for the first time. The ultra-fine particles (UFPs) are produced by fuel burning, particularly in diesel vehicles, and higher exposures significantly increase people's chances of getting the deadly cancer. Previous work has shown that nanoparticles can get into the brain and that they can carry carcinogenic chemicals. Brain cancers are rare, and the scientists have calculated that an increase in pollution exposure roughly equivalent to moving from a quiet city street to a busy one leads to one extra case of brain cancer for every 100,000 people exposed.

The discovery of abundant toxic nanoparticles from air pollution in human brains was made in 2016. A comprehensive global review earlier in 2019 concluded that air pollution may be damaging every organ and virtually every cell in the human body. Toxic air has been linked to other effects on the brain, including huge reductions in intelligence, dementia and mental health problems in both adults and children. The World Health Organization says air pollution is a “silent public health emergency”.

The new study, published in the journal *Epidemiology*, found that a one-year increase in pollution exposure of 10,000 nanoparticles per cubic centimeter – the approximate difference between quiet and busy city streets – increased the risk of brain cancer by more than 10%. The pollution levels in the cities studied – Toronto and Montreal – ranged from 6,000/cm<sup>3</sup> to 97,000/cm<sup>3</sup>. *Weichenthal* said people living with pollution of 50,000/cm<sup>3</sup> have a 50% higher risk of brain cancer than those living with 15,000/cm<sup>3</sup>.

## **CONCLUSION**

In recent years, rapid advances in nanotechnology have brought major developments in the areas of the environment, medicine, agriculture, industry, and other sciences. The nanoparticle technology has made an important contribution to the field and provided a basis for the development of nanotechnologies. Despite the fact that the major effect of particle size on materials' toxicities has been specified in the past, the effect of particle size on the behavior and reactivity of nanoparticles remains unclear. New issues and ideas about nanoparticles require the development of appropriate laboratory methods. Currently, there are several uses of nanoparticles in the environment, including the removal of contaminants from water, sewage, and air. Also, they have been used in environmental instruments, such as sensors, green nanotechnology, and the reduction of greenhouse gases. However, apart from the usefulness of nanoparticles, they can cause some hazards for the environment from their production to their disposal.

As a result, environmental risk assessments of nanoparticles during their lifecycles are essential. It is worth noting that the study of the effects of nanoparticles on industrial and non-industrial workplaces also is very important. Also, the measurement of exposures of workers in outdoor workplaces to nanoparticles released from various sources is essential. It is recommended that additional information be gathered on the characteristics of various nanoparticles, especially their toxicological properties, and placed in databases that can be made readily available to researchers. In plants that deal with engineered nanoparticles, safety measures should be considered to minimize occupational exposure. Also, some guidelines should be established concerning the safe handling and use of nanoparticles in research laboratories. Finally, while promoting the benefits of the use of nanoparticles in various fields, we should ensure that no adverse effects result from their use.

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## EULOPHID PARASITIDS AS BIOCONTROL AGENTS

Dr. K. Fousi\* and Dr. I. P. Abdul Razak

Associate Professors, Department of Zoology, KAHM Unity Women's College, Manjeri,  
Kerala-676122, India

\*E-mail: [drkfousi@gmail.com](mailto:drkfousi@gmail.com)

Eulophids are a group of small parasitic hymenopterans, mostly entomophagous parasitoids and few phytophagous forms. The family is large - sized with about 4260 nominal species occurring in 550 nominal genera. It is one among the twenty families coming under the Super family Chalcidoidea of the order Hymenoptera. They are found in abundance among the vegetation especially the green pastures. Entomophagous eulophids include several species emerging from egg-sacs of spiders and majority attacking insect Pterygota. Predominant among them are larval parasites. Egg parasitoids, egg-larval parasites and pupal parasites are also met with. Pupal parasites are usually gregarious, hundreds of them develop in a single lepidopterous pupa. Ectoparasitism is found in the subfamily Eulophinae and some Tetrastichinae. Eulophines are ectoparasitic on insects burrowing or mining on plant tissues. Bulk of Tetrastichines develops as parasites in galls and egg, larval or pupal parasites on lepidopterans and dipterans. Lepidoptera, Diptera, Coleoptera and Homoptera are the main host groups. A good number are suspected to show phytophagy. Almost all the species in Entedoninae are endoparasitic on coleopterous, lepidopterous and dipterous hosts developing in plant tissues. Little is known of the biology of the subfamily Euderinae. Still some are found to be parasitic on small beetles developing on bracket fungi growing on dead wood.



**Figure 1 : Eulophid parasitoid feeding on mealy bug host**

### **DIAGNOSTIC FEATURES**

Body weakly sclerotised, mostly less than 3mm. long with or without metallic reflections ; antenna with two to four funicle segments ; mesosoma with well developed prepectus ; mesoscutum with notauli complete , incomplete or absent ; scutellum often with a pair of sub-median grooves ; each leg with four-segmented tarsi.

### **IMPORTANCE**

Majority of Eulophids are entomophagous , either primary or secondary parasitoids of other insects including several major pests of agricultural crops. They attack Insecta Pterygota and egg- sacs of spiders. Most of them are larval parasites. Egg and pupal

parasitoids are also met with. The main host groups are Lepidoptera, Diptera, Coleoptera and Homoptera that are leaf-miners, gall makers and insect larvae burrowing in plant tissues.



**Figure 2: Eulophid parasitoid laying egg on host**

*Trichospilus pupivorus* Ferriere and *Tetrastichus howardii* (Oloff) (= *Tetrastichus Israeli* Mani & Kurian) are widely used pupal parasites to control the black headed caterpillar pest, *Opisina arenosella* Walker (= *Nephantis serinopa* Meyrick) of coconut in Kerala(India). *Elasmus nephantidis* Rohwer belonging to the family Eulophidae is a larval parasitoid of the above pest employed in biological control of the same. In order to control the sugarcane leaf hopper, *Pyrilla perpusilla* Walker, its egg parasitoid eulophid *Tetrastichus pyrillae* Crawford is made use of especially in states like Punjab(India).

*Tetrastichus howardii* (Oloff) (= *Tetrastichus ayyari* Rohwer) is a pupal parasitoid of the sugarcane shootborer, *Chilo infuscatellus* Snellen. The eggs of *Epilachna vigintioctopunctata* Fabricius and *E. dodecatigma* Mulsant, pests of brinjal, tomato, potato and cucurbits are hosts to *Tetrastichus ovularum* and *Achrysocharis appanai*. Pleurotropis epilachnae parasitise the larva of *E. vigintioctopunctata* Fabricius and *E. dodecatigma* Mulsant. Another species of *Pleurotropis*, *P. foveolatus* is parasitic on the pupa of *E. vigintioctopunctata* Fabricius and *E. dodecatigma* Mulsant. *Tetrastichus schoenobii* Ferriere is found to be parasitic on the eggs of paddy stem borer, *Scirpophaga incertulas* walker. The pupal parasite *Tetrastichus howardii* (Oloff) (= *Tetrastichus israeli* Mani& Kurian) is made use of in the control of Rice leaf roller pest, *Cnaphalocrocis medinalis* Guenee. A species of *Pediobius* and *Elasmus* are found to be parasitic on the Rice case worm, *Nymphula depunctalis* Guenee and a species of *Tetrastichus* parasitizes the Top shoot borer of sugarcane, *Scirpophaga nivella*.



**Figure 3: Eulophid parasitizing a host larva**

Among the pests mentioned in the table, except *Epilachna* beetles and *Pyrilla* bugs, all belong to the order Lepidoptera. Among the parasitoids mentioned, many species of

Tetrastichus like *T. howardii* (Oliff), *T. pyrillae* Crawford, *T. Schoenobii* Ferriere and *T. ovularum* are parasitic on Lepidopterans. *Tetrastichus* Haliday, thus is one of the important genera of the family Eulophidae with wide application in biocontrol of agricultural pests. The members of this genus show a subhorizontal propodeum with inverted Y-shaped median and paraspiracular carinae, densely reticulate sub median areas ; submarginal vein with one or two dorsal setae; and mesoscutum with a median longitudinal sulcus.

Table 1: Parasitoids of some common crop pests with bio- control potential

<b>Eulophid parasitoid</b>	<b>Pest species</b>	<b>Host plant</b>
<i>Trichospilus pupivorus</i>	<i>Opisina arenosella</i> (= <i>Nephantis serinopa</i> )	Coconut
<i>Tetrastichus howardii</i> (= <i>Tetrastichus israeli</i> )	<i>Opisina arenosella</i> (= <i>Nephantis serinopa</i> )	Coconut
<i>Elasmus nephantidis</i>	<i>Opisina arenosella</i> (= <i>Nephantis serinopa</i> )	Coconut
<i>Tetrastichus pyrillae</i>	<i>Pyrilla Perpusilla</i>	Sugarcane
<i>Tetrastichus howardii</i> (= <i>Tetrastichus ayyari</i> )	<i>Chilo infuscatellus</i>	Sugarcane
<i>Tetrastichus ovularum</i>	<i>Epilachna vignitioctopunctata</i> & <i>E. dodecastigma</i>	Brinjal/tomato/ potato/cucurbits
<i>Pleurotropis epilachnae</i>	<i>Epilachna vignitioctopunctata</i> & <i>E. dodecastigma</i>	Brinjal/tomato/ potato/cucurbits
<i>Achrysocharis appanai</i>	<i>Epilachna vignitioctopunctata</i> & <i>E. dodecastigma</i>	Brinjal/tomato/ potato/cucurbits
<i>Pleurotropis foveolatus</i>	<i>Epilachna vignitioctopunctata</i> & <i>E. dodecastigma</i>	Brinjal/tomato/ potato/cucurbits
<i>Tetrastichus sp.</i>	<i>Scirpophaga nivella</i>	Sugarcane
<i>Tetrastichus schoenobii</i>	<i>Scirpophaga incertulas</i>	Paddy
<i>Tetrastichus howardii</i> (= <i>Tetrastichus israeli</i> )	<i>Cnaphalocrocis medinalis</i>	Paddy
<i>Elasmus sp.</i> & <i>Pediobius sp.</i>	<i>Nymphula depunctalis</i>	Paddy

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**FIG: A KEYSTONE RESOURCE IN WESTERN GHATS**

Dr. I. P. Abdul Razak\* and Dr. K. Fousi

*Associate Professors, Department of Zoology, KAHM Unity Women's College, Manjeri, Kerala-676122, India**\*E-mail: [abdulrazakip@gmail.com](mailto:abdulrazakip@gmail.com)*

Kerala is one of the smallest states of India, is a narrow strip of land with its own natural boundaries, hemmed by Western Ghats on the east. The climate is almost uniform with very little variations. The temperature ranges normally from 25<sup>0</sup>-32<sup>0</sup>C and drops to 21<sup>0</sup> C or less in highlands and very occasionally it goes up to zero level on the peaks of the Western Ghats. The South-West monsoon brings shower during June-September and North-East monsoon brings rain during the months of October and November. The humidity ranges between 40-90%. The altitude decreases west wards from the majestic heights of Western Ghats through modulating country side to the coastal area. About 41 rivers and a number of rivulets and streams criss-cross the state throughout.

Tropically Kerala is divided into lowlands, midlands and highlands. The lowland stretches along the coastal plains of western side. Its soil is mainly alluvial. The high land or upland is constituted by the Western Ghats ranges that stretch throughout the eastern side. It is marked by the rising peaks of about 2400 m or above, the steeply rising hills and its thick forests, high altitude resorts, plantations etc. The vegetation types can be included as tropical evergreen forests, shoals, tropical moist deciduous forests and grass lands.



**Figure 4&2 : Fig trees with fruits**

There are about 23 species of *Ficus* found in Kerala, including three species endemic to Western Ghats. Eight sections belonging to all subgenera are present in this region. Fig trees have a vital role in the wildlife by contributing a major share in the tropical forests as trees, stranglers, epiphytes, shrubs, bushes and vines and by serving as a main food source for various types of vertebrates such as birds, mammals and several invertebrates including insects. Very many varieties of animals and plants are depended on fig trees for their food and shelter. The common species of *Ficus* with their pollinator wasps are shown in Table 1.

Table 1: The common species of *Ficus* with their pollinator wasps

Sl.No.	<i>Ficus</i> species	Pollinator wasp
1	<i>Ficus hispida</i>	<i>Ceratosolen solmsi marchali</i>
2	<i>F. exasperata</i>	<i>Kradibia gestroi</i>
3	<i>F. drupacea</i>	<i>E. belgaumensis</i>
4	<i>F. racemosa</i>	<i>C. fusciceps</i>
5	<i>F. microcarpa</i>	<i>E. verticillata</i>
6	<i>F. benghalensis</i>	<i>E. masoni</i>
7	<i>F. amplissima</i>	<i>Maniella delhiensis</i>
8	<i>F. talboti</i>	<i>E. (Parapristina) keralensis</i>

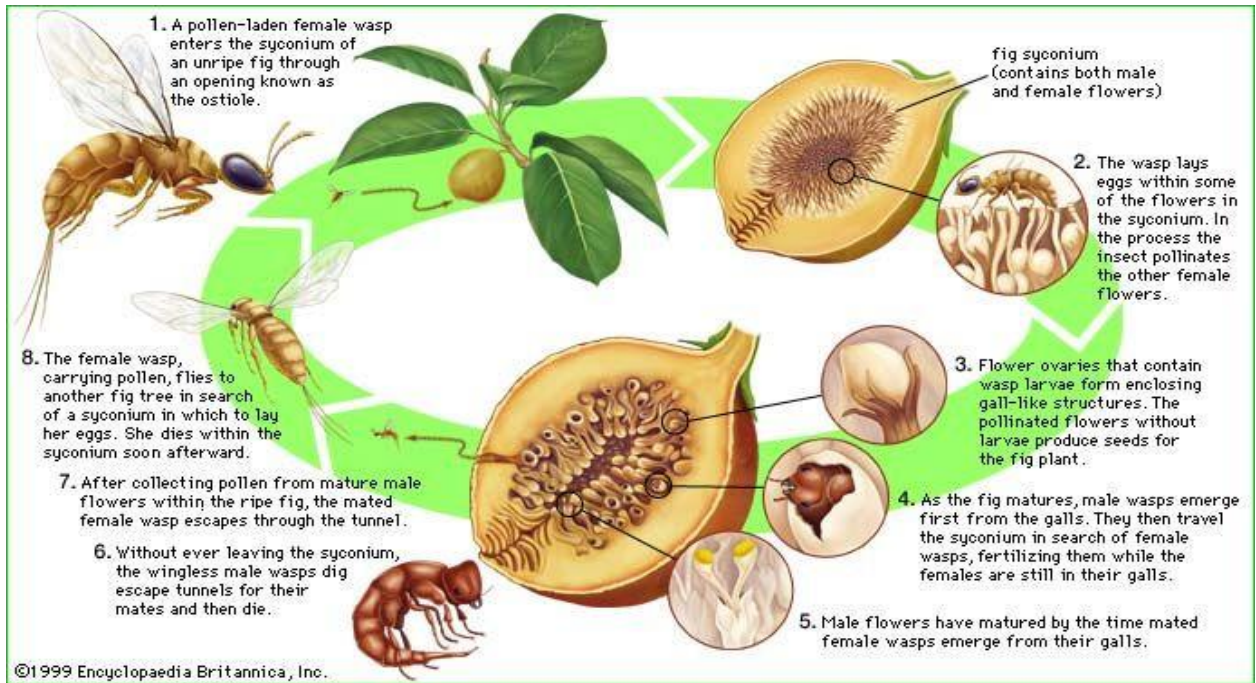
### **FIG POLLINATION SYSTEM**

Half of the 900 fig species belonging to the subgenus *Urostigma* are strangler figs. In tropical forests where strangler figs are most common have very dense canopies which allow only an occasional shaft of sunlight to illuminate the forest floor. In ecological point of view they are known as keystone resources. Their absence affects the survival of whole lot of other animal and plant species. The importance of *Ficus* plants to the ecosystem is due to their intimate relationship with their species specific, obligate pollinator wasps (Agaonidae, Chalcidoidea, Hymenoptera) as per the table cited. This is one of the best known plant-animal mutualisms. Fig wasps pollinate and lay eggs in the enclosed fig syconium. The pollinator's offspring subsequently feed on some of the developing seeds. In the monoecious figs, wasps and uneaten seeds mature together within the syconium. Several weeks later mating occurs within the syconium; the female wasp then collect pollen from newly mature anthers and departs in search of receptive, B phase fig in which to oviposit. Pollinators are known to be attracted to their host fig by a species specific volatile chemical signal that is emitted by the receptive syconium. The tiny adult fig wasps do not feed and they are short lived. Hence, there is a very brief period during which they must locate a syconium of the correct stage. So their life has clear consequences for the ecology and evolution of their interaction with figs.

### **RESOURCE UTILIZATION BY VERTEBRATE FAUNA**

The dependence of frugivorous birds, bats and primates on ripe fig is well known. Several insects are major seed predators. Such interactions have a major impact on the distribution of these associates. Ripe figs generally make attractive fruit resource with their easy edibility and high nutrient value per fruit flesh and also contributed by dead wasp inside the figs. The frugivores are attracted to the brightly coloured figs. There are birds like green pigeon, barbets feeding figs even in green colour. The great pied hornbill, Malabar grey hornbill, small quaker babblers, parakeets, Malabar trogon and cuckoo-shrike are known fig eaters. The mammals like monkeys, deer, bears, wild pigs and mongoose and the some nocturnal creatures like fruit bats, flying squirrels and civets visit the fig trees. Once the fruiting season is complete, the frugivores satiated with the fig feast disperse the fig seeds through their droppings.





**Figure 3: Schematic representation of fig pollination mechanism**



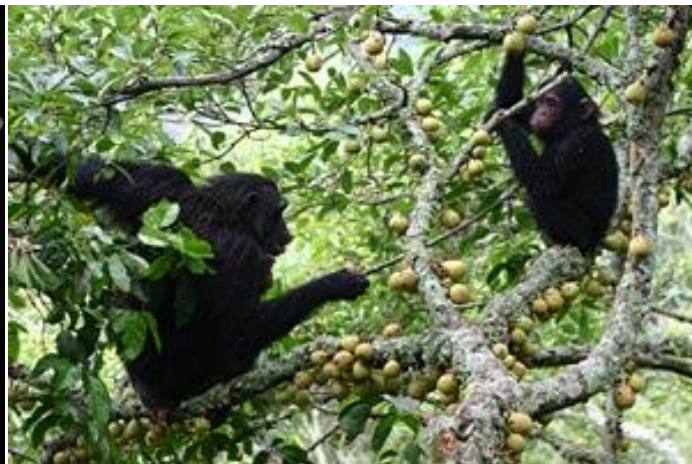
**Figure 4: Fig eating ants**



**Figure 5: Fig eating bird**



**Figure 6: Fig eating bat**



**Figure 7: Fig eating monkey**

## **CONCLUSION**

The biology and pollination ethology of only some species of *Ficus* have been studied so far. The combined efforts of entomologists and botanists of different parts of the world will enable to explore phylogeny and co-evolution of different sections of the genus *Ficus* and associated species of fig wasps. The pollinator wasp population is maintained through asynchrony in flowering which will ensure the food supply for the frugivores when other fruiting trees are scarce. So, the resource utilization by organisms and its implications has to be further evaluated.

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# **AUTOMOBILE EXHAUSTS IMPACT ON ENVIRONMENT- REMEDIATION STEPS TO REMOVE HARMFUL CONTAMINANTS FROM EXHAUSTS- THE ROLE OF THREE WAY CATALYTIC SYSTEMS**

Dr. Divya T

*Assistant Professor (Ad hoc), PG Department of Chemistry, KAHM Unity Women's College,  
Manjeri, Kerala-676122, India*

*E-mail: [divyapattambi.88@gmail.com](mailto:divyapattambi.88@gmail.com)*

## **INTRODUCTION**

Environmental pollution is a major issue faced by human beings. Among these, air pollution and water pollution cause serious health issues. Remediation from these undesirable conditions is highly demanding on considering their impact on human health. The effects of air pollution on health are very complex as there are many different sources and their individual effects vary from one to the other. Huge amount of noxious gaseous substances are expelled to the atmosphere as a result of transportation, power plants, anthropogenic or manmade activities and also through various industrial processes. Since the onset of the industrial revolution, there has been a steady change in the composition of the atmosphere mainly due to the combustion of fossil fuels used for the generation of energy and transportation. These pollutants even at parts per million levels will lead to several serious environmental and health hazards. Air pollutants that are inhaled have serious impact on human health affecting the lungs and the respiratory system; they are also taken up by the blood and pumped all-round the body. These pollutants are also deposited on soil, plants, and in the water, further contributing to human exposure. Ensuring good quality air is essential for the protection of public health. Governments worldwide have adopted a range of increasingly demanding measures to curb air pollution with a particular focus on the emissions from motor vehicles. An important part of this strategy has been the development of the three-way catalytic converter to remove exhaust pollutants such as carbon monoxide, unburnt hydrocarbons and nitrogen oxides. In urban areas, three way catalytic converters play a pivotal role in improving quality of air and offer a clean and healthy environment.

## **EXHAUST POLLUTANTS**

The most important chemical reaction in a petrol engine – that is, the one that provides the energy to drive the vehicle – is the combustion of fuel in air. In an ‘ideal’ system, combustion would be complete so that the only exhaust products would be carbon dioxide and steam. In practice, the complete oxidation of the fuel depends on a number of factors: first, there must be sufficient oxygen present; second, there must be adequate mixing of the petrol and air; and finally, there must be sufficient time for the mixture to react at high temperature before the gases are cooled. In internal combustion engines, the time available for combustion is limited by the engine’s cycle to just a few milliseconds. There is incomplete combustion of the fuel and this leads to emissions of the partial oxidation product, carbon monoxide (CO), and a wide range of volatile organic compounds (VOC), including hydrocarbons (HC), aromatics and oxygenated species. These emissions are particularly high during both idling and deceleration, when insufficient air is taken in for complete combustion to occur.

Another important result of the combustion process, particularly during acceleration, is the production of the oxides of nitrogen – nitric oxide (nitrogen monoxide, NO) and nitrogen dioxide (NO<sub>2</sub>). Conventionally, these two oxides of nitrogen are considered together and represented as NO<sub>x</sub>. At the high temperatures involved (in excess of 1 500 °C) nitrogen and oxygen in the air drawn in with the fuel may combine together to form NO. On leaving the engine, this monoxide cools down and is oxidized by oxidants in the atmosphere to form the dioxide. Although the ‘fixing’ of nitrogen from the air is the major source of NO<sub>x</sub>, it may also arise from the oxidation of any nitrogenous components in the fuel.

Primary pollutants are defined as those gases emitted directly from the exhaust of a vehicle. None of these is a desirable addition to the atmosphere, but perhaps the most notorious consequence of exhaust emissions is their role in the production of photochemical smog – a mixture of ozone, nitrogen dioxide, other secondary products and small particulates. These secondary pollutants can cause severe damage to human health.

The role of an emission control catalyst is to simultaneously remove the primary pollutants CO, VOCs and NO<sub>x</sub> by catalyzing their conversion to carbon dioxide (CO<sub>2</sub>), steam (H<sub>2</sub>O) and nitrogen (N<sub>2</sub>).

### **DANGEROUS EFFECT OF NOXIOUS EXHAUST GASES ON HUMAN HEALTH**

Nowadays exhaust gas emissions containing hazardous constituents is tremendously increasing due to population explosion. Negative impact of various hazardous pollutants on the green environment is not in our control. According to the World Health Organization, six major air pollutants include particle pollution, ground-level ozone, carbon monoxide, sulfur oxides, nitrogen oxides, and lead. Long and short term exposure to air suspended toxicants has a different toxicological impact on human including respiratory and cardiovascular diseases, neuropsychiatric complications, the eyes irritation, skin diseases, and long-term chronic diseases such as cancer. Several reports have revealed the direct association between exposure to the poor air quality and increasing rate of morbidity and mortality mostly due to cardiovascular and respiratory diseases. Exposure to these toxic pollutants is unbearable to human beings, which leads to some chronic disorders such as asthma, Alzheimer's and Parkinson's diseases, lung disorders, emphysema and mainly the malfunctioning of heart functions. Among these various air pollutants, carbon monoxide poses major threat to human beings. CO is one of the major constituents of exhausts from automobiles, industrial processes and coal fired power stations. Concentration of carbon monoxide in the environment increases as a result of certain natural and anthropogenic activities. Vehicular exhausts are contributing much (73%) to this effect. Increased population is the prime cause of the excessive emission of toxic gases from various sources. The maximum permissible level of carbon monoxide in the atmosphere is 40ppm and above this critical level it will cause adverse effects on the ecosystem. It is a major threat to plantations on earth by adversely affecting N<sub>2</sub> fixation, photosynthesis and plant respiration. Exposure to CO gas causes a lot of health hazard issues in human beings such as dizziness, headache, vomiting, nausea, heart diseases, anemia and various respiratory disorders. Carbon monoxide promotes the ground level ozone formation also.

Even trace amount of carbon monoxide is very harmful that will lead to brain damage or even death due to anoxia. Anoxia is the condition of oxygen starvation in tissues due to the inability of hemoglobin to carry enough oxygen to tissues. CO has 200 times higher binding capacity with iron in hemoglobin than oxygen leading to the deficiency of oxygen in the blood. Hence sufficient amount of oxygen cannot be pumped into brain which makes the victims unconscious. Carbon monoxide is recognized as a silent killer which possesses

remarkable affinity towards myoglobin also. The presence of carbon monoxide creates some unbalanced conditions in human beings related to oxygen deficiency. The CO abatement techniques continue to be a hot research topic in today's era owing to the hazardous impact of carbon monoxide.

The main effect of breathing in raised levels of nitrogen dioxide is the increased likelihood of respiratory problems. These compounds are of the same family as nitrogen dioxide, nitric acid, nitrous oxide, nitrates, and nitric oxide. When  $\text{NO}_x$  is released into the air, it reacts, stimulated by sunlight, with organic compounds in the air; the result is smog. Smog is a pollutant and has adverse effects on children's lungs.  $\text{NO}_x$  reacting with sulfur dioxide produces acid rain, which is highly destructive to everything it lands on. Acid rain corrodes cars, plants, buildings, national monuments and pollutes lakes and streams to an acidity unsuitable for fish.  $\text{NO}_x$  can also bind with ozone to create biological mutations (such as smog), and reduce the transmission of light. Nitrogen dioxide inflames the lining of the lungs, and it can reduce immunity to lung infections. This can cause problems such as wheezing, coughing, colds, flu and bronchitis.  $\text{NO}_2$  might be a marker for the contribution of  $\text{NO}_x$  to the formation of secondary pollutants such as secondary particles and  $\text{O}_3$ . Sulphur dioxide  $\text{SO}_2$  (sulphur dioxide) in the air is caused due to the rise in combustion of fossil fuels. It can oxidize and form sulphuric acid mist.  $\text{SO}_2$  in the air leads to diseases of the lung and other lung disorders such as wheezing and shortness of breath. Long-term effects are more difficult to ascertain as  $\text{SO}_2$  exposure is often combined with that of SPM. Inhaling hydrocarbons from gasoline, household cleaners, propellants, kerosene and other fuels can be fatal to children. Further complications include central nervous system impairments and cardiovascular problems.

### **THE THREE-WAY CATALYTIC CONVERTER**

The catalytic converter was first invented by Eugene Houdry in the 1950's. The catalytic converter has emerged as the emission-control method of the late 1970s and will probably continue that role well into the 1980s. Because the converter is an engine add-on that does not require fundamental changes in the conventional spark-ignition engine, the enormous technology and investment in these engines is retained. A catalytic converter is a simple device that uses basic redox reactions to reduce the pollutants a car makes. It converts around 98% of the harmful fumes produced by a car engine into less harmful gases. It is composed of a metal housing with a ceramic honeycomb-like interior with insulating layers. This honeycomb interior has thin wall channels that are coated with a washcoat of aluminum oxide. This coating is porous and increases the surface area, allowing more reactions to take place and containing precious metals such as platinum, rhodium, and palladium. No more than 4-9 grams of these precious metals are used in a single converter. The converter uses simple oxidation and reduction reactions to convert the unwanted fumes. Recall that oxidation is the loss of electrons and that reduction is the gaining of electrons. The precious metals mentioned earlier promote the transfer of electrons and, in turn, the conversion of toxic fumes.

There are two types of converters in use—the two-way and the three-way units. The two-way oxidation catalyst was first added to new cars in model year 1975. These units use platinum and palladium to oxidize the HC and CO and can meet the 0.41- and 3.4-g/mile standards specified for these constituents for 1981. Three way catalytic converter is a multicomponent material which primarily consist of a ceramic monolith ( $2\text{Mg} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ ), which withstand high temperature and allow thermal expansion, precious metals (Rhodium, platinum, palladium and gold),  $\text{CeO}_2$ , gamma alumina and other metal oxides. Ceramic monolith has strong walls enclosing an array of parallel channels, a typical monolith

has 4 channel openings per cm<sup>2</sup>, this type of design allows a high rate of flow of exhaust gases. Cordierite is used because it can withstand the high temperatures in the exhaust, and the high rate of thermal expansion encountered when the engine first starts – typically, the exhaust gas temperature can reach several hundred degrees in less than a minute. Metallic monoliths are also used, particularly for small converters, but these are more expensive

The satisfactory operation of both the two-way and the three-way catalysts depends on controlling the composition of the exhaust products entering the catalysts. The three-way catalysts can be either dual-bed or single-bed systems. A dual-bed system requires that the engine operate with a rich air/fuel mixture so that the NO<sub>x</sub> can be reduced in the first bed. Air is then added to the exhaust leaving the first bed so that the oxidation reaction to control HC and CO can proceed in the second bed. Three way catalytic converters are gaining more attraction when considering its role in environmental pollution abatement. On properly combining three way catalytic systems with automobile engine system, almost 90 % air pollution from automobile exhausts can be controlled effectively. The partially combusted hydrocarbons, CO, NO<sub>x</sub> are converted to environmentally friendly products CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> by three way catalytic reactions in a single step. Noble metals are widely investigated as promoters in three way catalytic systems due to its low temperature reducibility. But their ever increasing cost and poor thermal stability holds back its application from this field. An alternative to noble metals can be achieved by incorporating a low temperature reducible catalyst in three way catalytic converters.

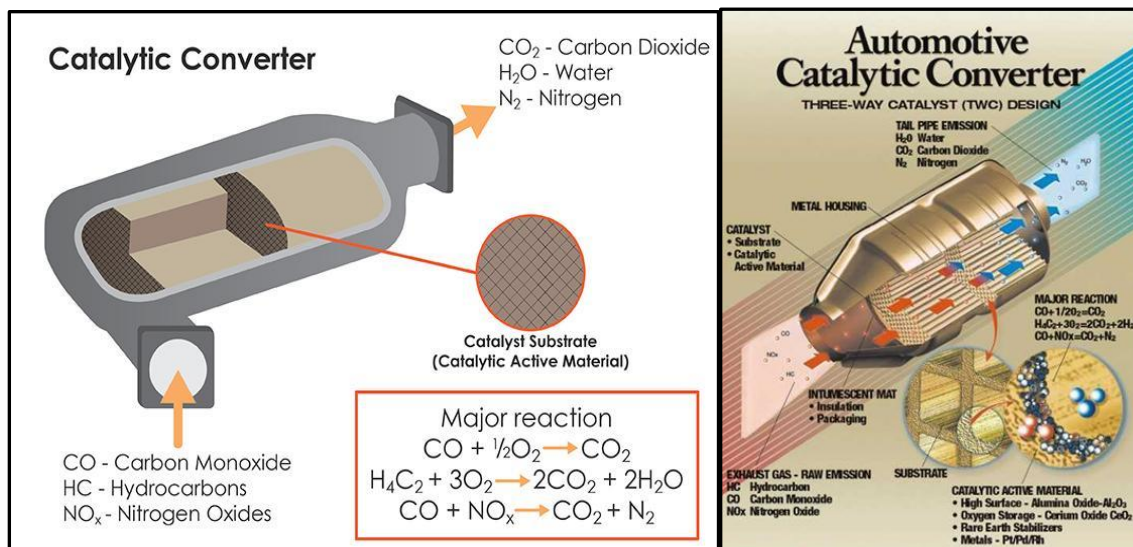
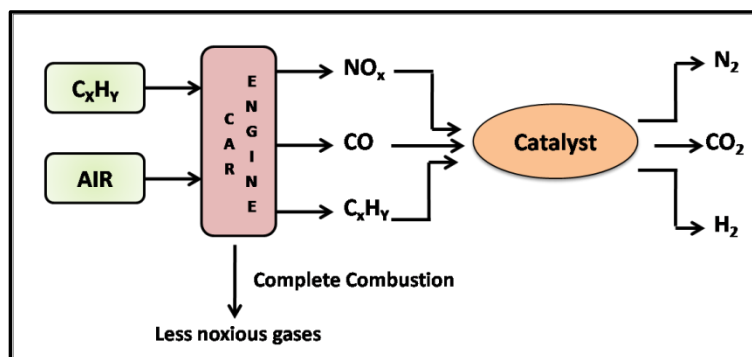


Fig.1. Three way catalytic reactions in exhaust gas engine of vehicles in the presence of catalyst

As a major and common component in three way automotive exhaust catalyst system, ceria plays an outstanding role in purification. High oxygen storage and buffering capacity, low cost and good thermal stability of ceria make it an elite member for this application. It can release oxygen under oxygen lean atmosphere and store oxygen at oxygen rich atmosphere. Surface defects, large surface to volume ratio of atoms, structural defects and oxygen vacancy in the system have positive contribution to the oxidation efficiency of the catalyst.

## **CONCLUSION**

A catalytic converter provides an environment for a chemical reaction wherein toxic combustion by-products are converted to less-toxic substances. Catalytic converters are most commonly used in motor vehicle exhaust systems. Catalytic converters are also used on generator sets, forklifts, mining equipment, trucks, buses, trains, and other engine-equipped machines. Although the catalytic converter has a significant role in reducing toxic emissions from car engines, it also has detrimental environmental effects. In the conversion of hydrocarbons and carbon monoxide, carbon dioxide is produced. Carbon dioxide is one of the most common greenhouse gases and contributes significantly to global warming. Along with carbon dioxide, the converters sometimes rearrange the nitrogen-oxygen compounds to form nitrous oxide. This is the same compound used in laughing gas and as a speed enhancer in vehicles. As a greenhouse gas, nitrous oxide is a 300 times more potent than carbon dioxide, and contributes proportionally to global warming. Tetra-ethyl lead present in gasoline "poisoned" the converter by forming a coating on the catalyst's surface, effectively disabling it. Some early converter designs created a great deal of restriction to the flow of exhaust, which negatively affected vehicle performance, drivability, and fuel economy. The use of precious metals in the coating of the inner ceramic structure, many catalytic converters has been targeted for theft. Initially, automakers believed the catalytic converter would make cars prohibitively expensive. On the contrary, catalytic converters only add about two percent to the cost of a vehicle. In 1985, the Environmental Protection Agency estimated that catalytic converters saved at least 10 times more in health costs than the price of a catalytic converter. It had been stated that catalytic converters are known in a lot of cases to have an excessively long warm-up time period, in a great deal of cases ranging up to thirty-minutes. Even though catalytic converters aren't 100% effective at cutting emissions, they are an essential step on the road to reducing pollution from automobiles.

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## CARBON DIOXIDE: THE HERO AND THE VILLAIN

Dr. Muhammed Basheer Ummathur

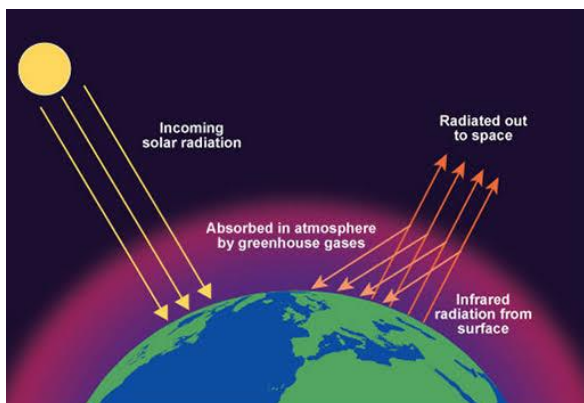
Associate Professor & Head, PG Department of Chemistry, KAHM Unity Women's College,  
Manjeri, Kerala-676122, India

E-mail: [mbummathur@gmail.com](mailto:mbummathur@gmail.com)

CO<sub>2</sub> is used as a refrigerant, in fire extinguishers, for inflating life rafts and life jackets, blasting coal, foaming rubber and plastics, promoting the growth of plants in greenhouses, immobilizing animals before slaughter, and in carbonated beverages. It is a colourless gas and at low concentrations it is odorless. At sufficiently high concentrations it has a sharp acidic odour. At standard temperature and pressure the density of CO<sub>2</sub> is 1.98 kg/m<sup>3</sup>, about 1.67 times that of air.

In a balanced ecosystem the CO<sub>2</sub> released into the atmosphere is removed regularly by the green plants by photosynthesis. The major consumers of CO<sub>2</sub> gas from the atmosphere are green plants and oceans. The green plants absorb CO<sub>2</sub> gas from the atmosphere to prepare their food through the process of photosynthesis, while the oceans dissolve CO<sub>2</sub> gas to form carbonate rocks.

### GREEN HOUSE EFFECT



A blanket of CO<sub>2</sub> gas exists in the lower part of the atmosphere (*i.e.* below 15 kms). When sunlight falls on the top of the atmosphere, the visible light and IR rays pass through the CO<sub>2</sub> layer and fall on the earth. Since the IR radiations have heating effect, they heat the earth and its various objects. The IR radiations of long wavelength emitted by the earth and its objects are absorbed by the CO<sub>2</sub> layer in the atmosphere. The layer of CO<sub>2</sub> gas in the atmosphere traps all the IR radiations coming from the earth's surface. These trapped IR rays heat the earth's atmosphere. This progressive warming up of the earth's surface and atmosphere due to the blanketing effect of CO<sub>2</sub> and certain other gases in the atmosphere is called Green House effect. Earth's atmosphere traps the heat from the sun and prevents it from escaping into the outer space.

The green house effect received its name because the earth's atmosphere acts much like the glass or plastic roof and wall of a green house. Sunlight enters a greenhouse through the transparent glass or plastic panes and heats the plants, but the heat emitted by the plants in



the form of IR radiation cannot pass through the glass or plastic panes. As a result, the inside temperature increases.

### **CAUSES OF GREENHOUSE EFFECT**

The earth's atmosphere allows most of the sunlight that falls on it to pass through and heat the surface. But the heat radiated by the heated surface cannot pass freely into space because greenhouse gases such as CO<sub>2</sub>, CH<sub>4</sub>, O<sub>3</sub>, chlorofluorocarbon compounds (CFCs) and water vapour in the atmosphere absorb it. Thus, they add to the heating of the atmosphere. The rise in temperature of the earth is very necessary for our existence on earth, because without it the whole earth would be converted into an extremely cold planet and consequently we shall not be able to have a normal life.

Very large quantities of CO<sub>2</sub> are introduced into the atmosphere through various processes. The burning of fossil fuels like coal, natural gas and petroleum is releasing about 6000 million tons of CO<sub>2</sub> in the atmosphere every year. Most man-made machines such as the automobile contribute more to the greenhouse effect, whether they run on petrol or diesel, release harmful gases into the atmosphere and damage the composition. These gases, in turn, create the greenhouse effect in the atmosphere.



The cultivation of land releases about 2000 million tons of CO<sub>2</sub> every year into the air, which is produced by bacteria. CO<sub>2</sub> is also discharged into the atmosphere through the eruption of volcanoes. Respiration of living organisms and decay of dead organisms also produce CO<sub>2</sub>. Global deforestation is also contributing to an increase in the CO<sub>2</sub> content of the atmosphere because trees are essential to maintain a balance in the CO<sub>2</sub> level. As per the report of World Resources Institute the loss of forests contributes between 12% and 17% of annual global greenhouse emissions.



The destruction of the ozone layer by human-made chemicals, such as CFCs, halons, are allowing increased levels of harmful UV-B radiation to reach the surface of the earth. Increased levels of UV-B radiation could reduce the density of plankton in the oceans. Since plankton are the primary carbon sink of the planet, reduction in their density could result in less CO<sub>2</sub> being absorbed from the atmosphere and ultimately the percentage of CO<sub>2</sub> increases in the atmosphere.

The high rate of population growth has been indirectly responsible and one of the major causes of the Greenhouse effect. With the increase in population, the needs and wants of the people increase, therefore, this increases the manufacturing as well as the industrial

processes along with deforestation for housing as well as agricultural/grazing purposes. This results in the increase of the release of greenhouse gases which catalyze the greenhouse effect.

### **CONSEQUENCES OF GREENHOUSE EFFECT**

The CO<sub>2</sub> gets confined exclusively to the troposphere. Hence, this large-scale increase in the atmospheric CO<sub>2</sub> concentration leads to abnormal global warming through enhanced greenhouse effect. It is estimated that if the input of CO<sub>2</sub> and other greenhouse gases into the atmosphere continues at the present rate, their atmospheric concentrations would double by about year 2050 and this would bring a 3°C rise in the surface temperature of the earth.

The evaporation of surface water increases, which further raises the temperature. Some areas of the world would experience abnormally high evaporation of water and unusual changes in oceanic currents and winds. Abnormal changes in weather patterns and seasons as well as increased desertification upset the ecosystem. Some regions of the world may lose up to 30% of the annual rainfall while some other region may experience very, high rainfall. Increased CO<sub>2</sub> levels in the atmosphere are also expected to cause plants, undergoing photosynthesis, to take up the gas at a greater rate so that plants in warmer climates with adequate rainfall would grow faster. The whole climatic pattern of the world would change which adversely affects plants and animals.

Climatic changes would affect agricultural production adversely. Since some regions would become increasingly dry and some others increasingly wet, the whole agricultural pattern would be upset with a consequent drop in agricultural products. The biological production of ocean is decreased. The patterns of cropping are changed and affect the world food production.

Increase in oceanic temperature may cause the melting of polar ice caps, leading to an abnormal rise in sea levels around the globe. This may result in the erosion and submergence of low-lying coastal lands and islands. It has been estimated that the sea level may rise by 0.5 to 1.5 m in the next 50 to 100 years. The polar ice sheet which was extending to 12 million square kilometers now decreasing on a fast rate as well as many mountainous glaciers has been vanished or decreasing day by day.



It is clear from World Health Organization report that extreme high air temperatures contribute directly to deaths from cardiovascular and respiratory disease, particularly among elderly people. In the heat wave of summer 2003 in Europe for example, more than 70 000 excess deaths were recorded. As per the record in 2005 about 150,000 annual deaths worldwide have been tied due to climate change already. Climate related deaths are expected to cause approximately 250,000 additional deaths per year, from malnutrition, malaria, diarrhea and heat stress between 2030 and 2050; 38,000 due to heat exposure in elderly people, 48,000 due to diarrhea, 60,000 due to malaria, and 95,000 due to childhood under

nutrition. The main causes for these deaths are heat waves & droughts as well as floods and more powerful storms linked to climate change.



Higher sea levels would increase the frequency and severity of flood damages coastal areas, cause loss of soil replenishment and seawater intrusion into rivers and other aquatic systems near the ocean. Fish and other aquatic organisms may not be able to withstand the high temperature of waters. So, they will perish.



Climatic changes resulting in flood or drought, agricultural loss, homelessness and starvation would force people to move within and between countries. These refugees would cause very serious social and economic problems. An increase in average global temperature is likely to increase the incidence of infectious diseases such as malaria, sleeping sickness, dengue and yellow fever.

### **CONTROL OF GREENHOUSE EFFECT**



The input of CO<sub>2</sub> into the atmosphere has to be controlled on a global basis and a global policy on industrialization, deforestation, *etc.* has to be adopted by all the nations of the world. We must develop industrial practices and means of transportation which are less dependent on fossil fuels and ultimately manage completely without them. Reducing use of fossil fuels would considerably reduce the amount of carbon dioxide produced as well as reducing the levels of the pollutants. Solar energy may be used as an alternative to the conventional fossil fuels. Planned forestation programmes should be implemented to reduce the CO<sub>2</sub> level, as trees act as natural 'sink' for CO<sub>2</sub> by utilizing it during photosynthesis.

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## RADIOACTIVE WASTE: AN OVERVIEW

Mrs. Haritha A K

*Assistant Professor (Ad hoc), PG Department of Chemistry, KAHM Unity Women's College,  
Manjeri, Kerala-676122, India  
E-mail: [harithaakashokan@gmail.com](mailto:harithaakashokan@gmail.com)*

Energy is the most important component of infrastructure essential for growth and economic development of any country. It is one of the most challenging issues currently facing most of the countries. Industries and all world communities require energy for daily needs. We live in a world that is just beginning to consume energy. If the population of the world grows at the present rate, in the next 50 years – as world population expands to 9 billion and the energy needs are not met – it will severely hamper the human growth.

Clean energy from 'new renewable' sources such as solar, wind, biomass and hydroelectric power deserves strong support. But the collective capacity of these technologies to produce electricity in the decades ahead is limited. The International Energy Agency projects that, even with continued subsidy and research support, these new renewable energy sources can provide only around 6% of world electricity by 2030. As the price of oil and global warming concerns continue to rise steadily both have forced many countries to look for alternative source of energy which is clean, sustainable and efficient. The search of alternative energy source among the developed nations has led to a renewed interest in nuclear energy. The renewed interest in the clean-burning properties of nuclear power is become much more attractive today. The nuclear energy market is expected to grow substantially over the next 20 years and expected to double by 2030.

Production of electricity per capita is considered as one of the major development index of a country. The per capita energy consumption in many countries including China and India has increased. Among the power generation technologies, nuclear fission is one of them. The nuclear power generation has been developed since 1960 and now around 450 number of atomic fission power reactors are there over the world. In nuclear power production, the power generated from 1 gram of U is equivalent to the power generated from 2083 kg of coal. A large amount of energy released in exchange of small amount of nuclear fuel but the major problem in producing nuclear power is its radioactive waste.

The nuclear experiments have led some areas on earth to a radioactive waste storage centre and certain accidents from the nuclear power stations such as Chernobyl in Ukraine and Fukushima Daiichinuclear power station in Japan indicates a warning of hidden danger of radioactive pollution which is a big threat for environment. Radioactive waste management is becoming a major research area all over the world and its importance is increasing day by day. If the radioactive waste is not treated properly, it will harm the surrounding environment as well as life forms in the nature. Radioactive waste requires sophisticated treatment and management in order to successfully isolate it from interacting with the biosphere. This usually necessitates different types of treatments, followed by a long-term management strategy involving storage, disposal or transformation of the waste into a non-toxic form. Therefore, radioactive waste management forms an important aspect of any nuclear establishment. Although the amount of radioactive waste generated is very small,

when compared to wastes produced by fossil fuel electricity generation, safe radioactive waste management must be the primary priority of any nuclear programme.

The future development of nuclear power largely depends on the success of programmed and management of radioactive waste generated at various stages of the nuclear fuel cycle. Apart from the biological pollution, the industrial and the chemical pollution of the soil, nowadays there is also the radioactive pollution and the man is guilty for all of them.

### **RADIOACTIVE WASTE**

Radioactive waste is any liquid, gas or solid that contains, or is contaminated with, radionuclides at concentrations or activities greater than clearance levels as established by individual countries and regulatory authorities. It is a type of hazardous waste that is usually obtained as a by-product of nuclear power generation and other applications of nuclear fission or nuclear technology, such as research and medicine.

Radioactive wastes comprise of a number of radioisotopes which are having unstable configurations of elements that decay emitting ionizing radiations which can be harmful to the environment. Those isotopes which emit different types and levels of radiation, will last for different periods of time not just a few years but for thousands of years. All radioisotopes contained in the waste have a half-life i.e. the time taken for any radionuclide to lose half of its radioactivity. Thus, all radioactive waste decays into non-radioactive elements i.e. stable isotopes. The nuclei of radioactive substances spontaneously disintegrate to emit alpha, beta and gamma rays. The alpha rays consist of particles (nuclei of helium atoms) carrying a positive charge, beta rays particles have negative charge (streams of electrons) and gamma rays are charge less electromagnetic radiation with shorter wavelengths than any X-rays. These rays can penetrate living tissues for short distances and affect the tissue cells. It could take just seconds to die from exposure to such radioactive materials. It must be handled in the right manner so that it will not cause a ton of devastation in the world.

### **SOURCES OF RADIOACTIVE WASTE**

Radioactive waste comes from a number of sources. In countries with nuclear power plants, or nuclear fuel treatment plants, the majority of waste originates from the nuclear fuel cycle and nuclear weapons reprocessing. Other sources where much smaller amounts of radioactive waste are produced by the medical, industrial, research and defence sectors.

The 'nuclear fuel cycle' is the sequence of industrial activities needed to generate electricity by nuclear power. It includes the manufacturing of nuclear fuel and management of spent nuclear fuel (used fuel). The nuclear fuel cycle is also called as nuclear fuel chain, is the progression of nuclear fuel through the front end of the reactor, where the preparation of fuel occurs, and in the service period in which the fuel is used during reactor operation, and in the back end, which are necessary to safely manage, contain, and either reprocess or dispose of spent nuclear fuel takes place. Primarily the radioactive waste originates from nuclear power plants as nuclear fuel that is produced after being used inside of a nuclear reactor contains the most dangerous long-lived radionuclides which can last even for a century.

Waste from nuclear weapons decommissioning is unlikely to contain much beta or gamma activity other than tritium and americium. It is more likely to contain alpha-emitting actinides such as Pu-239 which is a fissile material used in bombs, plus some material with much higher specific activities, such as Pu-238 or Po.

Radioactive wastes produced by the defence sector arise in three main areas like Operation of active nuclear-powered submarines and the decommissioning of retired

submarines; Clean-up of defence sites that may have been contaminated in the past; and Production, management and decommissioning of strategic deterrent nuclear weapons. The Ministry of Defence is responsible for the safe, secure and sustainable dismantling of retired submarines.

Radioactive materials are used for many purposes in the medical industry. In particular, radioactive materials are used to sterilise equipment, and help diagnose and treat medical illnesses. Relatively small amounts of radioactive waste are produced during the manufacture, use and recycling of radiopharmaceuticals. Radioactive medical waste tends to contain beta particle and gamma ray emitters. In diagnostic nuclear medicine a number of short-lived gamma emitters such as technetium-99m are used. Many of these can be disposed of by leaving it to decay for a short time before disposal as normal waste. Other isotopes such as I-131, Sr-89, Co-60 are also used in medicine.

The industrial sector uses radioactive sources in a number of ways. The most common use is for non-destructive testing of materials and components. For example, gamma rays are used to test the quality of welds or the thickness of products, such as paper. Industrial source waste can contain alpha, beta, neutron or gamma emitters. Gamma emitters are used in radiography while neutron emitting sources are used in a range of applications, such as oil well logging.

### **TYPES OF RADIOACTIVE WASTES**

The type of radioactive waste varies by country. Generally there are five types of radioactive waste- high level, low level, intermediate level, mining and milling and transuranic waste. All types of nuclear wastes have their own separate storage and clean-up procedures.

High-level waste is simply the spent fuel that is still present after it has been used inside of nuclear reactors. This radioactive waste has to cool off for several years and is considered to be very dangerous. The cooling process of this waste usually takes place inside of deep pools of water that are several hundred feet deep. This type of waste is hazardous to people for many reasons, but especially because it remains radioactive. High level waste accounts for 95% of the total radioactivity produced in the nuclear reactor. This type of nuclear waste is very dangerous. It must consistently go through a process to keep it cool and the radioactive material under control. High level waste can have short and long lived components depending upon the time it will take for the radioactivity to decrease to levels that is not considered harmful for humans and surrounding environment. In india, a key idea for the long term disposal of high level wastes is carried out by identifying suitable sites at which the waste could be buried, a process called deep geological repository (DGR) is followed by the department of atomic energy. Several areas of karnadaka and andra Pradesh were selected for the disposal and the after effects of improper disposal are still by the villagers.

Most of the radioactive waste that is around today is considered to be low level. About 90% of all nuclear waste is low level. Nuclear reactors, hospitals, dental offices, and similar types of facilities often use low-level nuclear waste materials on a daily basis. Low-level nuclear waste is not dangerous, and any of it can be disposed of inside of a landfill. It does not require shielding during handling and transport. The low level waste contains just 1% of the radioactivity of all radioactive waste.

Intermediate-level waste contains high amount of radioactivity than low-level and less than high-level. This type of waste typically requires shielding during handling and interim

storage. This type of waste typically includes refurbishment waste, ion-exchange resins, chemical sludges and metal fuel cladding. The intermediate level waste contains 4% of all the radioactivity.

Tailings and waste rock are generated by mining and milling of uranium ore. The tailings material is covered with water and has the consistency of fine sand, when dried. It is produced by grinding the ore and the chemical concentration of uranium. After few months, the tailings material contains 75% of the radioactivity of the original ore.

Transuranic wastes defined as waste that is contaminated with alpha-emitting transuranic radionuclides with half-lives greater than 20 years. Elements that have an atomic number greater than uranium are called transuranic ("beyond uranium"). Because of their long half-lives, it is disposed more cautiously than either low- or intermediate-level waste. Transuranic waste is much heavier than uranium. This type of waste is produced through nuclear waste reprocessing procedures in most cases.

### **DISPOSAL OF RADIOACTIVE WASTE**

Radioactive waste is extremely varied in terms of physical and chemical form, radioactivity and the half-life of the radioactive elements it contains, as well as volume. A specific process is adopted for each category of waste, including a series of operations such as sorting, treatment, conditioning, storage and disposal.

**Sorting:** This consists in separating waste according to its different properties, in particular the half-lives of the radionuclides it contains. It also involves separating waste that can be compacted, incinerated or melted down to reduce the volume.

**Treatment and conditioning:** Different types of waste undergo different types of treatment (incineration, calcination, melting, compacting, cementation, vitrification, etc.). It is then sealed in a container. The result is a radioactive waste package.

**Storage and disposal:** Storage facilities are designed to accommodate waste packages for a limited period of time. Disposal is the final stage of the waste management process and should ensure that the packages must protect people and the environment both in the short and very long term.

In some countries, for very short-lived waste the radioactivity level of which disappears almost entirely in a few weeks to a few hundred days, is stored long enough to decay before disposal. High-level and long-lived waste which is in a liquid form, is mixed with molten glass and poured into stainless steel containers, then hermetically sealed by a welded lid. Once the glass has cooled down, the radioactivity is trapped inside the matrix. These waste packages are currently stored by the organisations that generated the waste.

India has adopted closed fuel cycle option if the spent fuel is reprocessed, it is referred to as a closed fuel cycle fuel. During reprocessing, only about two to three percent of the spent fuel becomes waste and the rest is recycled. At the end the high level waste will be emplaced in geological disposal facilities. The processing technologies adopted for management of radioactive waste are summarized below:

- *Solid waste:* Solid waste generated from nuclear power plants after suitable conditioning are disposed off in Near Surface Disposal Facilities (NSDF) located within the exclusion zone boundary of nuclear power plants. Near Surface Disposal Facilities are designed and constructed to contain the radionuclides within the disposal system until the radionuclides decay to negligible activity level.



- *Liquid waste:* Low level liquid waste generated from nuclear power plants are discharged to the environment after suitable treatment and ensuring compliance with the regulatory limit. The treatment system essentially comprises chemical treatment, evaporation, ion exchange, filtration etc.
- *Gaseous waste:* Gaseous waste is treated at the source of generation. The gaseous wastes are discharged to the environment through 100 m high stack after filtration and dilution with continuous monitoring of radionuclides and compliance with the regulatory limits.

### **WHY IS RADIOACTIVE WASTES DANGEROUS FOR US?**

Eventhough many countries are trying to achieve the goal of safe disposal of radioactive wastes, certain limitations exis regarding the dangerous drawbacks such as

**There is no long-term storage solution:** Even though nuclear power plants supply 11 percent of the world's electricity from 449 operating nuclear reactors, there are no safe long-term waste storage repositories. Our primary way of dealing with radioactive waste at the moment is to simply store it somewhere, and try to figure out what to do with it later. One commonly used "storage place" for decades have been our seas and oceans for their great capacity to dilute radiation. Clearly, this way of dealing with such a dangerous material is not safe, as the radioactive contamination spreads through our marine ecosystem.

**Reprocessing nuclear waste is harmful:** Nuclear waste reprocessing is highly polluting and is one of the largest sources of human-generated radioactivity on the planet. During this process, plutonium is separated through a series of chemical reactions from the spent uranium fuel. Plutonium is then used as a new fuel or to build nuclear weapons. Plutonium ranks amongst the most toxic substances ever known to humans. It accumulates in bones and liver, and makes it difficult to estimate its effects on individuals. Waste reprocessing is not an answer to the waste problem. In fact, the amount of waste left behind is higher. Chemical processes used to dissolve spent fuel rods generate significant volume of radioactive liquid waste, which needs to be safely stored.

Addressing the public's concerns and negotiating acceptable solutions is an important challenge regarding the radioactive wastes. At present, no single energy source excels in all measures. Each has some pros and cons. Although nuclear power has some challenges – notably waste disposal – it appears to be one of the most attractive sources in terms of a small environmental footprint, reliable energy generation, security of the energy supply, and other important measures. It should, therefore, be considered in this light in decision-making on future energy-supply options.

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## PHYSICOCHEMICAL TREATMENT OF WASTE WATER

Mrs. Najeera P C

*Assistant Professor (Ad hoc), PG Department of Chemistry, KAHM Unity Women's College,  
Manjeri, Kerala-676122, India  
E-mail: [najeerapc@gmail.com](mailto:najeerapc@gmail.com)*

Environment is the surroundings in which we live. But the contamination of our environment by pollutants is environmental pollution. The current stage of the earth that we are seeing is the cause of centuries of exploitation of earth and its resources. The environmental pollution, directly and indirectly, affects the lives of humans and other species. These living beings co-existed on the earth with human from centuries. Carbon and dust particles string up with the air in the form of smog, damaging respiratory system, haze, and these factors affect the immune system smoke. These are caused by the emission of industrial and manufacturing units by burning of fossil fuels, vehicle combustion of carbon fumes. Moreover, of birds which become a carrier of viruses and infections. Besides, it also affects the body system and body organs. Water gets contaminated easily with any pollutant whether it is human waste or chemical discharge from factories. Also, we use this water for irrigation of crops and drinking. But, because of infection they become contaminated too. Besides, an animal dies because they drink this same contaminated water. Moreover, around 80% of pollutants of land such as chemical, industrial and agricultural waste end up in the water bodies. Besides, these water bodies ultimately connect to the sea which means it indirectly pollutes the biodiversity of the sea. Because of contaminated soil and water, the crop or agricultural produce also get toxic. Furthermore, this contaminated food effect our health and organs. From the beginning of their life, these crops are laced with chemical components that reach a mass level until the time of harvest. Climate change is also a cause of environmental pollution. Also, it affects the physical and biological components of the ecosystem.

Moreover, ozone depletion, greenhouse gases, global warming all these climate changes are a cause of environmental pollution. Besides, their effect can be fatal for our upcoming generations. The irregular extreme cold and hot climate affect the ecological system of the earth. In conclusion, man has exploited the wealth of nature at the cost of his and environments health. Also, the effect that is now emerging rapidly is all because of the activities of humans for hundreds or thousands of years. Above all, if we wish to survive and continue our life on earth then we have to take measures. These measures will help is securing our as well as our next generation future .Numerous process exist for the treatment of gaseous ,liquid and solid pollutants.

In this chapter I give an overview of several key principles for treatment of waste water. The ultimate goal of waste-water management is the protection of the environment in a manner commensurate with public health and socio-economic concerns.

### **PHYSICAL TREATMENT OF WATER POLLUTANTS**

Water pollution is a serious problem in India as almost 70 per cent of its surface water resources and a growing percentage of its groundwater reserves are contaminated by biological, toxic, organic, and inorganic pollutants.

The most commonly used physical treatment of waste water are:

**(a) Screening:** The screening of waste-water, one of the oldest treatment methods, removes gross pollutants from the Waste stream to protect downstream equipment from damage, avoid interference with plant operations and prevent objectionable floating material from entering the primary settling tanks. Screening devices may consist of parallel bars, rods or wires, grating, wire mesh, or perforated plates, to intercept large floating or Suspended material. The openings may be of any shape, but are generally circular or rectangular. The material retained from the manual or mechanical cleaning of bar racks and screens is referred to as Screenings, and is either disposed of by incineration, or returned into the waste flow after grinding.

**(b) Flow equalization:** It is the process of controlling hydraulic velocity, or flow rate, through a wastewater treatment system. The equalization of flow prevents short term, high volumes of incoming flow, called surges, from forcing solids and organic material out of the treatment process. Flow equalization also controls the flow through each stage of the treatment system, allowing adequate time for the physical, biological and chemical processes to take place. This technology has only recently begun to be used in residential treatment systems. The flow patterns of residential treatment systems are intermittent and variable in nature, generating frequent hydraulic and organic surges. These surges can result in large quantities of solids being washed out of the system.

**(c) Sedimentation:** Sedimentation, a fundamental and widely used unit operation in wastewater treatment, involves the gravitational settling of heavy particles suspended in a mixture. This process is used for the removal of grit, particulate matter in the primary settling basin, biological floc in the activated sludge settling basin, and chemical floc when the chemical coagulation process is used. Sedimentation takes place in a settling tank, also referred to as a clarifier. There are three main designs, namely, horizontal flow, solids contact and inclined surface. In designing a sedimentation basin, it is important to bear in mind that the system must produce both a clarified effluent and a concentrated sludge. Four types of settling occur, depending on particle concentration, namely, discrete, flocculent, hindered and compression. It is common for more than one type of settling to occur during a sedimentation operation

**(d) Flotation:** Flotation is a unit operation used to remove solid or liquid particles from a liquid phase by introducing a fine gas, usually air bubbles. The gas bubbles either adhere to the liquid or are trapped in the particle structure of the suspended solids, raising the buoyant force of the combined particle and gas bubbles. Particles that have a higher density than the liquid can thus be made to rise. In waste-water treatment, flotation is used mainly to remove suspended matter and to concentrate biological sludge. The chief advantage of flotation over sedimentation is that very small or light particles can be removed more completely and in a shorter time. Once the particles have been floated to the surface, they can be skimmed out. Flotation, as currently practiced in municipal waste-water treatment, uses air exclusively as the floating agent. Furthermore, various chemical additives can be introduced to enhance the removal process.

**(e) Granular medium filtration:** The filtration of effluents from waste-water treatment processes involves removal of suspended solids from waste-water effluents of biological and chemical treatment processes, in addition to the removal of chemically precipitated phosphorus. The complete filtration operation comprises two phases: filtration and cleaning or backwashing. The waste-water to be filtered is passed through a filter bed consisting of granular material (sand, anthracite and/or garnet), with or without added chemicals. Within the filter bed suspended solids contained in the waste-water are removed by means of a

complex process involving one or more removal mechanisms such as straining, interception, impaction, sedimentation, flocculation and adsorption. The Cleaning/backwashing phase differs, depending on whether the filter operation is continuous or semicontinuous. In semicontinuous filtration, the filtering and cleaning operations occur sequentially, whereas in continuous filtration the filtering and cleaning operations occur simultaneously.

### **CHEMICAL TREATMENT OF WASTE WATER**

Chemical processes used in waste-water treatment are designed to bring about some form of change by means of chemical reactions. They are always used in conjunction with physical unit operations and biological processes. In general, chemical unit processes have an inherent disadvantage compared to physical operations in that they are additive processes. That is to say, there is usually a net increase in the dissolved constituents of the waste-water. This can be a significant factor if the waste-water is to be reused. These are the main chemical unit processes, such as chemical precipitation, adsorption, disinfection, chlorination and other applications.

**(a) Adsorption with activated carbon:** Adsorption is the process of collecting soluble substances within a solution on a suitable interface. In Wastewater treatment, adsorption with activated carbon is aimed at removing a portion of the remaining dissolved organic matter. Particulate matter present in the water may also be removed. Activated carbon is produced by heating char to a high temperature and then activating it by exposure to an oxidizing gas at high temperature. The gas develops a porous structure in the char and thus creates a large internal surface area. The activated char can then be separated into various sizes with different adsorption capacities. The two most common types of activated carbon are granular activated carbon (GAC), which has a diameter greater than 0.1 mm, and powdered activated carbon (PAC), which has a diameter of less than 200 mesh. A fixed-bed column is often used to bring the waste-water into contact with GAC. The water is applied to the top of the column and withdrawn from the bottom, while the carbon is held in place. Backwashing and surface washing are applied to limit head loss build-up. Expanded-bed and moving-bed carbon contactors have been developed to overcome the problem of head loss build-up. In the expanded-bed system, the influent is introduced at the bottom of the column and is allowed to expand. In the moving-bed system, spent carbon is continuously replaced with fresh carbon. Spent granular carbon can be regenerated by removal of the adsorbed organic matter from its surface through oxidation in a furnace. The capacity of the regenerated carbon is slightly less than that of the virgin carbon.

**(b) Disinfection:** Disinfection refers to the selective destruction of disease-causing microorganisms. This process is of importance in waste-water treatment owing to the nature of waste-water, which harbours a number of human enteric organisms that are associated with various waterborne diseases. Commonly used disinfection methods are the following:

- (i) Physical agents such as heat and light;
- (ii) Mechanical means such as screening, sedimentation, filtration, and so on;
- (iii) Radiation, mainly gamma rays;
- (iv) Chemical agents including chlorine and its compounds, bromine, iodine, ozone, phenol and phenolic compounds, alcohols, heavy metals, dyes, soaps and synthetic detergents, quaternary ammonium compounds, hydrogen peroxide, and various alkalis and acids. The most common chemical disinfectants are the oxidizing chemicals, and of these, chlorine is the most widely used.

**(c) Dechlorination:** Dechlorination is the removal of free and total combined chlorine residue from chlorinated wastewater effluent before its reuse or discharge to receiving waters. Chlorine compounds react with many organic compounds in the effluent to produce undesired toxic compounds that cause long-term adverse impacts on the water environment and potentially toxic effects on aquatic micro-organisms. Dechlorination may be brought about by the use of activated carbon, or by the addition of a reducing agent such as sulfur dioxide (SO<sub>2</sub>), sodium sulphite (Na<sub>2</sub>SO<sub>3</sub>) or sodium metabisulfite. It is important to note that dechlorination will not remove toxic by-products that have already been produced.

### **CONCLUSIONS**

Physical and chemical treatments are very important within the waste water treatment systems and prior to any biological and advanced treatment technologies. Its understanding and conceptual knowledge is essential for any waste water treatment systems.

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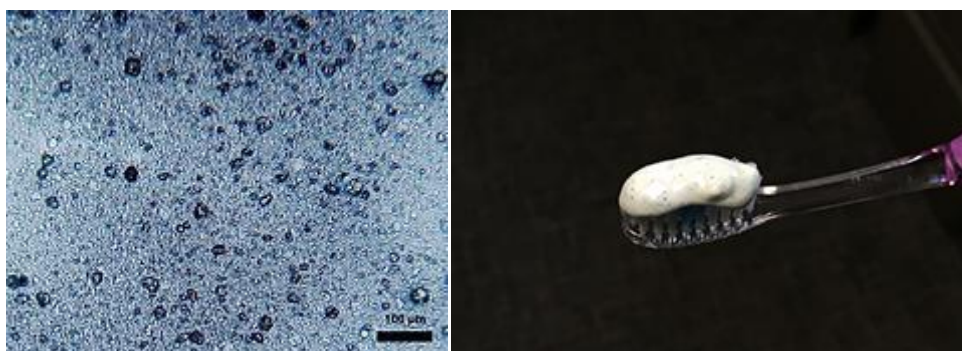
## MICROPLASTIC POLLUTION IN WATER AND SOIL

Mrs. Suhada K M

*Assistant Professor, PG Department of Chemistry, KAHM Unity Women's College, Manjeri, Kerala-676122, India*

*E-mail: [kmsuhada591989@gmail.com](mailto:kmsuhada591989@gmail.com)*

Plastic is everywhere. Nowadays plastics have penetrated every aspect of everyday life from clothing to coatings and from transport vehicles to cleaning products. Plastic is a cheap, durable, lightweight, malleable material and has a practically unlimited number of possible applications. A large quantity of these ends up in the ocean and soil. Most plastics in the ocean break up into very small particles which are called "microplastics." There are other plastics which are intentionally designed to be small. They're called microbeads and are used in many health and beauty products. Microplastics are defined as small plastic pieces less than five millimeters long which can be harmful to our ocean and aquatic life. They enter natural ecosystems from a variety of sources, including cosmetics, clothing, and industrial processes. The term "microplastics" was introduced in 2004 by Professor Richard Thompson, a marine biologist at the University of Plymouth in the United Kingdom.



*Polyethylene based micro spherules in toothpaste*

Microplastics are divided into two types: primary and secondary

### **PRIMARY MICROPLASTICS**

Primary microplastics are small pieces of plastic that are purposefully manufactured and used in facial cleansers and cosmetics, or in air blasting technology. Micro beads are tiny pieces of polyethylene plastic added to health and beauty products, such as some cleansers and toothpastes.

### **SECONDARY MICROPLASTICS**

Secondary plastics are small pieces of plastic derived from the breakdown of larger plastic debris, both at sea and on land. Over time, a culmination of physical, biological, and chem photo degradation, including photo degradation caused by sunlight exposure, can reduce the structural integrity of plastic debris to a size that is eventually undetectable to the naked eye. This process of breaking down large plastic material into much smaller pieces is known as fragmentation.

## **MICROPLASTICS IN WATER**

Society has used the ocean as a convenient place to dispose of unwanted materials and waste products for many centuries, either directly or indirectly via rivers. The volume of material increased with a growing population and an increasingly industrialized society. The demand for manufactured goods and packaging, to contain or protect food and goods, increased throughout the twentieth century. Large-scale production of plastics began in the 1950s and plastics have become widespread, used in a bewildering variety of applications. The many favorable properties of plastics, including durability and low cost, make plastics the obvious choice in many situations. Unfortunately, society has been slow to anticipate the need for dealing adequately with end-of-life plastics, to prevent plastics entering the marine environment. As a result there has been a substantial volume of debris added to the ocean over the past 60 years, covering a very wide range of sizes (metres to nanometres in diameter). This is a phenomenon that has occurred wherever humans live or travel. As a result there are multiple routes of entry of plastics into the ocean, and ocean currents have transported plastics to the most remote regions. It is truly a global problem.

50% of the plastic manufactured items are used once and then discarded which ends in ocean, soil and even drinking water. The disadvantages of plastics however are becoming more and more visible. Large quantities of plastics are released into rivers and oceans with various adverse effects to ecosystems and related economic activities. MPs emerged as a new type of pollutant and it is widely distributed in the aquatic environment. MPs on fresh water environment were studied.

Due to the widespread use and durability of synthetic polymers, plastic debris occurs in the environment worldwide. In the present work, information on sources and fate of MP particles in the aquatic and terrestrial environment, and on their uptake and effects, mainly in aquatic organisms, is reviewed. MPs in the environment originate from a variety of sources. Quantitative information on the relevance of these sources is generally lacking, but first estimates indicate that abrasion and fragmentation of larger plastic items and materials containing synthetic polymers are likely to be most relevant. MPs are ingested and, mostly, excreted rapidly by numerous aquatic organisms. So far, there is no clear evidence of bioaccumulation or biomagnification.

MP was present in the water phase of storm water retention ponds. The most common polymers are PVC, PS, PP, PE and polyester. This study of seven storm water ponds is amongst the first investigations on the abundance of MP in storm water runoff from urban and highway areas. It shows that urban and highway runoff contributes the MP to the aquatic environment even though it is treated with storm water ponds. It also proves that the land use of the contributing area should be taken into account when assessing MP load to the aquatic environment.

Waste water treatment plants serves to collect and treat waste that are known to include MP. Recent studies determine that the MP load and removal efficiencies of WWTPs with different treatment size. It is found that WWTPs are the one of the main source of MP in water and soil. Determination of MPs emission in the effluent of a municipal WWTP using Raman micro spectroscopy was done.

The process of MP fiber pollution in ground water is known. The research on this contaminant threat is focused on surface waters. While the aquifer contamination is only marginally mentioned, needing further investigation. Synthetic microfibers can be introduced into soil in different ways such as Waste water treatment plant, grey water discharge, septic tank outflow and can be reach aquifer system due to leaching or infiltration in soil pores.

As a new type of pollutant, MPs are an emerging scientific and social concern in the environment and are widely distributed in the aquatic environment and organism. Nowadays, researches on MP pollution mainly focus on the marine environment. As a bridge for the migration of MPs from the terrestrial environment to the marine environment, the freshwater environment has been deserved more attention. Four typical behaviors of MPs were summarized: biological ingestion, biological attachment, adsorption of pollutants and release of plasticizers. In addition, the progress in research and results on the ecological toxicity of MPs to freshwater organisms was also analyzed. Finally, emphasis on future research on the toxicity of MPs to freshwater aquatic organisms was made throughout this review as a tool in MP risk assessment research.

### **MICROPLASTICS IN SOIL**

Recently, research on environmental impact of MPs was conducted exclusively in marine environment and in shoreline. A substantial portion of microplastics are expected to end up in the world's soil, yet very little research has been conducted on microplastics in soil. 80 % of plastics found in marine environments and disposed of on land. MP contamination on soil is estimated 4-32 times higher than in the ocean. Just like water, soil is also the major component in the terrestrial ecosystem, which is under a strange threat of pollution. MPs affect the soil biodiversity very badly. MPs contamination is increasingly recorded in our Nation. Recent studies are the proof for soil contamination. The MP influences the soil and associated qualities of soil in the worse manner. Various types of MPs such as the polyester fibers, polyamide beads, poly acrylic fibers, polythene fragments etc influence the water holding capacity, soil bulk density, soil microbial activities and soil structure and function. This create imbalance in the equilibrium of soil. A special property called carbon sequestration, i.e. process of capturing and storing atmospheric CO<sub>2</sub> which reduces carbon concentration in atmosphere with the goal of reducing global climate change. But due to MP interference, this property of soil got damaged. This influences in process of life , biodiversity conservation and food security.

When particle size became less than 5 mm in diameter, they are categorized as MPs by National Oceanic and Atmospheric Administration (NOAA). The effects of MPs on soil are poorly understood. Higher concentration of MP inhibited the growth and increased the mortality of earth worm. Effect of MPs on soil-plant system were studied and found that MP affected both above and below ground parts of the wheat plant during both vegetative and reproductive growth. Now a days MP has entered into food chain: animals including echinoderm, molluscus and fish, plants including algae and microorganisms including bacteria. Effect of MPs in soil system is not clear. Nutrient release, soil wettability, water binding, and matrix rigidity of soil organic matter (SOM) can be affected by cross-links between segments of SOM, cations, and water molecule bridges (WaMB). A soil's cation exchange capacity (CEC) is expected to be relatively inert against changes in cation loading. Adsorption is the main mechanism of capturing water in soil organic matter (SOM) under arid conditions. This is governed by hydrophilic sites, which are gradually bridged via water molecule bridges (WaMB). Presence of MPs in Alps and Arctic snow were also studied and identified the presence of MP at Arctic snow. Earth worm keeps soil healthy. Presence of MP in soil also retard the growth of earth worm and there by the plant growth.

Studies reveal that the sludge from waste water treatment plants are the main source of MP in soil. Waste water treatment plants efficiently remove MPs from sewage and preventing their movement into aquatic environments. WWTP concentrates MP in their sludge and when we use sludge on agricultural soil as fertilizer, MP contaminates soil



environment. Determination of MPs emission in the WWTP can be done using Raman micro spectroscopy.

Adsorption is the main mechanism of capturing water in soil organic matter (SOM) under arid conditions. This is governed by hydrophilic sites, which are gradually bridged via water molecule bridges (WaMB).

It is observed that the MP can change the soil's biophysical environment such as bulk density, water holding capacity etc. The widespread occurrence of MP has studied and found that MPs are present throughout the globe. Extend of distribution of MP in the world depends on many factors such as geography, location, time etc. It is concluded that without appropriate laws and regulations, MP pollution will be dangerous and threaten human life.

MP detection in soil can be done using Transmission Electron Microscopy (TEM-EDX) and Pyrolysis. Urban compost application enhances the soil fertility in a successful way. But it is a major source of MP pollution in water and soil. Mps are damaging the soil qualities. This is new method of confining soil fraction, MP observation and chemical characterization of soil to follow the fate of plastic in soil.

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## ACID DEPOSITION: AN ENVIRONMENTAL ISSUE

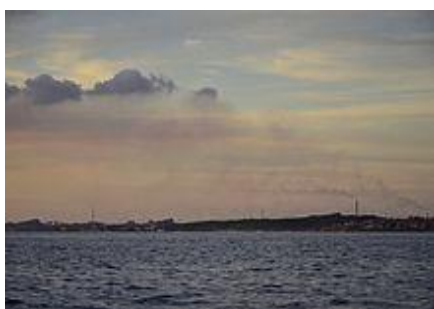
Mrs. Shabana K

*Assistant Professor (Ad hoc), PG Department of Chemistry, KAHM Unity Women's College,  
Manjeri, Kerala-676122, India*

*E-mail: [shabshabana@gmail.com](mailto:shabshabana@gmail.com)*

### INTRODUCTION

Acid rain was discovered in the 19<sup>th</sup> century by Robert Angus Smith, a pharmacist from Manchester (England), who measured high levels of acidity in rain falling over industrial regions of England and contrasted them to the much lower levels he observed in less polluted areas near the coast. Little attention was paid to his work until the 1950s, when biologists noticed an alarming decline of fish populations in the lakes of southern Norway and traced the problem to acid rain. Similar findings were made in the 1960s in North America (the Adirondacks, Ontario, Quebec). These findings spurred intense research to understand the origin of the acid rain phenomenon. Rain is naturally acidic due to the dissolution of carbon dioxide forming weak carbonic acid. Acid rain refers to rain that has a higher hydrogen ion concentration than about  $10^{-5}$  M. Acid rain occurs due to the dissolution of acidic oxides in the atmosphere. Sulfur dioxide is one such acidic oxide which is produced by natural means such as volcanoes and geothermal hot springs and industrial processes such as the burning of fossil fuels (brown coal) and metal extraction from sulfide ores. The acidity of solutions is measured on a logarithmic pH scale from 0 to 14 with 0 being most acidic and 14 being most alkaline and 7 as neutral. Distilled water is at 7 with normal rainwater naturally being from 5.3 to 6.0. Any measurement below 5.3 is commonly considered to be acid rain. Sulfur dioxide and nitric oxides can be produced either by human activity or by nature. Burning coal and oil and volcanic eruptions produce sulfur dioxide while the cars and lightning strikes produce nitric oxides.



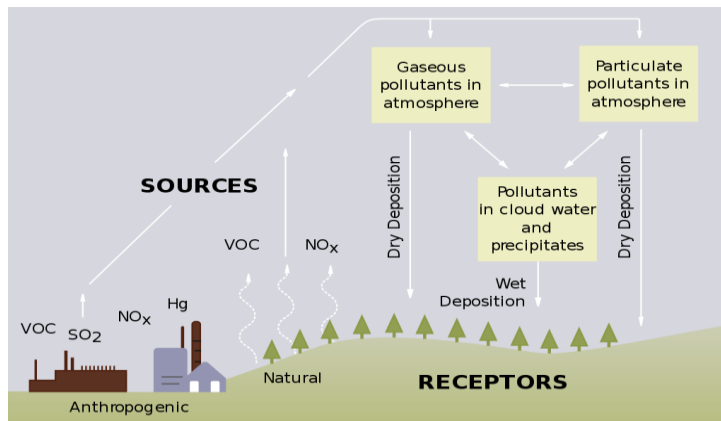
*Acid clouds can grow on SO<sub>2</sub> emissions from refineries, as seen here in Curaçao*

### FORMATION OF REACTANTS

Burning of Fossil Fuels:  $S_{(\text{in compounds})} + O_{2(g)} \rightarrow SO_{2(g)}$

Burning of Zinc Sulfide:  $2ZnS_{(s)} + 3O_{2(g)} \rightarrow 2ZnO_{(s)} + 2SO_{2(g)}$

The other major acidic oxide that contributes to the formation of acid rain is nitrogen dioxide. Nitric oxide is formed in high localized temperatures created by lightning strikes and naturally reacts in the atmosphere to produce nitrogen dioxide. Nitrogen dioxide is also produced in the high temperatures of combustion chambers of power stations and motor vehicles.



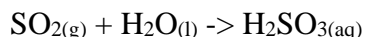
Processes involved in acid deposition (only SO<sub>2</sub> and NO<sub>x</sub> play a significant role in acid rain)

**CHEMICAL EQUATIONS FOR THE FORMATION**

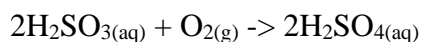
Formation of Nitrogen Dioxide:  $N_{2(g)} + 2O_{2(g)} \rightarrow 2NO_{2(g)}$

Both sulfur dioxide and nitrogen dioxide are acidic oxides and react with water to form acids.

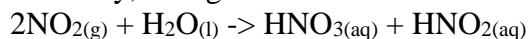
Sulfur dioxide reacts with water to form sulfurous acid.



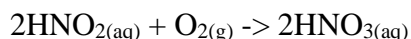
Substances in the upper atmosphere then catalyse the reaction between sulfurous acid and oxygen to form sulfuric acid.



Similarly, nitrogen dioxide reacts with water to form a mixture of nitric acid and nitrous acid.



Substances in the atmosphere then catalyse the reaction between nitrous acid and oxygen causing the formation of more nitric acid.



Both sulfuric acid and nitric acid are soluble in water and are the major acids present in acid rain. As this forms and falls onto the Earth's surface, these strong acids are also brought to the surface causing harmful effects on the built and the natural environment.

**EFFECTS OF ACID RAIN**

**On Ecosystems:** An ecosystem is a community of plants, animals and other organisms along with their environment including the air, water and soil. Everything in an ecosystem is connected. If something harms one part of an ecosystem – one species of plant or animal, the soil or the water – it can have an impact on everything else.

**On Fish and Wildlife:** The ecological effects of acid rain are most clearly seen in aquatic environments, such as streams, lakes, and marshes where it can be harmful to fish and other wildlife. As it flows through the soil, acidic rain water can leach aluminum from soil clay particles and then flow into streams and lakes. The more acid that is introduced to the ecosystem, the more aluminum is released.

Some types of plants and animals are able to tolerate acidic waters and moderate amounts of aluminum. Others, however, are acid-sensitive and will be lost as the pH declines.

Animal	Critical pH Level
Snails	6
Clams	6
Bass	5.5
Crayfish	5.5
Mayfly	5.5
Trout	5
Salamanders	5
Perch	4.5
Frogs	4

Generally, the young of most species are more sensitive to environmental conditions than adults. At pH 5, most fish eggs cannot hatch. At lower pH levels, some adult fish die. Some acidic lakes have no fish. Even if a species of fish or animal can tolerate moderately acidic water, the animals or plants it eats might not. For example, frogs have a critical pH around 4, but the mayflies they eat are more sensitive and may not survive pH below 5.5.

**On Plants and Trees:** Dead or dying trees are a common sight in areas affected by acid rain. Acid rain leaches aluminum from the soil. That aluminum may be harmful to plants as well as animals. Acid rain also removes minerals and nutrients from the soil that trees need to grow.

At high elevations, acidic fog and clouds might strip nutrients from trees' foliage, leaving them with brown or dead leaves and needles. The trees are then less able to absorb sunlight, which makes them weak and less able to withstand freezing temperatures.

**Buffering Capacity:** Many forests, streams, and lakes that experience acid rain don't suffer effects because the soil in those areas can *buffer* the acid rain by neutralizing the acidity in the rainwater flowing through it. This capacity depends on the thickness and composition of the soil and the type of bedrock underneath it. In areas such as mountainous parts of the Northeast United States, the soil is thin and lacks the ability to adequately neutralize the acid in the rain water. As a result, these areas are particularly vulnerable and the acid and aluminum can accumulate in the soil, streams, or lakes.

**Episodic Acidification:** Melting snow and heavy rain downpours can result in what is known as episodic acidification. Lakes that do not normally have a high level of acidity may temporarily experience effects of acid rain when the melting snow or downpour brings greater amounts of acidic deposition and the soil can't buffer it. This short duration of higher acidity (i.e., lower pH) can result in a short-term stress on the ecosystem where a variety of organisms or species may be injured or killed.

**Nitrogen Pollution:** It's not just the acidity of acid rain that can cause problems. Acid rain also contains nitrogen, and this can have an impact on some ecosystems. For example, nitrogen pollution in our coastal waters is partially responsible for declining fish and shellfish populations in some areas. In addition to agriculture and wastewater, much of the nitrogen produced by human activity that reaches coastal waters comes from the atmosphere.

**On Materials:** Not all acidic deposition is *wet*. Sometimes dust particles can become acidic as well, and this is called *dry deposition*. When acid rain and dry acidic particles fall to earth, the nitric and sulfuric acid that make the particles acidic can land on statues, buildings, and other manmade structures, and damage their surfaces. The acidic particles corrode metal and cause paint and stone to deteriorate more quickly. They also dirty the surfaces of buildings and other structures such as monuments.

The consequences of this damage can be costly:

- damaged materials that need to be repaired or replaced,
- increased maintenance costs, and
- Loss of detail on stone and metal statues, monuments and tombstones.
- Limestone and Marble
  - $\text{CaCO}_{3(s)} + \text{H}_2\text{SO}_{4(aq)} \rightarrow \text{CO}_{2(g)} + \text{H}_2\text{O(l)} + \text{Ca}(\text{NO}_3)_{2(aq)}$
- Metal Corrosion

- Metal + Acid  $\rightarrow$  Salt + Water
- i.e.  $\text{Fe}_{(\text{II})}(\text{s}) + \text{H}_2\text{SO}_{4(\text{aq})} \rightarrow \text{FeSO}_{4(\text{aq})} + 2\text{H}^+$

**Visibility:** In the atmosphere,  $\text{SO}_2$  and  $\text{NO}_x$  gases can be transformed into sulfate and nitrate particles, while some  $\text{NO}_x$  can also react with other pollutants to form ozone. These particles and ozone make the air hazy and difficult to see through. This affects our enjoyment of national parks that we visit for the scenic view such as Shenandoah and the Great Smoky Mountains.

**Human Health:** Walking in acid rain, or even swimming in a lake affected by acid rain, is no more dangerous to humans than walking in normal rain or swimming in non-acidic lakes. However, when the pollutants that cause acid rain — $\text{SO}_2$  and  $\text{NO}_x$ , as well as sulfate and nitrate particles— are in the air, they can be harmful to humans.

$\text{SO}_2$  and  $\text{NO}_x$  react in the atmosphere to form fine sulfate and nitrate particles that people can inhale into their lungs. Many scientific studies have shown a relationship between these particles and effects on heart function, such as heart attacks resulting in death for people with increased heart disease risk, and effects on lung function, such as breathing difficulties for people with asthma.

### **CONTROL MEASURES**

The numbers of possible solutions for acid rain that are available to us are plenty:

1. One of the most fundamental acid rain solutions is to utilize fuels that burn more cleanly, or to burn coal more efficiently. This will greatly reduce the possibilities of acid rain developing in the atmosphere.
2. As far as industrial power plants are concerned, the best solution is to attach devices known as ‘scrubbers’ in the chimneys of these plants. These scrubbers reduce the amount of sulfur produced in the smoke by 90 – 95%.
3. Vehicles and cars must be mandatory required to comply with very tight and efficient emission standards. Fitting catalytic converters into the exhaust pipes of vehicles also reduces the amount of sulfur dioxide produced by the vehicles.
4. For industrial power plants, there are many more acid rain solutions that must be enforced, as they are clearly the biggest contributors to the formation of acidified water droplets in the atmosphere. Industries must regularly inspect and clean all their emission equipment and chimneys and pipes.
5. All these acid rain solutions will be pointless unless people are informed and educated about the ill-effects and harms of acid rain. A widespread and nationwide effort must be made to make people aware. Only after that is done will all the acid rain solutions actually make a difference.

### **CONCLUSION**

Acid rain is one of the biggest environmental hazards that we are facing today, and strong measure must be taken to prevent it, before it is too late. Governments need to sit up and take notice, and do much more than what they are already doing. Acid rain adversely affects plants, animals and human beings, and as a result it is not something that we can afford to ignore. It is our duty towards ourselves and towards our fellow human beings to do all we can to prevent and reduce the presence and increase of acid rain in our environment.

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## SAVE OUR XAVIOUR

Dr. Jyothi P

Associate Professor, PG Department of Chemistry, KAHM Unity Women's College, Manjeri,  
Kerala-676122, India

E-mail: [jyothipuramana@gmail.com](mailto:jyothipuramana@gmail.com)

Now a days, we are very much concerned about the effects of ozone layer and its depletion because of its immense contribution towards sustaining life on our earth. It acts as a shelter for our earth from hazardous radiations from sun. Ozone, by virtue of its chemical properties becomes the Xaviour of all living organisms on our planet. Saving this xaviour is essential for the healthy existence of us and for the coming generations

The breakdown of ozone in the stratosphere results in reduced absorption of ultraviolet radiation. Consequently, unabsorbed and dangerous ultraviolet radiation is able to reach the Earth's surface at a higher intensity. Ozone levels have dropped by a worldwide average of about 4 percent since the late 1970s. For approximately 5 percent of the Earth's surface, around the north and south poles, much larger seasonal declines have been seen, and are described as "ozone holes". The discovery of the annual depletion of

The ozone layer was discovered in 1913 by the French physicists Charles Fabry and Henri Buisson. Measurements of the sun showed that the radiation sent out from its surface and reaching the ground on Earth is usually consistent with the spectrum of a black body with a temperature in the range of 5,500–6,000 K (5,227 to 5,727 °C), except that there was no radiation below a wavelength of about 310 nm at the ultraviolet end of the spectrum. It was deduced that the missing radiation was being absorbed by something in the atmosphere. Eventually the spectrum of the missing radiation was matched to only one known chemical, ozone. Its properties were explored in detail by the British meteorologist G. M. B. Dobson, who developed a simple spectrophotometer (the Dobsonmeter) that could be used to measure stratospheric ozone from the ground. Between 1928 and 1958, Dobson established a worldwide network of ozone monitoring stations, which continue to operate to this day. The "Dobson unit", a convenient measure of the amount of ozone overhead, is named in his honor.

### **WHAT IS OZONE?**

Ozone is an inorganic molecule with the chemical formula  $O_3$ . It has a pale blue colour and has a distinctively pungent smell. It is an allotrope of oxygen that is much less stable than the diatomic allotrope  $O_2$ . It is also termed as Trioxygen by IUPAC. The Molar mass of ozone is 48 g/mol and has a density 2.14 kg/m<sup>3</sup>. its boiling point is -112 °C. Ozone is soluble in

### **WATER, SULFURIC ACID, CARBON TETRACHLORIDE**

The ozone layer or ozone shield is a region of Earth's stratosphere that absorbs most of the Sun's ultraviolet radiation. It contains high concentration of ozone ( $O_3$ ) in relation to other parts of the atmosphere, although still small in relation to other gases in the stratosphere. The ozone layer contains less than 10 parts per million of ozone, while the average ozone concentration in Earth's atmosphere as a whole is about 0.3 parts per million. The ozone layer is mainly found in the lower portion of the stratosphere, from approximately



15 to 35 kilometers (9.3 to 21.7 mi) above Earth, although its thickness varies seasonally and geographically.

When chlorine and bromine atoms come into contact with ozone in the stratosphere, they destroy ozone molecules. Ozone depleting substances, that release chlorine include chlorofluorocarbons (CFCs). Since they are not destroyed in the lower atmosphere, CFCs drift into the upper atmosphere.

### **ACTION OF OZONE**

The ozone layer absorbs 97 to 99 percent of the Sun's medium-frequency ultraviolet light (from about 200 nm to 315 nm wavelength), which otherwise would potentially damage exposed life forms near the surface. In 1976, atmospheric research revealed that the ozone layer was being depleted by chemicals released by industry, mainly chlorofluorocarbons (CFCs). Concerns that increased UV radiation due to ozone depletion threatened life on Earth, including increased skin cancer in humans and other ecological problems, led to bans on the chemicals, and the latest evidence is that ozone depletion has slowed or stopped.

The United Nations General Assembly has designated September 16 as the International Day for the Preservation of the Ozone Layer. The photochemical mechanisms that give rise to the ozone layer were discovered by the British physicist Sydney Chapman in 1930. Ozone in the Earth's stratosphere is created by ultraviolet light striking ordinary oxygen molecules containing two oxygen atoms ( $O_2$ ), splitting them into individual oxygen atoms (atomic oxygen); the atomic oxygen then combines with unbroken  $O_2$  to create ozone,  $O_3$ . The ozone molecule is unstable (although, in the stratosphere, long-lived) and when ultraviolet light hits ozone it splits into a molecule of  $O_2$  and an individual atom of oxygen, a continuing process called the ozone-oxygen cycle. Chemically, this can be described as:



About 90 percent of the ozone in the atmosphere is contained in the stratosphere. Ozone concentrations are greatest between about 20 and 40 kilometres (66,000 and 131,000 ft), where they range from about 2 to 8 parts per million. If all of the ozone were compressed to the pressure of the air at sea level, it would be only 3 millimetres ( $\frac{1}{8}$  inch) thick.

Although the concentration of the ozone in the ozone layer is very small, it is vitally important to life because it absorbs biologically harmful ultraviolet (UV) radiation coming from the sun. Extremely short or vacuum UV (10–100 nm) is screened out by nitrogen. UV radiation capable of penetrating nitrogen is divided into three categories, based on its wavelength; these are referred to as UV-A (400–315 nm), UV-B (315–280 nm), and UV-C (280–100 nm).

UV-C, which is very harmful to all living things, is entirely screened out by a combination of dioxygen (< 200 nm) and ozone (> about 200 nm) by around 35 kilometres (115,000 ft) altitude. UV-B radiation can be harmful to the skin and is the main cause of sunburn; excessive exposure can also cause cataracts, immune system suppression, and genetic damage, resulting in problems such as skin cancer. The ozone layer (which absorbs from about 200 nm to 310 nm with a maximal absorption at about 250 nm) is very effective at screening out UV-B; for radiation with a wavelength of 290 nm, the intensity at the top of the atmosphere is 350 million times stronger than at the Earth's surface. Nevertheless, some UV-B, particularly at its longest wavelengths, reaches the surface, and is important for the skin's production of vitamin D.

Ozone is transparent to most UV-A, so most of this longer-wavelength UV radiation reaches the surface, and it constitutes most of the UV reaching the Earth. This type of UV radiation is significantly less harmful to DNA, although it may still potentially cause physical damage, premature aging of the skin, indirect genetic damage, and skin cancer.<sup>[8]</sup>

The thickness of the ozone layer varies worldwide and is generally thinner near the equator and thicker near the poles. Thickness refers to how much ozone is in a column over a given area and varies from season to season. The reasons for these variations are due to atmospheric circulation patterns and solar intensity.

The majority of ozone is produced over the tropics and is transported towards the poles by stratospheric wind patterns. In the northern hemisphere these patterns, known as the Brewer-Dobson circulation, make the ozone layer thickest in the spring and thinnest in the fall. When ozone is produced by solar UV radiation in the tropics, it is done so by circulation lifting ozone-poor air out of the troposphere and into the stratosphere where the sun photolyzes oxygen molecules and turns them into ozone. Then, the ozone-rich air is carried to higher latitudes and drops into lower layers of the atmosphere.

Research has found that the ozone levels in the United States are highest in the spring months of April and May and lowest in October. While the total amount of ozone increases moving from the tropics to higher latitudes, the concentrations are greater in high northern latitudes than in high southern latitudes, due to the ozone hole phenomenon. The highest amounts of ozone are found over the Arctic during the spring months of March and April, but the Antarctic has their lowest amounts of ozone during their summer months of September and October.

### **DEPLETION OF OZONE LAYER**

The ozone layer can be depleted by free radical catalysts, including nitric oxide (NO), nitrous oxide (N<sub>2</sub>O), hydroxyl (OH), atomic chlorine (Cl), and atomic bromine (Br). While there are natural sources for all of these species, the concentrations of chlorine and bromine increased markedly in recent decades because of the release of large quantities of man-made organohalogen compounds, especially chlorofluorocarbons (CFCs) and bromofluorocarbons. These highly stable compounds are capable of surviving the rise to the stratosphere, where Cl and Br radicals are liberated by the action of ultraviolet light. Each radical is then free to initiate and catalyze a chain reaction capable of breaking down over 100,000 ozone molecules. By 2009, nitrous oxide was the largest ozone-depleting substance (ODS) emitted through human activities. One above the Antarctic was first announced by Joe Farman, Brian Gardiner and Jonathan Shanklin, in a paper which appeared in *Nature* on May 16, 1985.

Ozone is an unstable compound and decomposes at about 573K to form oxygen. When UV radiation reaches ozone layer, ozone molecules present at the layer absorb its energy and decompose to form oxygen which is more stable than ozone. One ozone molecule decomposes to form one oxygen atom and a normal oxygen molecule. Hence the energy of UV radiation is absorbed in ozone layer even before reaching earth's surface. That's how ozone layer protects us from UV radiation.

Now, this does not deplete ozone layer since reverse reaction can also take place. That is, high energy UV radiation hits oxygen molecules and each decompose into two free oxygen atoms. Each oxygen atom combines with one oxygen molecule each and forms ozone molecules.

UV light creates ozone at wavelengths less than ~240 nm. While UV light from ~240 - 315 destroys ozone. In the process of creating and destroying ozone the UV light is absorbed in those wavelengths. The most severe case of ozone depletion was first documented in 1985

in a paper by British Antarctic Survey (BAS) scientists Joseph C. Farman, Brian G. Gardiner, and Jonathan D. Shanklin. Beginning in the late 1970s, a large and rapid decrease in total ozone, often by more than 60 percent relative to the global average, has been observed in the springtime (September to November) over Antarctica. Farman and his colleagues first documented this phenomenon over their BAS station at Halley Bay, Antarctica. Their analyses attracted the attention of the scientific community, which found that these decreases in the total ozone column were greater than 50 percent compared with historical values observed by both ground-based and satellite techniques. As a result of the Farman paper, a number of hypotheses arose that attempted to explain the Antarctic "ozone hole." It was initially proposed that the ozone decrease might be explained by the chlorine catalytic cycle, in which single chlorine atoms and their compounds strip single oxygen atoms from ozone molecules. Since more ozone loss occurred than could be explained by the supply of reactive chlorine available in the polar regions by known processes at that time, other hypotheses arose. A special measurement campaign conducted by the National Aeronautics and Space Administration (NASA) and the National Oceanic and Atmospheric Administration (NOAA) in 1987, as well as later measurements, proved that chlorine and bromine chemistry were indeed responsible for the ozone hole, but for another reason: the hole appeared to be the product of chemical reactions occurring on particles that make up polar stratospheric clouds (PSCs) in the lower stratosphere.

### **MEASURES TO REDUCE OZONE DEPLETION**

Avoid the consumption of gases dangerous to the ozone layer, due to their content or manufacturing process. Some of the most dangerous gases are CFCs (chlorofluorocarbons), halogenated hydrocarbon, methyl bromide and nitrous oxide.

Minimize the use of cars. The best transport option is urban, bicycle, or walking. If you use a car to a destination, try to carpool with others to decrease the use of cars in order to pollute less and save.

Do not use cleaning products that are harmful to the environment and to us. Many cleaning products contain solvents and substances corrosive, but you can replace these dangerous substances with non-toxic products such as vinegar or bicarbonate.

Buy local products. In this way, you not only get fresh products but you avoid consuming food that has traveled long distances. As the more distance traveled, the more nitrous oxide is produced due to the medium used to transport that product.

Maintain air conditioners, as their malfunctions cause CFC to escape into the atmosphere.

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## PHASE TRANSFER CATALYSIS IN ENVIRONMENTAL ANALYSIS

Dr. Bijudas K\* and Mrs. Bashpa P

Assistant Professors, Department of Chemistry, N. S. S. College, Manjeri, Kerala-676122,  
India

\*E-mail: [bjudask@gmail.com](mailto:bjudask@gmail.com)

### PHASE TRANSFER CATALYSIS

The introduction of phase transfer catalysts (PT catalysts) about fifty decades ago has revolutionised organic synthesis in respect of anion dissolution in non-polar solvents coupled with their ability to catalyse the reactions. The choice of phase transfer catalysts helped in the synthesis of many organic materials in a big way, especially related to pharmaceuticals and fine chemicals. This unique ability to catalyse certain reactions selectively has many advantages in synthetic processes. The fact that these materials in the form of quaternary ammonium or phosphonium salts have many advantages compared to the classical phase transfer catalysts, viz the crown ethers: which are toxic, costly and relatively difficult to prepare.

Phase transfer catalysis (PTC) is a technique which can be used to carry out a variety of chemical reactions under mild conditions with improved results. PTC technique is now utilized in many applications, from research in chemistry to full-scale synthetic production of chemicals like pharmaceuticals, fine chemicals, polymers, dyes etc. It is also of great importance to develop technological methods to minimize problems related to environmental pollution. PTC technique is used in pollution prevention, pollution treatment and removal or destruction of impurities in waste and product streams. Cost reduction and pollution prevention are the two most powerful driving forces in the chemical industry today, and these can be achieved to a great extent by the phase transfer catalysis technique, if properly adopted.

The technique of phase transfer catalysis has been in use for the commercial manufacture of chemicals worth \$ 10 billion or more per year. The scope of PTC technology is most appropriately understood by considering a range of reactions for which PTC is made applicable. The 1800 patents and the nearly 9000 publications on PTC fall into 30 or so major reaction categories, most of which are used in the production of monomers, polymers, agricultural chemicals, pharmaceuticals, additives, flavours and fragrances, dyes, explosives, surfactants, petrochemicals, rubber and wide range of other products related to fine organic chemicals.

### NATURE OF PHASE TRANSFER CATALYSIS

The phase transfer catalyst is a vehicle and it transfers anionic reactants into non-polar media and the transferred anions make the reaction to take place with ease. This is quite significant when we see that reactions between substrate located in an organic phase and reactant located in the aqueous phase are slow and ineffective.

The simple approach used earlier to accelerate rates of reactions of a two-phase process (aqueous phase-organic phase) was to effect rapid stirring, so as to increase interaction between the reactants. A different approach was to employ a dipolar aprotic solvent such as dimethyl sulphoxide (DMSO), dimethylformamide (DMF), acetonitrile,

hexamethylphosphoramide (HMPA) etc. which are effective in liberating reactive anions by solvating cations. These solvents ensure mutual miscibility and solubility of both ionic salts and organic substrates and help to increase the rate of reaction. They solvate cationic part of the salt leaving the anion in a relatively 'bare' or desolvated situation. However, there are considerable practical disadvantages connected with the use of these solvents. The drawbacks of using these solvents are that they are costly, difficult to purify, and toxic in nature. Moreover, it is difficult to keep such solvents in anhydrous state and difficult to recover.

Phase transfer catalysis can easily overcome the problems in such situations. This technique has been shown to enhance the reactivity in different types of reactions. The method involves transfer of anions from the polar medium into the non-polar organic media in the form of an ion-pair with the cationic moiety of the catalyst with appropriate size and lipophilicity. The anions thus transferred and poorly solvated in the organic media exhibit greater reactivity. This enables the substrate to react faster in the non-polar media in the presence of PT catalyst.

The commonly used phase transfer catalysts are quaternary ammonium or phosphonium salts (generally known as quaternary onium salts). Compounds like n-alkyl phosphoramides (particularly n-dodecyl orn-hexadecyl), methylene bridged phosphorous and sulphur oxides, tris[2-(2-methoxyethoxy) ethyl] amine (TDA-1) are also used as phase transfer catalysts. The classical phase transfer catalysts are the crown ethers, cryptates etc. when used in catalytic quantities can act as phase transfer materials. Polyethylene glycols, otherwise known as poor chemist's crown also has the properties, though to a much lower extent as PT catalysts.

The advantages of PTC over the conventional methods are as follows.

- Use of expensive and toxic anhydrous dipolar aprotic solvents can be avoided.
- High reactivity and selectivity of the species ensured.
- Elimination of dangerous, inconvenient and expensive reactants such as NaH, NaNH<sub>2</sub>, t-BuOK, R<sub>2</sub>NLi etc. can be done and NaOH, KOH, K<sub>2</sub>CO<sub>3</sub> etc. can be used.
- Synthetically easier to work up as the reaction requires lower temperature.
- Activation energies are considerably reduced.
- Ensure high yield of the desired product and minimise industrial waste.

The simplicity of the procedure, the increased reaction rates, high yield of the product and the comparatively low cost of the process make PTC a pervasive and widely accepted technique in the chemical industry. The PTC technique has been found to be applicable to a variety of reactions like nucleophilic substitution, elimination, carbene reactions, esterification, etherification, alkylation, condensation, addition, polymerization, isomerisation, hydrolysis, oxidation-reduction etc.

### **BRIEF HISTORY OF PHASE TRANSFER CATALYSIS**

The technique of phase transfer catalysis, a convenient synthetic method has originated only in the later part of the last century. The foundations of the technique were laid by M. Makosza, C.M. Starks and A. Brandstrom in the mid 1960's.

Makosza and coworkers in 1965 initiated a systematic exploration of alkylations and subsequently of other reactions in two phase systems containing mainly concentrated aqueous

alkali metal hydroxides. The descriptive term they originally used were 'catalytic two-phase reactions', 'catalytic alkylation of anions' and 'catalytic generation of carbenes'.

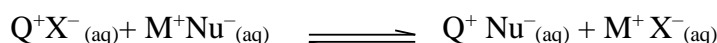
Simultaneously Charles M. Starks took patents on 'catalysis of heterogeneous reactions. Starks has introduced the term 'phase transfer catalysis' for the first time. Furthermore, he gave a mechanistic concept unifying the different reactions under PTC. This provided an enormous impetus to the development of this technique.

At the same time A. Brandstrom developed a process called 'ion-pair extraction' and this method logically leads to PTC technique. The ion-pair extraction method is used to extract anions from an aqueous layer into non-polar organic solvents like chloroform or methylene chloride. Most of the anions can be extracted as ion-pairs into the organic phase, with quaternary ammonium as cationic part. The ion-pairs have a tendency to associate in the organic phase and hence to overcome the unfavourable extraction barriers.

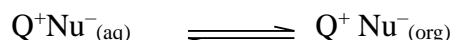
Another piece of work related to phase transfer catalysis is that of Gibson and Hosking. They showed that triphenylmethylarsonium permanganate can be prepared, isolated and dissolved in chloroform, where it can act as an excellent oxidising agent.

### **PRINCIPLE OF PHASE TRANSFER CATALYSIS**

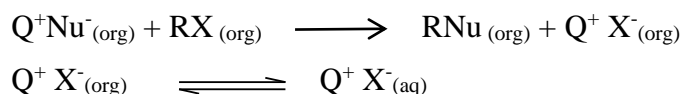
The working of phase transfer catalysis involving quaternary onium salts is based on the formation of certain equilibria. Usually PT catalysts are soluble in water as well as in non-polar media. However, most of the organic substrates dissolve only in organic solvents. When a solution of the reactant inorganic anion is mixed with a solution of the organic substrate in organic medium, they form two phases. The aqueous phase is a reservoir of the nucleophile and the organic phase contains the substrate. Since the anionic aqueous phase is immiscible with the substrate containing organic phase, there will be practically no reaction in the absence of any interfacial phenomena. In such circumstances if a small amount of quaternary ammonium or phosphonium halide or bisulphate, which contains a lipophilic cation is added to the heterogeneous two-phase system, rapid reaction takes place. Since the lipophilic cation enjoys solubility both in aqueous and in organic phases, it exchanges its anion with the excess of anion in the aqueous salt solution and bring it for reaction in the organic phase. The quaternary ion is often called as 'quat' and is represented by the symbol 'Q'. The exchange of anion is an equilibrium process as shown in equation below.



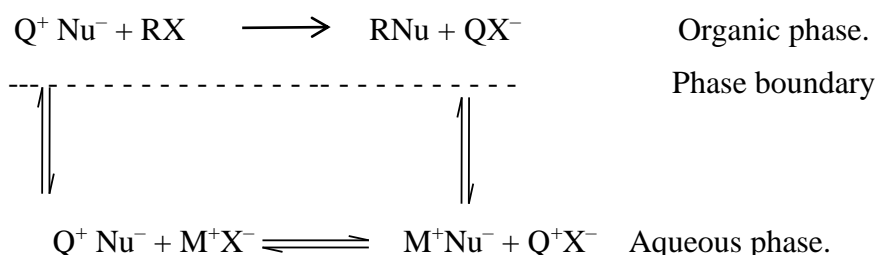
The anion paired with  $Q^+$  is transferred into the organic phase. A second equilibrium termed phase transfer equilibrium then follows and is shown below.



Once the nucleophile or base (represented by Nu) is in non-polar organic media, the reaction (equation 1.3) takes place leading to product formation. In the case of a nucleophilic substitution reaction,  $Q^+$  would ultimately be paired with the nucleophile, thus generating the  $Q^+X^-$ , which is subjected to further equilibrium as shown in equation below



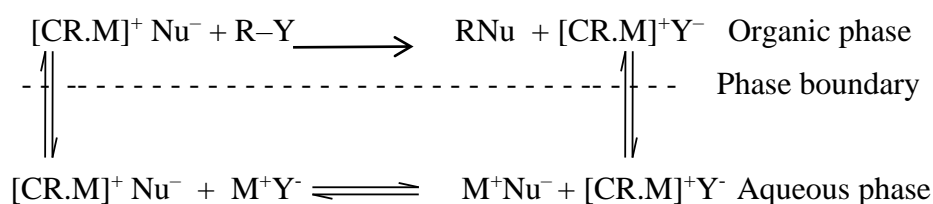
These equilibria and consequent chemical process have been shown by Starks in a classic diagram of phase transfer catalytic cycle shown in scheme below and is known after him.



### Stark's phase transfer catalytic cycle

It is not necessary that the ion pair,  $\text{Q}^+\text{X}^-$ , generated in the organic phase be identical to that of originally added as PT catalyst. It is only necessary that lipophilic cation,  $\text{Q}^+$  should be present in solution and whatever be the  $\text{X}^-$ , it must be exchangeable with Nu.

Crown ethers also act in a similar manner to act as phase transfer agents. However, the mode of action is different. They envelop the cation and make it larger, softer and more soluble in the organic phase. The phase transfer cycle using a crown ether can be represented in scheme below in which CR represents the crown.



### Phase transfer catalytic cycle with crown ethers

It is clear that, the onium cation replaces the cation added to the reaction mixture with the nucleophilic salt whereas the crown simply complexes with the cation. In either case, a positively charged hydrophobic species is solvated by a non-polar solvent. This cation,  $\text{Q}^+$  or  $[\text{CR.M}]^+$  provides the anion only weak stabilising interactions and the anion is therefore more nucleophilic than it would be in water or in alcohol. These anions are known as 'naked' anions or 'bare' anions.

There are two basic requirements for a substance to act as a PT catalyst. The catalyst must be able to transfer one of the reactants from its normal phase into the normal phase of the other reactant and the transferred reagent in the new phase must be available in a highly active form. In order to fulfil these requirements, at first, the PT catalyst must be cationic and must have enough organic structure so that the catalyst can be substantially partitioned into the organic phase with the desired anion. Secondly the effective cation-anion binding must be 'loose' enough to allow high anion reactivity. In addition to the above essential requirements, additional parameters like stability of the catalyst under the reaction conditions, availability of the catalyst, cost, ease of removal or recovery and selectivity in catalytic activity etc. are to be considered.

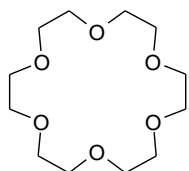
### QUATERNARY SALTS AS PT CATALYSTS

Numerous quaternary ammonium, phosphonium, antimonium, bismathonium and tertiary sulphonium salts have been claimed to be PT catalysts. However, in practice only a limited number of ammonium and phosphonium salts are widely being used. This is based on some factors involved in their anion transfer ability, reactivity, stability etc. The simple notation,  $\text{R}_4\text{N}^+\text{X}^-$  and  $\text{R}_4\text{P}^+\text{X}^-$  are used for ammonium and phosphonium salts respectively.

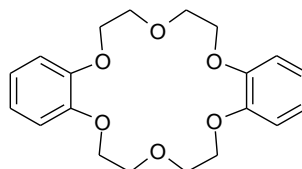
## **CROWN ETHERS AS PT CATALYSTS**

Crown ethers (macrocyclic ethers) are large heterocyclic ring compounds having several oxygen atoms usually in a regular pattern. They have the property of forming complexes with a variety of cationic substrates, like alkali metal cations, alkaline earth cations or ammonium ions and can dissolve homogeneously in an organic solvent. The cavity in the crown ether can accommodate an alkali metal cation through the ion-dipole interaction to form an alkali cation-crown ether complex with a counter ion.

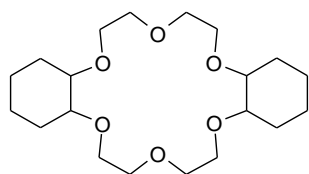
The common commercially available crown ethers are 18-crown-6, dibenzo-18-crown-6, dicyclohexano-18-crown-6 and 15-crown-5.



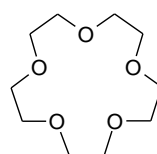
18-crown-6



Dibenzo-18-crown-6



Dicyclohexano-18-crown-6



15-crown-5

Using the simple 'lock and key' approach, it is evident that 18-crown-6 has cavity dimension of the same magnitude as that of  $K^+$  ion, while the 15-crown-5 has cavity size suited for the ionic diameter of  $Na^+$  ion. Therefore, in principle a particular crown should be more specific for a particular metal ion than the others.

Crown ethers are recovered by washing the reaction mixture repeatedly with an acidified saturated KCl solution. This solution is evaporated and the solid residue is extracted with methylene chloride, dried with anhydrous  $MgSO_4$  and evaporated. The resulting solid is recrystallised from acetonitrile to remove KCl.

The crown ethers and the quaternary ammonium salts have many similarities in activity as phase transfer catalysts. However, the high cost, high toxicity and difficulty in preparation are some of the factors against crown ethers for their choice as PT catalysts.

## **POLLUTION PREVENTION USING PHASE TRANSFER CATALYSIS**

Phase-transfer catalysis is an extremely effective technology for improving environmental standards through pollution prevention, green chemistry and pollution treatment. PTC technology can help to meet ever tightening environmental goals. Phase-transfer catalysis excels at reducing the cost of manufacture of organic chemicals, many of the benefits of PTC have very direct and compelling impact on pollution prevention and green chemistry. Four of the many pollution prevention benefits of PTC include increasing yield, reducing excess reactants, conducting reactions under solvent-free PTC conditions and dramatically reducing reaction temperature. These benefits of PTC can often be absolutely crucial to reducing BOD, COD, TDS, air emissions and other forms of pollution.



## **EXAMPLES OF PTC IN POLLUTION PREVENTION**

### **1. DMSO cyanation Vs PTC cyanation**

One of the classical examples that illustrate the ability of phase-transfer catalysis to reduce non-product output is the replacement of a DMSO cyanation process with a PTC-toluene cyanation process. Dimethyl sulfoxide was originally chosen as the solvent due to its outstanding ability to co-dissolve and react inorganic sodium cyanide and an organic benzyl chloride derivative. One major problem with the DMSO process is that the workup requires multiple and lengthy aqueous washes to separate the DMSO from the product. These washes not only create large volumes of aqueous waste, but the wastewater contains much DMSO (affects COD/BOD), entrains organic product due to the presence of DMSO (results yield loss & non-product output) and contains the excess cyanide from the reaction (TDS and major safety hazard that combines highly toxic cyanide with the effective skin penetrating DMSO solvent). Moreover, the DMSO procedure reported using a 70 mole % excess of sodium cyanide and afforded only 81% isolated yield. Clearly, there were multiple reasons to improve upon the DMSO process.

When the DMSO cyanation process was replaced with a PTC-toluene cyanation process, the following compelling environmental advantages were achieved:

1. 85 % less aqueous waste!
2. 19 % higher isolated yield which in addition to the major cost advantage means that all that organic material becomes product instead of non-product output!
3. 95 % reduction of cyanide waste (70 mole % excess reduced to 2 mole % excess), which has huge impact on COD/BOD and nitrogen content!
4. The totally non-recoverable DMSO solvent (non-product output) with its huge cyanide load in the large volume of waste water was eliminated! In contrast, the toluene in the PTC process was used in the next step of the process and was fully recoverable.

Other polar aprotic solvents: While we are on the subject of nucleophilic substitutions performed in high boiling polar aprotic solvents, we should note that DMF (dimethyl formamide), NMP (N-methylpyrrolidinone) and DMAc (dimethyl acetamide) are likely to suffer from similar waste characteristics as DMSO. These solvents are almost always preferentially replaced by PTC conditions. PTC generates much less waste achieving higher yield with much lower excess of nucleophile and uses easily recoverable solvents.

Pollution prevention benefits: major reductions in wastewater volume, BOD/COD, TDS, TKN, sulphur and cyanide

### **2. Polycarbonate**

Polycarbonate is one of the largest volume commercial phase-transfer catalysis processes. Since the global capacity of polycarbonate is more than 1 million tons/year, even small improvements in the efficiency of raw material usage can have a huge positive impact on environmental performance. GE Plastics (now SABIC Innovative Plastics) patented a PTC process that significantly reduces the excess of one of the highly hazardous raw materials which results in greatly reduced air and water emissions as well as cost savings.

Polycarbonate is produced by the phosgenation of bisphenol A in the presence of base (to form the nucleophilic phenoxide). Prior to the use of PTC, triethylamine was used as the catalyst to activate the carbon-chlorine bond of phosgene and the chloroformate intermediate

toward the nucleophilic attack of the phenoxide. However, that activation also promotes hydrolysis of these water sensitive compounds. To quote from the patent, “in a phosgene hydrolysis rate study, it was found that at a triethylamine concentration of  $6.64 \times 10^{-3}$  M, triethylamine affected phosgene hydrolysis at a relative rate of greater than 200 compared to a reference value of 1 without catalyst.”

The GE patent describes a PTC procedure which avoids the use of triethylamine as the catalyst. This in turn dramatically reduces hydrolysis to the point that the process impressively uses only 1 mole% excess of phosgene to achieve the desired yield, molecular weight and other polycarbonate properties. This represents a reduction of the excess phosgene by at least 90% relative to the procedures using triethylamine described in previous patents. The reduced levels of phosgene and chloroformate hydrolysis result in much lower waste load in wastewater and air emissions and greatly enhanced safety.

The conclusion is that it is possible to achieve extremely significant improvements in phosgene utilization by retrofitting the non-PTC process with PTC and avoiding hydrolysis of the water sensitive compounds. This represents breakthrough performance from environmental, safety and cost standpoints.

Pollution prevention benefits: major reductions of excess phosgene usage, resulting byproducts and TDS

### 3. p-nitrophenetole

p-nitrophenetole is an intermediate for dyes and other compounds of industrial importance. Prior to PTC, a British patent reported an attractive 90% yield for p-nitrophenetol produced by the reaction of p-chloronitrobenzene with ethanol in the presence of sodium hydroxide. However, the other 10% was the undesirable byproduct 4,4'-dichloroazoxybenzene. Separation of this chlorinated azoxybenzene not only requires much expenditure but it constitutes an environmentally undesirable non-product output. Furthermore, the purity of the p-nitrophenetole is insufficient for most application fields, especially that of dyestuff intermediates. So, there are multiple strong driving forces to improve this process that include pollution prevention, cost reduction and product quality improvement.

A PTC process reported in a patent uses an inexpensive phase-transfer catalyst and achieves a 95% isolated yield with impurity levels of under 0.1% for 4,4'-dichloroazoxybenzene, p-chloronitrobenzene, 4,4'-diethoxy-azoxybenzene and p-nitrophenol.

In summary, this patent describes the use of phase-transfer catalysis to avoid the formation of hazardous and corrosive chlorinated aromatic waste while increasing yield and quality of the product.

### 4. Transesterification

Pollution prevention benefits: Major reduction in fuel to heat large volumes of reactant.

The production of 50,000 tons/year of monoglycerides and diglycerides for use as emulsifiers is performed at a temperature of about 250° C. The reaction is a base-catalyzed transesterification that requires such a high temperature for two reasons: to partially solubilize polar glycerol in nonpolar triglyceride (vegetable oil) and to promote the reaction of the hydrogen-bonded hydroxyls of glycerol with the ester functional group. The amount of energy required to heat 50,000 tons to 250° C is obviously great.

Halpern et al of PTC Organics patented a phase-transfer catalysis process that reduces the reaction temperature by 150° C to only 100° C! This represents huge savings in fuel which in

turn reduces greenhouse gas generation. The concept is based on the ability of PTC to transfer small amounts of the glycerol monoanion into the organic phase where there is no hydrogen bonding that could reduce the nucleophilicity of the glycerol monoanion. In fact, the reaction actually proceeds at 60° C. Veterans in this field find this to be remarkable.

One lesson from this patent is that there are many potential applications waiting to be discovered that can use phase-transfer catalysis to reduce the temperature of high-temperature non-PTC reactions. The greatest environmental benefit is saving on burning of fuel, but there are also usually concurrent benefits for reducing reaction temperature by 200-150° C such as better selectivity, better colour and reduced pressure.

Pollution prevention benefits: major reductions in chlorinated aromatic waste & TKN

### **5. Use of PTC for Converting waste anion into useful product**

The previous examples illustrated the use of PTC for pollution prevention. Sometimes, it is difficult or impossible to avoid the generation of waste anions. In many of these cases, it is possible to leverage the strengths of PTC to simultaneously extract and react waste anions from an aqueous stream and produce value added products that can be sold at a profit while cleaning up the waste stream. Sometimes this is called reactive separation.

Joyce, Bielski and Halpern of Value Recovery (formerly PTC Value Recovery Inc.) patented a phase-transfer catalysis process which extracts waste anions from dilute aqueous waste streams and reacts them with a variety of alkyl halides or acyl halides to produce saleable product. The many examples described in the patent include effective reactive separation for many problematic waste anions including cyanide, phenoxide, acrylate, iodide, sulphide and others.

Environmental benefits: major reduction of waste organic and inorganic anions in aqueous waste streams

### **CONCLUSION**

There are hundreds of examples of the use of phase-transfer catalysis that achieve pollution prevention, green chemistry and pollution treatment. There are hundreds more potential applications that are waiting to be identified and developed by the creative and technically competent readers of this article. So, the question is how can you identify opportunities at your company to use PTC technology to achieve breakthrough improvements in environmental performance and maybe even save your production plant from closure due to non-compliance. The following section will provide some easy guidelines for identifying pollution prevention opportunities using phase-transfer catalysis.

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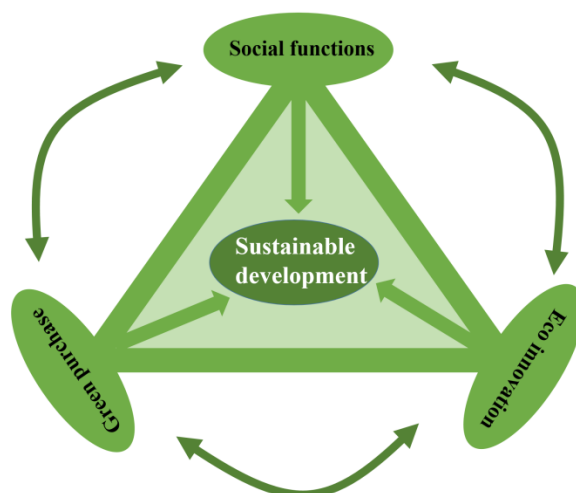
## GREEN CONSUMERISM: A CALL FOR SOCIAL CONSCIOUSNESS

Dr. Yamuna Kunhi Mouvenchery

*Assistant Professor, Department of Chemistry, N. S. S. College, Manjeri, Kerala-676122, India*

*E-mail: [shyamayamuna@gmail.com](mailto:shyamayamuna@gmail.com)*

The tremendously increasing consumption of goods and services across the world leads to massive depletion of natural resources and serious damage to the environment. Global warming, floral and faunal declination and increased level of environmental pollution are among the serious consequences. It is in this context that the idea of 'sustainable development' emerged. The idea was first put forth by the Brundtland Commission of the United Nations in 1987, as 'development that meets the needs of the present without compromising the ability of future generations to meet their own needs. The concept encourages sustainability through minimisation of environmental and social impacts, aiming at long term economic growth and consistency in environmental as well as social needs. The most important aspects of sustainable development are social and economic development within the carrying capacity of ecosystems, de-linking economic growth from resource use and environmental degradation, improved efficiency and sustainability in the use of resources and production processes and reduced resource degradation, pollution and waste. In short, social needs and environmental needs are the two faces of the coin: sustainable development targets social needs, but without compromising on environmental needs. Thus, a trilateral relationship exists between the three: sustainable development, social needs and environmental needs. This article focuses mainly on the environmental aspects of sustainability.



Environmental sustainability stands on the feet of sustainable production and sustainable consumption, ensured through eco innovation and green consumption, respectively. Eco innovation focuses on incorporating environmental sustainability practices at every stage of creation of goods and services. Green consumption, on the other hand, is normally related to environmentally responsible consumption where consumers consider the environmental impact of purchasing, using, and disposing of various products, or using various green services.

## **ECO INNOVATION**

The term comprises development of new ideas, behaviour, products and processes that contribute to reduction in environmental burden or to ecologically specified sustainability targets. *Hines and Marin* point out that most innovation appears to build on ‘repurposing, improving or renewing existing ideas and practices’. This encompasses innovation in technological, social and institutional aspects. Mainly five cases of innovations are addressed while talking about ecological/environmental sustainability. They are, (1) the introduction of a new good, (2) the introduction of a new method of production, (3) the opening of a new market, (4) the seek for a new source of raw materials and (5) the carrying out of new organisation of any industry.

Innovation in any of such cases leads to green product – one which satisfies consumers’ needs without damaging the environment and contributes towards a more sustainable system. These products are environmentally superior and have low environmental impact. Green products use materials safer to the environment, are recyclable and require less packaging. Organic products, energy efficient light-bulbs, eco-friendly washing machine, etc., are among the green products. The following features define a product ‘green’: products those are originally grown, products those are recyclable, reusable and/or biodegradable, products with natural ingredients, products containing recycled contents and non-toxic chemical, products that do not harm or pollute the environment, products that will not be tested on animals, products that are manufactured and marketed in environmentally conscious way and have eco-friendly packaging (i.e. reusable, refillable containers etc.). The following functions define a product ‘green’: conservation of water and energy, prevention of contributions to air, water and land pollution, protection of indoor air quality, using of renewable, responsibly sourced materials, contributing little environmental impact. Other than green manufacturing, green marketing (packaging, transportation and advertising) contribute to the greenness of a product.

## **GREEN CONSUMPTION**

The sustainability practice at both the stages of production and consumption can be ensured by the consumers. Green consumption refers to the purchase of environmentally friendly products and avoiding products that harm the environment. Green purchase intention, i.e., willingness to purchase green products, is a complex form of ethical decision-making behaviour reflecting socially responsibility. Being socially responsible, the green consumer “takes into account the public consequences of private consumption and attempts to use his or her purchasing power to bring about social change”. Nevertheless, the environmental awareness of the consumer is not fully translated into action, leading to attitude-behaviour gap.

## **ATTITUDE-BEHAVIOUR GAP**

It has been reported that although consumers’ attitude towards environmental protection and willingness to purchase green products has increased dramatically in recent years, on the global scale, it is reflected in purchasing only to a nominal extent. The global market share of green products is below 3% of the entire market. A 2007 study shows that 67% of the consumers expressed interest towards organic food products, but only 4% actually purchased them. This is indicative of that consumer decisions are only weakly influenced by environmental considerations and there exists a discrepancy between attitude and behaviour. That is, environmental impacts of consumer decisions are largely overlooked and the positive attitude is not translated into action, except for rare exceptions. This discrepancy between the

consumer's positive attitude towards the environment and actual purchasing behaviour is termed 'attitude-behaviour gap'.

A number of factors were identified to be responsible for the attitude-behaviour gap, including price, availability, social influences, etc. *Joshi and Rahman*, based on a thorough literature review, classified the determinants of green purchase behaviour into individual factors (emotions, habits, perceived consumer effectiveness, perceived behavioural control, values and personal norms, trust, knowledge) and situational factors (price, availability, product attribute and quality, store-related attributes, brand image, eco-labelling and certification). These factors are largely discussed in literatures. However, one important social aspect that needs special attention, but remain almost unattended is the discrepancy between the knowledge level/education status of the consumer and his/her attitude, the knowledge-attitude gap.

### **THE KNOWLEDGE-ATTITUDE GAP**

The most extensively studied determinant for consumer behaviour is consumer knowledge. It is important to note that knowledge level of the consumer does not always reflect in their choice of products. In a literature review, 28% of the reviewed literature showed no correlation between environmental knowledge and green purchase intention of the consumer. Even though individuals are aware of environmental issues, need for environmental protection and impact of their purchase on the environment, this awareness or knowledge is not always reflected in consumer-attitude. Even well-learned consumers and those having highest level of environmental consciousness do not always purchase green. This is especially relevant for under-developed and developing countries, including India. People are aware of the consequences of pollution, ozone depletion, climate change, etc. and it is found that the awareness increases recently among Indians, especially youth. But the awareness is not seriously reflected in the attitude and behaviour.

One reason could be the inappropriate knowledge. It is expected that the level of environmental knowledge mediates the relationship between green attitude and environmental behaviour. Therefore, increased consumer knowledge might strengthen consumers' trust in green products and reinforce the attitude-behaviour relationship. One possible explanation for this may be that only a basic understanding of ecological and social problems might not be enough to motivate consumers towards adopting sustainable consumption practices. A deeper understanding of the consequences of irresponsible consumption might prove to be more effective in making the consumer shift towards green consumption.

Secondly, subjective/social norms can influence individual's behaviour as they may exert pressure on an individual to act in a certain way. Thus social norms and attitude of reference group may contribute significantly to the knowledge-attitude gap. It is interesting to note that this dependence is strongly influenced by the societal standards: social norms influence green purchase behaviour positively in developed Western countries while a negative influence can be observed in developing- and under-developed countries. Strong environmental and social values motivate consumers for green purchase, decreasing the gap between knowledge and attitude and between attitude and behaviour, as observed in developed Western countries. To them, 'going green' appears to be a fashion and consumers engage in green issues. However, studies on relationship between social norms and consumer attitude revealed mixed results, in the Indian context, possibly due to the highly heterogeneous and complex nature of Indian societal and cultural arena. As for many other

social parameters, a generalisation across the entire India may not be possible, in case of environmental awareness and attitude-behaviour relationship.

To an average middle-class Indian, the choice of costumes, cosmetics, automobiles, construction, among others, are counted as indicators of individual's societal value. People opt for synthetic clothing materials instead of more climate-friendly cotton and private vehicles instead of public transport available in plenty; use cosmetics which impart serious (and mostly unknown) environmental impact to show up 'fair', although the Indian ethnicity basically is for coloured skin; houses are constructed just as a matter to announce one's financial achievement to the society, not on need. On the other hand, middle-class Indians contributes greatly to the world's brain capacity. The country capital (populated largely by the highest educated, highest level employees of the country) had to call for environmental emergency for several weeks due to life style-driven high pollution pressure and India figures among the 30 most populated countries. This manifests the knowledge-attitude gap and the need to address it, in precedence to the higher level attitude-behaviour gap. The problem is that environmental awareness and formal education are not always correlated and individual's attitude is determined by so many other social factors than scientific outlook. Thus it is alarmingly important to address the issue through proper and scientific approach to environment education. Obviously, the problem with green consumerism and attitude-behaviour gap in Indian community does not lie solely on the shoulders of societal outlook, but on so many other factors including high price, accessibility, availability, reliability of product quality, etc. Above all, attitude matters and it is important to recognise and emphasis the borderline between socially conscious consumer and socially responsible consumer. The socially conscious consumer participates in consumption behaviours consistent with his/her standards of responsibility, whereas the socially responsible individual adheres to generally accepted values of the society.

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## HEAVY METAL CONTAMINATION IN SOIL: EFFECTS, SOURCES AND REMEDIATION TECHNIQUES

Dr. Deepa K

Assistant Professor, PG Department of Chemistry, KAHM Unity Women's College, Manjeri,  
Kerala-676122, India  
E-mail: [deepakarat08@gmail.com](mailto:deepakarat08@gmail.com)

Heavy metal contamination refers to the excessive deposition of toxic heavy metals in the soil caused by human activities. Heavy metals in the soil include some significant metals of biological toxicity, such as mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr), arsenic (As), etc. They also include other heavy metals of certain biological toxicity, such as zinc (Zn), copper (Cu), nickel (Ni), stannum (Sn), vanadium (V), etc. In recent years, with the development of the global economy, both type and content of heavy metals in the soil caused by human activities have increased gradually, resulting in the deterioration of the environment. Heavy metal pollution of soil has become a worldwide environmental issue that has attracted considerable public attention, largely from the increasing concern for the security of agricultural products. Heavy metals enter the soil agro-ecosystem through natural processes derived from parent materials, and through anthropogenic activities. Heavy metal pollution poses a great threat to the health and well-being of organisms and human beings due to potential accumulation risk through the food chain.

In the past, soil contamination was not considered as important as air and water pollution, because soil contamination was often with wide range and was more difficult to be controlled and governed than air and water pollution. However, in recent years the soil contamination in developed countries come to be serious. Heavy metals thus paid more and more attention and became a hot topic of environmental protection worldwide.

### **CHARACTERISTICS OF HEAVY METAL CONTAMINATION OF SOILS**

- ***Strong latency heavy metal contamination is colorless and odorless, so it is difficult to be noticed.***

Heavy metals do not explicitly damage the environment in a short period. Nevertheless, when it exceeds the environmental tolerance, or when environmental conditions have changed, heavy metals in the soil may be activated and cause serious ecological damage. So heavy metal contamination is usually chemical Time Bombs.

- ***Irreversibility and remediation hardness***

If the air and water are polluted, the pollution problem can be reversed certainly by dilution and self-purification after switching off the sources of pollution. However, it is difficult to use dilution or self-purification techniques to eliminate heavy metal contamination and to get soils improved. Some soils contaminated by heavy metals are likely to take one or two hundred years to be remediated. Therefore, heavy metal contamination needs relatively high cost of remediation and the remediation cycle is relative long.

- ***Complex heavy metal contamination***

In the past, soil contamination was mainly caused by a single heavy metal. However, in recent years more cases are found to be caused by a variety of heavy metals. The complex

contamination caused by a variety of heavy metals will always amplify the contamination by heavy metals separately.

### **SOURCES OF HEAVY METALS IN SOIL**

Excess heavy metals in the soil originate from many sources, which include atmospheric deposition, sewage irrigation, improper stacking of the industrial solid waste, mining activities, the use of pesticides and fertilizers, etc.

- ***Atmosphere to soils pathway***

Heavy metals in the atmosphere are mainly from gas and dust produced by energy, transport, metallurgy and production of construction materials. Excepting mercury, heavy metals basically go into the atmosphere in the form of aerosol and deposit to the soil through natural sedimentation and precipitation, etc.

- ***Sewage to soils pathway***

Wastewater can be divided into several categories, sanitary sewage, chemical waste water, industrial mining wastewater and urban mining mixed sewage, etc. Heavy metals are brought to the soil by irrigative sewage and are fixed in the soil in different ways. The heavy metal contamination caused by sewage irrigation must be paid enough attention. Quality of irrigative sewage must be strictly controlled within the national quality standard for irrigation water.

- ***Solid wastes to soils pathway***

There are a variety of solid wastes which have complex composition. Of which mining and industrial solid waste contamination is the most serious. When these wastes are in the process of being piled or governed, heavy metals move easily due to the facilitation of sunlight, raining and washing. And they spread to the surrounding water and soils at the shape of funnel and radiation. With the development of industry and the acceleration of urban environmental construction, sewage treatment is continuing to be strengthened.

- ***Agricultural supplies to soils pathway***

Fertilizers, pesticides and mulch are important agricultural inputs for agricultural production. Nevertheless, the long-term excessive application has resulted in the heavy metal contamination of soils. The vast majority of pesticides are organic compounds, and a few are organic - inorganic compound or pure mineral, and some pesticides contain Hg, As, Cu, Zn and other heavy metals. Heavy metals are the most reported pollutants in fertilizers. Heavy metal content is relatively low in nitrogen and potash fertilizers, while phosphoric fertilizers usually contain considerable toxic heavy metals. Heavy metals in the compound fertilizers are mainly from master materials and manufacturing processes. The content of heavy metals in fertilizers is generally as follows: phosphoric fertilizer > compound fertilizer > potash fertilizer > nitrogen fertilizer. Cadmium is an important heavy metal contaminant in the soil. Cadmium is brought to soils with the application of phosphoric fertilizers. Many studies showed that, with the application of a large amount of phosphate fertilizers and compound fertilizers, the available content of Cadmium in soils increases constantly, and Cadmium taken by plants increases accordingly.

### **IMPACT OF HEAVY METAL CONTAMINATION OF SOILS**

- ***Impact on soil microorganisms and enzymatic activity***

Microbial activity and enzymatic activity of the soil can sensitively reflect the quality of the soil. The microbial biomass of the soil was an important indicator of determining the

extent of soil contamination. Microbial activity is inhibited significantly in the heavy metal contaminated soil. The microbial biomass in the soil contaminated by Cu, Zn, Pb and other heavy metals were inhibited severely. The soil's microbial biomass near the mine was significantly lower than that far away from the mine. The activities of almost all enzymes in the soil were significantly reduced by 10 to 50 times with the increase of the concentration of heavy metals.

- ***Impact on the plants***

Low concentration of soil heavy metals, regardless of necessary or unnecessary to plants, will not affect the growth of plants in a certain range. But if the concentration is too high, the content of heavy metals enriched by the plant exceeds its tolerance threshold, and thus the plant will be poisoned and it even leads to death of the plant. Cadmium may interfere in crop photosynthesis and protein synthesis, and may cause membrane damage, etc.

- ***Impact on humans***

Existing research showed that heavy metals in urban soils may go into the human body through skin absorption and inhalation of dust, etc., and thus directly damage, especially children's health. They also affect the urban environmental quality and damage human health indirectly through polluting the food, water and atmosphere. Cadmium may damage the metabolism of calcium, which will cause calcium deficiency and result in cartilage disease and bone fractures, etc. Agency for Toxic Substances Management Committee has listed Cadmium as the sixth most toxic substance that damages human health. Lead mainly enters human body through the digestive tract and respiratory tract, and then goes into the blood circulation in the form of soluble salts, protein complexes or ions, etc. 95% of the insoluble phosphate lead accumulates in bones. Lead is strongly pro-organizational. It affects and damages many of the body organs and systems, such as kidney, liver, reproductive system, nervous system, urinary system, immune system and the basic physiological processes of cells and gene expression. Cu, Zn and Ni are essential trace metals in the human body, but if the body takes excessive Cu, Zn and Ni from the outside environment, they will damage human health. Ni and Cu are tumor promoting factors, whose carcinogenesis effect has attracted global concerns. Workers who are in close contact with the nickel powder are more likely to suffer from respiratory cancer, and the content of Ni in the environment is positively correlated with nasopharyngeal carcinoma.

## **REMEDICATION OF HEAVY METAL CONTAMINATED SOILS**

Remediation using chemical, physical, and biological methods has been adopted to solve the problem. Phytoremediation has proven to be a promising alternative to conventional approaches as it is cost effective, environmentally friendly, and aesthetically pleasing.

### **Engineering remediation**

Engineering remediation refers to using physical or chemical methods to control heavy metal contamination of soils.

- ***Replacement of contaminated soil, soil removal and soil isolation***

Replacement of contaminated soil means adding large amount of clean soil to cover on the surface of the contaminated soil or to blend with the latter. Soil removal refers to remove the contaminated soil and renew it with the clean soil, which is necessary for the seriously contaminated soil with little area. Soil isolation means that to isolate the contaminated soil from the uncontaminated soil, but to completely remedy it still needs other auxiliary

engineering measures. All of these methods will cost large amount of manpower and material resources, so they can only be applied to small area of soils.

- ***Electrokinetic remediation***

Soil electrokinetic remediation is a new economically effective technology. The principle is that the DC-voltage is applied to form the electric field gradient on both sides of the electrolytic tank which contains the contaminated soil; contaminants in the soil is taken to the processing chamber, which is located at the two polar sides of electrolytic cell, through the way of electro-migration, electric seepage or electrophoresis, and thus reduce the contamination. The method performs well in the soil with low permeability.

- ***Soil leaching***

The principle of soil leaching is to wash the heavy metal contaminated soil with specific reagents and thus remove the heavy metal complex and soluble ions adsorbed on the solid phase particles. By using this method, heavy metals are separated from the soil, and heavy metals are then recycled from extracting solution.

- ***Adsorption***

Adsorption method is based on the fact that almost all heavy metal ions can be fixed and adsorbed by clay mineral, a steel slag, furnace slag, etc.

- ***Other methods***

Other engineering methods include washing and compounding, heat treatment, physical solidification, chemical improvers, chemical curing lamp remediation, etc.

### **Bioremediation**

- ***Phytoremediation***

Grow specific plants in the soil contaminated by heavy metals. These plants have the certain hyper-accumulation ability for the contaminants in the soil (accumulated mainly in the root or above the root). When the plants are ripe or reach certain enrichment level of heavy metals, remove heavy metals in the contaminated soil layer thoroughly by harvesting, burning and curing plants. Using plants and their coexisting microbial system to remove heavy metals is a new technology. The key of the method is to find the suitable plants with strong ability for heavy metal accumulation and tolerance.

- ***Microbial remediation***

Microbial remediation refers to using some microorganisms to perform the absorption, precipitation, oxidation and reduction of heavy metals in the soil. Fungi could secrete amino acids, organic acids and other metabolites to dissolve heavy metals and the mineral containing heavy metals. Fungi, *Gomus intraradices*, may improve the tolerance and absorption of Chromium to sunflower. Cultivating microorganisms that have degradation capacity on heavy metals by using biotechnology (genetics, genetic engineering, etc.) are one of the current focuses in this area.

- ***Animal remediation***

Some animals living in the soil (maggots, earthworms, etc.) can take heavy metals in the soil. Modern civilization is completely dependent on a large range of metals for all aspects of daily life. There is a long history of association between metals and human development. Copper has been used since about 8000 b.c., initially as native copper, but smelting of copper

from oxide ores is thought to date from about 6000 b.c. Lead was used before 5000 b.c., zinc and mercury by about 500 b.c., and nickel in alloys by 200 b.c. Cadmium was discovered comparatively recently. Regardless of the carcinogenic or non – carcinogenic risk, children were found to be more susceptible to the potential health risk; children were therefore likely under a higher health risk than adults. There were no significant carcinogenic and non – carcinogenic risks for adults, while children showed significant non – carcinogenic effect.

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## THERMAL POWER AND ENVIRONMENT

Mr. Muhammed Abdul Hakkeem C

*Assistant Professor & Head, Department of Physics, KAHM Unity Women's College,  
Manjeri, Kerala-676122, India  
E-mail: [hakeemchatholi@gmail.com](mailto:hakeemchatholi@gmail.com)*

### **INTRODUCTION**

Thermal Power plants (TPPs) are the major source of generation of electricity for any developing country. Around 70% of electricity generation in our country is met by thermal power plants. Fuel is blown into the combustible chamber of the boiler where it is burnt at high temperature where Heat energy converts water into steam. High energy steam is passed through the turbine and the steam creates force on the turbine causing the shaft to rotate at high speed. A generator is coupled at one end of the turbine shaft which generates power. The thermal power plant has serious impacts on land, soil, air and various social impacts. The thermal power plant are also said to emit large amount of mercury and generate large quantity of fly ash which destroys the surrounding environment. These plants also consume a large amount of water. Due to these problems they require a proper Environmental impact assessment.

Possible fuel sources include Fossil fuels such as coal, petroleum products and natural gas, Residual and waste materials such as domestic and industrial refuse and fuel made from recovered oil. Anthracite coal is the largest source of fuel for electricity generation followed by brown coal, natural gas and petroleum oils. Non-fossil sources of fuel such as landfill gas and biogases are also used. In some cases, these non-fossil fuels are co-fired with coal. The major components of TPP include the power system (i.e., power source, turbine and generator and associated facilities, which may include the cooling system, stack gas cleaning equipment, fuel storage handling areas, fuel delivery systems, solid waste storage areas, worker colonies, electrical substations and transmission lines, etc. The type of facility and size of thermoelectric projects, as well as technological configuration of generation system and also other associated facilities besides, environmental and social concerns of plant location, will determine the nature and intensity of environmental impacts of proposed TPP facility.

### **COAL AS A FUEL**

Coal is the only natural resource and fossil fuel available in abundance in India. Consequently, it is used widely as a thermal energy source and also as fuel for thermal power plants producing electricity. Power generation in India has increased manifold in the recent decades to meet the demand of the increasing population, of which more than 65% is produced by coal-based thermal power plants. The only fossil fuel available in abundance is coal, and hence its usage will keep growing for another 2–3 decades at least till nuclear power makes a significant contribution. The coal available in India is of poor quality, with very high ash content and low calorific value, and most of the coal mines are located in the eastern part of the country. The coal supplied to power plants is of the worst quality.. Combustion process converts coal into useful heat energy, but it is also a part of the process that produce greatest environmental and health concerns. Combustion of coal at thermal power plants emits mainly carbon dioxide, sulphur oxides, nitrogen oxides, and air borne

inorganic particulates, such as fly ash and suspended particulate matter (SPM). High ash content in Indian coal and inefficient combustion technologies contribute to India's emission of air particulate matter and other trace gases, including gases that are responsible for the greenhouse effect. And mercury which is a dangerous metal released by this coal combustion.

But the projected rapid growth in electricity generation in the country over the next couple of decades is expected to be met by using coal as the primary fuel for electricity generation, because of its abundance and deficiency of other fossil fuels.

### **ENVIRONMENTAL IMPACTS OF THERMAL POWER PLANTS**

The impacts of TPPs on the environment are influenced by processes used and the location characteristics in different ways. Coal-based power plants significantly impact the local environment. Direct impacts resulting from construction and ongoing operations include:

- i) Ambient Air Pollution – particulates, sulphur oxides, nitrous oxides, and other hazardous chemicals and toxic metals like Hg, As, etc.
- ii) Water Pollution – occurs in local water streams, rivers and ground water from effluent discharges and percolation of hazardous materials from the stored fly ash
- iii) Land Degradation – occurs due to alterations of land used for storing fly ash

The indirect impacts result mainly from coal mining, which includes degradation and destruction of land, water, forests, habitats, and societies. In addition to the impact of the coal-power plants, there is also a larger issue of the environmental and social impact of coal mining. In a typical TPP, environmental impacts are likely to comprise the following principal components:

- transportation of raw material
- preparing and storing raw material
- burning fuel and generating steam
- generating electricity and available heat
- treating exhaust gases and solid and liquid residues
- cooling infrastructures
- safe handling and disposal of wastes

### **Exhaust Gases**

Initially, perceptions of objectionable effects of air pollutants were limited to those easily detected like odour, soiling of surfaces and smoke stacks. Later, it was the concern over long-term/chronic effects that led to the identification of six criteria pollutants. These six criteria pollutants are sulphur di-oxide (SO<sub>2</sub>), Carbon Mono-oxide (CO), Nitrogen oxide (NO<sub>2</sub>), Ozone (O<sub>3</sub>), suspended particulates and non-methane hydrocarbons (NMHC) now referred to as volatile organic compounds (VOC). There is substantial evidence linking them to health effects at high concentrations. Three of them namely O<sub>3</sub>, SO<sub>2</sub> and NO<sub>2</sub> are also known phytotoxicants (toxic to vegetation). In the later part Mercury (Hg) has been added to that list.

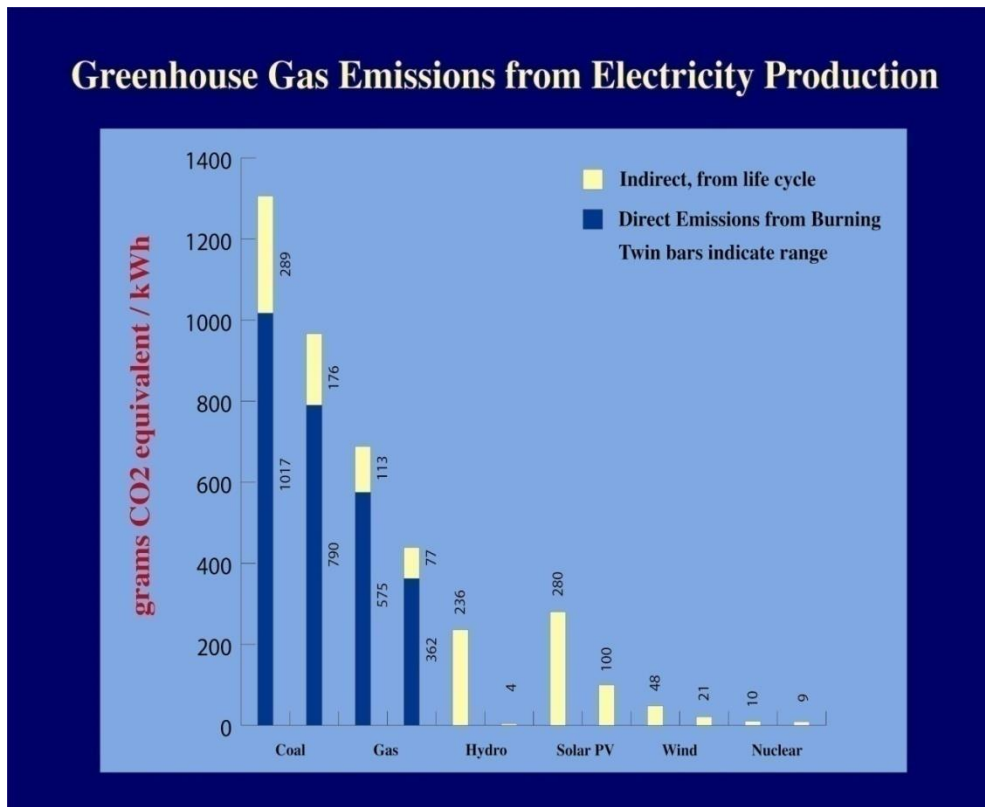
*Sulphur Oxide:* The combustion of sulphur containing fossil fuels, especially coal is the primary source of SO<sub>x</sub>. About 97 to 99% of SO<sub>x</sub> emitted from combustion sources is in the



form of  $\text{SO}_2$ , which is a criteria pollutant, the remainder is mostly  $\text{SO}_3$ , which is in the presence of atmospheric water is transformed into Sulphuric Acid at higher concentrations, produce deleterious effects on the respiratory system. In addition,  $\text{SO}_2$  is phytotoxicant.

*Particulate matter:* The terms particulate matter, particulate, particles are used interchangeably and all refer to finely divided solids and liquids dispersed in the air.

*Carbon Oxide:* Increasing  $\text{CO}_2$  levels have significant implications such as changes in monsoon precipitation patterns as well as rise in extreme rainfall events, coastal storms, droughts and global warming. Such changes in the climate could have enormous human, ecological, and economic impacts.



The particulate and noxious gas emissions from TPPs primarily and directly pollute the air. Eventually, the particulate emissions and, for the most part, the noxious gases and any atmospheric transformation products that may have formed (e.g.,  $\text{NO}_2$  and nitrate from  $\text{NO}$ ) fall to earth either by a way of precipitation or by dry deposition, thereby imposing a burden on the water and/or soil, with resultant potential damage to flora and fauna.

Emissions from thermoelectric projects can act as precursors of acid precipitation, particularly when coal with its high sulphur content is the fuel. Acid precipitation accelerates the deterioration of buildings and monuments, radically alters aquatic ecosystems of certain lakes, and damages vegetation in forest ecosystems.

### **Land Degradation**

The thermal power stations are generally located on the non-forest land and do not involve much resettlement and rehabilitation problems. However its effects due to stack emission etc, on flora and fauna, wild life sanctuaries and human life etc., have to be studied for any adverse effects. One of the serious effects of thermal power stations is land requirement for ash disposal and hazardous elements percolation to ground water through ash

disposal in ash ponds. According to the studies carried out by International consultants thousands of sq. km of land should be required for ash disposal only.

### **Cooling Water Sources And Issues**

Aquatic organisms drawn into cooling water intake structures are either impinged on components of the cooling water intake structure or entrained in the cooling water system itself. In case of either impingement or entrainment, aquatic organisms may be killed or subjected to significant harm. In some cases (e.g., sea turtles), organisms are entrapped in the intake canals.

### **Hot Water Ejection**

The effect on biological environment can be divided into two parts, viz. the effect on flora and the effect on fauna. Effect on flora is due to two main reasons, land acquisition and due to flue gas emissions. Land acquisition leads to loss of habitat of many species. The cooling water being at higher temperature (by 4 - 5°C) when discharged can harm the local aquatic biota. The primary effects of thermal pollution are direct thermal shocks, changes in dissolved oxygen, and the redistribution of organisms in the local community. Because water can absorb thermal energy with only small changes in temperature, most aquatic organisms have developed enzyme systems that operate in only narrow ranges of temperature. These stenothermic organisms can be killed by sudden temperature changes that are beyond the tolerance limits of their metabolic systems.

### **Waste Water**

The wastewater streams in a TPP include cooling tower blow down; ash handling wastewater; material storage runoff; metal cleaning wastewater; and low-volume wastewater, such as air heater and precipitator wash water, boiler blow down, boiler chemical cleaning waste, floor and yard drains and sumps, laboratory wastes, and back flush from ion exchange boiler water purification units. Such wastewater is usually generated in power plants which burn coal or biomass. The characteristics of the wastewaters generated depend on the ways in which the water is used.

The discharge of waste water causes water quality problems and has a high impact on the aquatic environment, which vary widely, depending on the type of fuel used, the abatement technique applied, the cooling technique and consequently the amount of water used, and the chemical and biological treatment reagents added for cleaning and maintenance purposes. These substances can impart significant toxicity to the receiving water. For instance, water from slag flush and ash transport has an alkaline character due to the composition of the ash, whereas water from boiler washing is acidic. Wastewater from the wet desulphurisation plant contains salts such as chlorides and sulphates. Salt derived from the sea is found in most coastal waters. However, discharges from industrial activities such as energy generating facilities provide a further source of salt. This effect is even more significant if the water is discharged to a river or lake.

The withdrawal of such large quantities of water and discharge with elevated temperature along with various pollutants, chemical contaminants picked up during process such as biocides or other additives may affect aquatic organisms, including phytoplankton, zooplankton, fish, crustaceans, shellfish, and many other forms of aquatic life. In Oil or Gas-based TPP, the same wastewater sources are usually present in plants except some of these streams (e.g., ash handling wastewater) may not be present at all. Apart from their cooling-water consumption, power plants have very modest water requirements.

**Noise**

Noise is another air pollution and the principal source of noise in a TPP includes the turbine generators and auxiliaries; boilers and auxiliaries, such as coal pulverisers; reciprocating engines; fans and ductwork; pumps; compressors; condensers; precipitators, including rappers and plate vibrators; piping and valves; motors; transformers; circuit breakers; and cooling towers. TPPs used for base load operation may operate continually while smaller plants may operate less frequently but still pose a significant source of noise if located in urban areas.

**Fly Ash and Bottom Ash**

Coal or biomass-fired Thermal power plants generate the greatest amount of solid wastes due to the relatively high percentage of fly ash in the fuel. The other solid waste from large-volume coal combustion wastes includes bottom ash, boiler slag. Fly ash removed from exhaust gases makes up more than 60–85% of the coal ash residue in pulverised-coal boilers. Bottom ash includes slag and particles that are coarser and heavier than fly ash.

Thermal power stations in India, where poor quality of coal is used, add to environmental degradation problems through gaseous emissions, particulate matter, fly ash and bottom ash. Growth of manufacturing industries, in public as well as private sectors has further aggravated the situation by deteriorating the ambient air quality. Abundance of ash content in Indian coal results in increase of fly ash and bottom ash content for disposal. The fly ash generated in thermal power station causes many hazardous diseases like asthma, tuberculosis, etc.

The particles of Fly ash are generally spherical in shape and range from 0.5 to 100 micron in size. The fine particles of fly ash reach the pulmonary region of the lungs and remain there for long periods of time; they behave like cumulative poisons. The submicron particles enter deeper into the lungs and are deposited on the alveolar walls where the metals could be transferred to the blood plasma across the cell membrane fly ash can be disposed off in a dry or wet state. Studies show that wet disposal of this waste does not protect the environment from migration of metal into the soil. Heavy metals cannot be degraded biologically into harmless products like other organic waste.

**COLLECTION OF FLY ASH**

After the combustion of the coal in the boiler, 20% of the ash is collected at the bottom of the boiler called bottom ash and 80% is carried along with flue gases called fly ash. Bottom ash is mixed with water and made into sludge form and sent through pumps into the ash ponds. The Electro Static Precipitator is used to collect the ash particles in the flue gases. The era after the introduction of the Electro Static Precipitator has partly protected the environment from harmful gases and hazardous chemicals. Generally dust is collected from the waste in two processes that is mechanically and electrically.

Mechanically is by using filters and electrically is by using Electro Static Precipitators. The ESP is efficient in precipitation of particles from sub microns to large sizes of particles and hence they are preferred to mechanical precipitators. The efficiency of modern ESP's is of the order 99.9%. The Electro Static Precipitators have high collecting efficiency, low sensitivity to high temperatures, low pressure drop, limited process controls and an easy and reduced maintenance make the electro static precipitators one of the most reliable and appreciated units available at the moment in the market. Electrostatic precipitators can be used for collecting virtually all kinds of dust coming from coal and oil fired power stations, blast furnaces and industrial furnaces, iron and steel processes, cement

factories, municipal solid wastes incinerators, paper mills, wood factories, textile industries, food and pharmaceuticals industries.

**Principle of Electro Static Precipitator:** The electro static precipitator utilizes electrostatic forces to separate dust particles from the gas to be cleaned. The flue gas is ionized in the electro static field and large quantities of positive and negative ions are formed. The positive ions are immediately attracted towards the negative wires by the strength of the field. The negative ions however attracts towards the positive plates.

### **UTILIZATION OF FLY ASH**

**Fly ash bricks:** The Central Fuel Research Institute, Dhanbad has developed a technology for the utilization of fly ash for the manufacture of building bricks. Fly ash bricks have a number of advantages over the conventional burnt clay bricks. Unglazed tiles for use on footpaths can also be made from it

**Fly ash in manufacture of cement:** In the presence of moisture, fly ash reacts chemically with calcium hydroxide and  $\text{CO}_2$  present in the environment attack the free lime causing deterioration of the concrete. A cement technologist observed that the reactive elements present in fly ash convert the problematic free lime into durable concrete. Fly ash can substitute up to 66% of cement in the construction of dams. Fly ash in R.C.C. is used not only for saving cement cost but also for enhancing strength and durability. Fly ash can also be used in Portland cement concrete to enhance the performance of the concrete. Portland cement is manufactured with Calcium oxide, some of which is released in a free state during hydration. Utilization of fly ash in cement concrete minimizes the carbon dioxide emission problem to the extent of its proportion in cement.

**Fly ash-based ceramics:** Ceramic products with up to 50 wt% of mullite and 16 wt% of feldspars were obtained from binary mixtures of fly ash from the Teruel power station(N-E Spain) and plastic clays from the Teruel coal mining district. The firing behaviour of fly ash and the ceramic mixtures was investigated by determining their changes in mineralogy and basic ceramic properties such as colour, bulk density, water absorption and firing shrinkage. To determine the changes on heating suffered by both the fly ash and the ceramic bodies, firing tests were carried out at temperatures between 900 and 1200°C in short firing cycles. The resulting ceramic bodies exhibit features that suggest possibilities for use in paving stoneware manufacture, for tiling and for conventional brick making. The National Metallurgical Laboratory; Jamshedpur has developed a process to produce ceramics from fly ash having superior resistance to abrasion

**Fly ash as fertilizer:** Fly ash provides the uptake of vital nutrients/minerals (Ca, Mg, Fe, Zn, Mo, S and Se) by crops and vegetation, and can be considered as a potential growth improver. Because it can be a soil modifier and enhance its moisture retaining capacity and fertility the improvement in yield has been recorded with fly ash doses varying from 20 tone / hectare to 100 tone / hectare . On an average 20-30% yield increase has been observed. Out of 150 million hectare of land under cultivation, 10 million hectares of land can safely be taken up for application of fly ash per year. The fly ash treated fields would give additional yield of 5 million tone food grains per year valued at Rs.3000 per year.

**Fly ash in road construction:** The use of fly ash in large quantities making the road base and surfacing can result in low value–high volume utilization technology demonstration projects at New Delhi, Dadri (U.P.) and Raichur (Karnataka) have been successfully completed for use of fly ash in road / flyover embankments.

**Roads and Embankments:** Another area that holds potential for utilization of large volumes of fly ash is road and flyover embankments. Fly ash embankments at Okhla, Hanuman Setu, Second Nizamuddin bridge in Delhi and roads at Raichur, Calcutta, Dadri etc. have established that on an average Rs. 50 to 75 per MT of earth work cost can be saved by using fly ash (in lieu of soil) in such works, primarily due to reduction in excavation & transportation costs.

### **ENVIRONMENTAL IMPACT OF FLY ASH UTILIZATION**

Utilization of fly ash will not only minimize the disposal problem but will also help in utilizing precious land in a better way. Construction of road embankments using fly ash, involves encapsulation of fly ash in earthen-core or with RCC facing panels. Since there is no seepage of rain water into the fly ash core, leaching of heavy metals is also prevented. When fly ash is used in concrete, it chemically reacts with cement and reduces any leaching effect. Even when it is used in stabilization work, a similar chemical reaction takes place which binds fly ash particles. Hence chances of pollution due to use of fly ash in road works are negligible.

### **CLEAN COAL TECHNOLOGIES**

Clean Coal Technologies (CCTs) offer the potential for major improvements in efficiency and significant reduction in the environmental emissions when used for power generation. These technologies may be utilized in new as well as existing plants and are therefore, an effective way of reducing emissions in the coal fired generating units. Several of these systems are not only very effective in reducing emissions of noxious gases, but because of their higher efficiencies they also emit lower amount of CO<sub>2</sub> per unit of power produced. CCTs can be used to reduce dependence on foreign oil and to make use of a wide variety of coal available. To meet increasing demand of power with minimal environmental impact for sustainable development, adoption of clean coal technologies with enhanced power plant efficiency, fuel switching, use of washed coal, efficient pollution control systems and proper by product and waste handling & utilization, is necessary.

### **PRE-COMBUSTION TECHNOLOGIES**

**Coal Beneficiation:** Ash, sulphur and other impurities can be reduced from the coal before it is burnt.

**Combustion Technologies:** Generation of emissions of SO<sub>2</sub>, NO<sub>x</sub> & CO<sub>2</sub> can be minimized by adopting improved combustion technologies

**Super-critical Technology:** By increasing steam temperature and pressure, the efficiency of the steam turbine (and hence, of electricity generation) can be increased. As the steam-pressure and temperature increases to a critical point, the characteristics of steam are altered such that water and steam are no longer distinguishable and it is known as super-critical steam and this technology is more efficient.

### **POLLUTION CONTROL TECHNOLOGIES**

Air pollutants emitted from combustion process from boilers consists mainly of particulates, sulphur oxides, nitrous oxides, heavy metals, and CO<sub>2</sub> – chemicals that cause serious health and environmental damages. There are a range of flue gas treatment technologies for reducing such flue gas emissions of these pollutants; they are now typically a part of specific coal-utilization technology packages. The add-on pollution-reducing technologies are broadly installed at three stages namely: pre-combustion, in-combustion and post-combustion. In pre-combustion stage coal beneficiation/washing is carried out to reduce

the overall amount of coal ash and also increase energy efficiency. The pollution cleanup technologies to remove particulates and sulphur from the combustion gas are also viewed as pre-combustion mechanisms. During in-combustion stage, low NO<sub>x</sub> to reduce NO<sub>x</sub> emissions, dry limestone scrubbing for sulphur removal in fluidized-bed combustion and gasification are incorporated as pollution control measures.

### **CONCLUSION**

Environmental pollution by the coal based thermal power plants all over the world is cited to be one of the major sources of pollution affecting the general aesthetics of environment in terms of land use, health hazards and air, soil and water in particular and thus leads to environmental dangers. Fly ash also affects environment because it is in direct contact with water. Heavy metals can also adversely affect the growth rate in major crops. Coal combustion residues (CCRs) are a collective term referring to the residues produced during the combustion of coal regardless of ultimate utilization or disposal. It includes fly ash, bottom ash, boiler slag, and fluidized bed combustion ash and other solid fine particles. In India, presently coal based thermal power plants are releasing 105MT of CCRs which possess major environmental problems. Presently from all these thermal power plants, dry fly ash has been collected through Electrostatic Precipitator (ESP) in dry condition as well as pond ash from ash ponds in semi-wet condition. In India most of the thermal power plants do not have the facility for automatic dry ash collection system. Commonly both fly ash and bottom ash together are discharged as slurry to the ash pond/lagoon these affect on environment, economy, and social factor. The disposable management of fly ash from thermal power plant is necessary to protect our environment. It is advisable to explore all possible applications for fly ash utilization. All possible mitigation measures should be employed at each and every thermal power plant in order to reduce its adverse environmental impacts.

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## **IMPACT OF AGROCHEMICAL USE IN AGRICULTURE: THEIR BENEFITS AND HAZARDS**

Dr. Anees Rahman K N

*Assistant Professor (Ad hoc), PG Department of Chemistry, KAHM Unity Women's College,  
Manjeri, Kerala-676122, India  
E-mail: [anmailr@gmail.com](mailto:anmailr@gmail.com)*

### **INDRODUCTION**

Agriculture is essential for human survival, in order to meet the demand of food created by exponential growth of population. But the food production via conventional agricultural method was insufficient. The absence of modern techniques, different plant diseases and the pest infections, climate events and natural disasters further prevented the agricultural productivity. These lack of sufficiency and efficiency created different famines around the world. The great Chinese famine (1959-61) is one of the most severe and saddest example, which caused the death of 15 to 43 million people. So in order to defeat the far reaching severity of the food scarcity, new techniques were introduced in agriculture, which then known as "Green Revolution"

Green Revolution is a movement which refers to a series of research, development, and technology transfer initiatives. This happened between the 1960s and 1980s. It started with use of new high-yielding varieties of food crop, and the widespread use of machineries, irrigation techniques and agrochemicals such as fertilizers sufficient rapid supply of nutrients and pesticides and herbicides to control the pests and weeds respectively to maximize the productivity. The outcome was the unprecedented gains in the production of grains and other food products particularly in developing countries. In India the Green Revolution started in the late 1960s and with its success India attained food self-sufficiency within a decade.

### **AGROCHEMICALS**

An agrochemicals are general name for the chemicals used in agriculture and are consist of pesticides including insecticides, herbicides, fungicides and nematocides. It also include synthetic fertilizers, various plant hormones and other chemical growth agents. Over the past few decades, the heavy reliance on agrochemicals have been witnessed in order to enhance the crop production. In India, these agrochemicals acted a very crucial role in the success of the green revolution.

Agrochemicals have various beneficial effects. These include supplementation of plant nutrients, crop protection, growth promoters, and growth retardants, preservation of food and materials, and prevention of vectorborne diseases as a primary effect. The most important benefits include the protection of human, animal, and crop health as secondary benefits.

### **HARMFUL EFFECTS OF AGROCHEMICALS**

Agrochemical use raises numerous environmental concerns, including human health and animal health hazards. Pesticides are ubiquitous in the environment and most are synthetic. Food toxicity due to pesticides is associated with severe effects on human health. Actually, the mode of action of pesticides involves targeting the systems or enzymes in pests which may be identical or similar to the systems or enzymes in human beings and they, therefore, pose risks to human and livestock health as well as to the environment.



Pesticide toxicity can result from a high level of exposure, mishandling, ingestion, inhalation, or dermal absorption. Sustained exposure to such agrochemicals for a long period of time may result in various dangerous diseases, such as:

- Hormonal imbalances, leading to infertility and breast pain;
- neurological, psychological, and behavioral dysfunctions;
- reproductive system defects;
- immune system dysfunction;
- blood disorders;
- genotoxicity;
- cancers.

Pesticides can pollute soil, water, grasslands, and other vegetation. In addition to killing insect-pests, pathogens, or weeds, pesticides can be toxic to nontargeted organisms, like birds, fish, beneficial insects, and other plants. A number of toxicological studies in animals demonstrate that pesticides, to which the general population may be chronically exposed, are potential carcinogens, neurotoxins, reproductive toxins, and immunotoxins, besides the involvement of pesticides in the development of neurodegenerative diseases. Several articles and reports evaluated toxicological and epidemiological evidences for various health effects associated with pesticides. Pesticide contamination can affect aquatic fauna and flora, as well as human health when water is used for public consumption. Aquatic organisms are directly exposed to chemicals resulting from agricultural production via surface runoff or indirectly through trophic chains.

### **Impact on environment**

Pesticides can contaminate soil, water, turf, and other vegetation. In addition to killing insects or weeds, pesticides can be toxic to a host of other organisms including birds, fish, beneficial insects, and non-target plants. Insecticides are generally the most acutely toxic class of pesticides, but herbicides can also pose risks to non-target organisms.

### **Surface water contamination**

Surface waters are the main receptors of pesticides contamination from agricultural use. Pesticides can contaminate surface water through runoff from treated plants and soil. Contamination of water by pesticides is widespread. The studies done by the U.S. Geological Survey (USGS) on major river basins across the country reveals that, More than 90 percent of water and fish samples from all streams contained one, or more often, several pesticides. Pesticides were found in all samples from major rivers with mixed agricultural and urban land use influences and 99 percent of samples of urban streams. The USGS also found that concentrations of insecticides in urban streams commonly exceeded guidelines for protection of aquatic life.

### **Ground water contamination**

Groundwater pollution due to pesticides is a worldwide problem. According to the USGS, at least 143 different pesticides have been found in ground water, including pesticides from every major chemical class. During one survey in India, 58% of drinking water samples drawn from various hand pumps and wells around Bhopal were contaminated with Organochlorine pesticides above the EPA standards. Once ground water is polluted with toxic chemicals, it may take many years for the contamination to dissipate or be cleaned up.

### **Soil contamination**

Soil, a natural environment for the growth and development of plants, consists of a mixture of organic and mineral components occurring in gaseous, aqueous and solid states. Genetically and environmentally, soils differ significantly, yet, they tend to perform the function of reservoirs of water and nutrients necessary for a suitable development of the plant root system and microorganism. Soil has the capacity of retaining various pollutants, such as heavy metals, pesticides hence they impart to the contamination of the food chain, which can also potentially threaten human health

The active substances of pesticides produce pollution in soil environment, affecting microorganisms living there. Thus, they may also interfere with the correct sequence of biochemical pathways in soil biogeochemical cycles.

Heavy treatment of soil with pesticides can cause populations of beneficial soil microorganisms to decline. According to the soil scientist Dr. Elaine Ingham, "If we lose both bacteria and fungi, then the soil degrades. Overuse of chemical fertilizers and pesticides have effects on the soil organisms that are similar to human overuse of antibiotics. Indiscriminate use of chemicals might work for a few years, but after awhile, there aren't enough beneficial soil organisms to hold onto the nutrients" (Savonen, 1997). For example, plants depend on a variety of soil microorganisms to transform atmospheric nitrogen into nitrates, which plants can use.

### **CONCLUSION**

Although pesticides are applied to the soil, these substances can be transported over long distances through evaporation and precipitation. In addition, pesticides also reach water bodies by surface runoff and by percolation through the soil and into the groundwater. In this way, many compounds have been detected in high concentrations in surface waters worldwide. The occurrence of these contaminants in the aquatic environment, especially in high concentrations, can cause adverse effects on non-target organisms, including humans. Some of the compounds identified can induce endocrine dysfunction, oxidative stress, immune and neurological system problems, and chromosomal changes among other effects that may be more severe in pregnant women and children. In addition, pesticides generally occur in surface waters as complex mixtures that are difficult to evaluate, and may have additive and synergistic effects. It is noteworthy that some revised toxicological studies observed effects on organisms after exposure to herbicides, fungicides, and insecticides at concentrations found in surface waters .

For these reasons, it is very important that drinking water is treated in order to remove contaminants before distribution to the population. Many examples of pesticides resistant to conventional water treatment methods were observed. These compounds remained stable throughout all of the steps in the process with few exceptions. Among several advance treatment techniques for pesticide removal, the adsorption process presents high efficiency and high adsorption capacity for a wide range of pesticides and may be a process with great potential.

Also more sustainable and environmental friendly system of cultivation needs to be practiced and it should have been called Organic Farming. For that the should be another wave of green Revolution has to occur with focus on to feed a growing world population and to do so sustainably without compromising the environment.

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## APPLICATIONS OF ECO-FRIENDLY POLYMERIC MATERIALS

Mrs. Smitha M

*Assistant Professor, Department of Chemistry, N. S. S. College, Manjeri, Kerala-676122,  
India*

*E-mail: m.smitha.saj@gmail.com*

### **INTRODUCTION**

In recent days polymer based materials have applied on every phase of our life and conferred great impact on the society. But most of them used are non-biodegradable and after usage accumulated on the environment from a variety of sources and furthermore these materials are now believed to be contributing to the release of some chemicals in the environment causes pollution. So the development of biodegradable synthetic polymers and bio composites being promoted in every applications including packaging, biomedical, textiles, agriculture, household use etc. due to growing awareness of environmental and waste management issues. This chapter introduces some eco-friendly polymeric materials and presents the applications of these polymer based materials in various fields.

The polymer based materials used in society today are made from a broad class of materials that are both natural and synthetic in origin and are complex organic molecules composed of repeating carbon-based units or chains possessing wide range of properties which influences their behaviour in the environment. Biodegradable polymers are polymers that are capable of being broken down quite readily into fragments by different mechanisms, which is influenced by the environmental setting and is facilitated by the presence of microorganisms. Under the influence of these conditions polymer degrades to non-toxic natural components. Mainly two types of chemical reactions, those based on hydrolysis and those based on oxidation occurred during bio degradation. Degradation of condensation polymers occurred through hydrolysis reactions and decomposition of polymers containing only carbon atoms occurred through oxidation followed by hydrolysis of the products of oxidation. Susceptibility of a polymer to undergo bio degradation depends on the polymer structure; enzymes produced by the microorganisms, variable reaction conditions etc.

The advantages of biodegradable polymer is that they do not require separate collection, sorting, recycling or any other waste disposal solution as is the case with non-biodegradable plastics. So one of the primary aims of recent research is the development of biodegradable polymeric materials as waste management options for polymers in the environment because these materials do not affect the environment in any harmful way as they decomposes into natural components and are now being applied in various fields of our life. Packaging represents the most important application followed by building and construction, automotive electrical and electronic equipment, medicine and agriculture. Some synthetic biodegradable polymers currently used and their applications in various areas are discussed here.

### **FOOD PACKAGING APPLICATIONS**

Attitude towards traditional plastic bags has turned to negative all over the world due to the environmental problems caused by them. As a result, governments have taken action to limit their use. Conventional polymers such as Polyethylene and polypropylene, which are used for the production of plastic bags after disposal last in the environment for many hundred

years. Furthermore, Physical recycling of many polymeric packaging materials for food and other biological substances is impractical and generally undesirable. Science offers biodegradable polymers, capable of degrading after disposal in bioactive environments as a solution to these problems. Cellulose is one natural biodegradable material, which on chemical modification improves their properties and can be applied in this area. Some thermoplastic polyester like Poly ( $\epsilon$ -caprolactone) (PCL), polyhydroxylalkanoates (PHAs) and poly(lactic acid) (PLA) are the biodegradable polymers, which are water resistant and may be processed with melt-extrusion method into sheets, bottles, and diverse shaped products, which makes these plastics very promising for use as biopolymers. Polyhydroxylalkanoates, poly lactic acid, Poly ( $\epsilon$ -caprolactone) (PCL) alone or in a blend with synthetic polymer or with starch give packaging films.

### **BIO MEDICAL APPLICATIONS**

The need for the bio degradable polymers with tailored physico-chemical and degradable properties increased with the development of biomedical technologies like tissue engineering and controlled drug release. Both natural and synthetic biodegradable polymers are used in this area. Among those, natural polymers such as collagen, fibrin and hyaluronic acid (HA) synthetic polymers, including biodegradable and bioresorbable polymers such as poly(lactic-co-glycolic acid) (PLGA) and poly( $\epsilon$ -caprolactone) (PCL), polyhydroxylalkanoates (PHAs), polyurethanes (PURs) have been used. Due to biodegradability, relatively low antigenicity, cell-binding properties, mechanical strength, collagen in combination with many natural and synthetic polymers has been extensively applied for biomedical applications. Carbon fibre reinforced PLA composites are widely used in medical applications like ligament replacement. Collagen and PCL nano fibrous composite, with mechanical properties similar to skin have been developed as scaffold in tissue engineering. PCL-based fibrous scaffolds obtained by electrospinning method have shown favourable physical and biological characteristics, such as the maintenance of scaffold structure in physiological buffer and the support of cell proliferation and differentiation. Polycaprolactone (PCL) is a very good material for sustained drug delivery applications due to high permeability. Owing to the significant tissue compatibility of polyurethanes, they have been explored as cardiac pacemakers and vascular implants.

### **AGRICULTURAL FIELDS**

The primary aim of agricultural development during the 20th century all over the world was the increasing productivity per unit area of land used for crop production. This was accomplished by the excessive use of fertilizers and pesticides along with natural resources such as water and plant resources. Although this practice resulted in considerable increase in crop yields, causes the depletion of natural water resources and pollution with hazardous pesticides and chemical fertilizers, which threatened the survival and well-being of all life forms on earth. The use of polymer in agriculture is gaining popularity in science. Functionalized polymers were used to increase the efficiency of pesticides and herbicides, allowing lower doses to be used and to indirectly protect the environment by reducing pollution and clean-up existing pollutants. Polymeric biocides and herbicides are now being used in this area. It allows lower amount of conventional biocides to enter into the agricultural fields. Many polymers like chitosan, ethyl cellulose, alginate, chitosan-clay mixture, cellulose etc. are applied as controlled release polymeric materials. Some super adsorbent polymers and composites are also used to improve the physical properties of the soil such as water-holding capacity, soil permeability and infiltration rates, water use efficiency, instopping erosion and water run-off etc. Starch copolymer, cellulose based polymers and polyacrylamide and poly(vinyl alcohol) is used as superabsorbent polymers in

the soil. Water-soluble polymers (WSP) have been used extensively for the removal or recovery of contaminated metal ions from aqueous solutions. Polysaccharides such as cellulose, chitin and chitosan are a group of polymers most commonly applied for the purpose of metal sorption. Thus biodegradable polymers have now increasingly been used as plastics substitutes for several applications in agriculture.

### **AUTOMOTIVE INDUSTRY**

Application of biodegradable and green composites in automotive industry is increased much due to environmental consideration to reduce disposal of waste from vehicles. Recently in automotive industry most of the structural part is made of materials like steel other than plastic materials. But the usage of plastic materials become high when we considering non-structural parts such as front and rear bumpers and interior trim components etc. Initially many materials applied in automotive industry were not eco-friendly materials and but now due to increase in the awareness of environmental consideration, on-going researches are concentrated to manufacture eco-friendly materials for both exterior and interior components. However, due to the current material property constraints, only interior components are being developed using bio-based polymeric materials. Currently, many works reported polylactic acid composite and blends of cellulose and starch as replacements for commodity plastics such as polypropylene (PP) and polyethylene (PE). New and promising bio-polymer polyhydroxyalkanoates (PHA), and biopolyurethane foam is also being developed, and commercialization of PHA has just begun. Natural fiber reinforced composites, in particular sisal/PLA, flax/PHB, coir/PLA, jute/PLA, hemp/PHB, and jute/PHB composites, can be used in car bumpers, seats, door, and window panels, insulation, and so on.

### **CONCLUSIONS**

Due to growing environmental awareness, development and applications of biodegradable polymeric materials in different sectors are enhancing in recent days. The sectors of packaging, agriculture, automotive and medicine all need eco-friendly materials owing to the harmful effects of conventional materials. So the current researches in this area are focussed for the development of biodegradable eco-friendly materials with good mechanical and functional properties. A wide range of biodegradable polymeric materials are now available in these areas performing their function effectively. Looking ahead these materials could become commodity plastics of the future and save our environment from detrimental effects.

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