GENERAL OVERVIEW

WATER POLLUTION PROBLEM

The major part of scientific and technological development has been directed towards the elevation of standard of living. The living conditions today have surely improved to a great extent. Markets are flooded with new avenues of human comforts to its citizens. The industrialization and urbanization is gaining momentum in all developing countries at the cost of environmental degradation. The development is dominated by two prime factors. Firstly, each developed or developing countries are facing unprecedented problem in the environmental areas, like, issues of population, extremes of affluences, drinking water, global warming, stratospheric ozone depletion, ground water contamination, management of wastes and other pollution problems. Secondly, these problems invoke opportunities of parallel scope. The natural resources are not only getting depleted day by day but also getting polluted. The air, water and soil are getting filled up with hazardous wastes. The very nature of environmental problems has changed. So the time has reached to visualize the whole process at a different angle.

The human society is more critically dependent than ever on the environmental resource base, water, topsoil, vegetation, biodiversity, climate etc. which ultimately underpins all our economic activities. Yet these environmental resource bases are being developed and degraded at rates far surpassing to an extent that is serving a severely impoverished planet. The environmental underpinnings are much more valuable in strictly scientific and economic terms than it is expected. Because most of the environmental goods and services are not traded in the market place and hence have no price evaluations. They have been treated as not only priceless but worthless. That is the reason why they have been misused and overused as if with impunity. The human society can embark on a shift from an approach that has over exploited and utilized the environment to a strategy that derives full and sustainable benefits from the environments. However, the following few facts would underline the needs to tackle the environmental problem.
Chapter-1 Introduction and Literature Review

- The southern ozone hole remained as large as ever, seven times the size of India.
- CO₂ emission has increased more than ever.
- The average global temperature rose by a record amount of 1.2%.
- Economic losses from freak weather are more than ever.
- The global grain harvest fell by 1%.
- Two thirds of the world’s coral reefs revealed a terminal threat in the form of bleaching from rising temperature.
- The world lost more species than ever.
- More people are being affected due to drinking of contaminated water.
- More people are being affected with airborne diseases.
- The world is losing a number of species and creating a number of dreaded species.

Most essential for all life forms, but diminishing availability with each passing! The amount of water isn't diminishing, but the demand for it is steadily increasing. In addition, the amount of water that is clean and drinkable is steadily decreasing because of pollution caused by us. Water is the only substance that occurs naturally in all three common states of matter Solid (ice), Liquid and Gas (water vapor). It is the most abundant compound on Earth’s surface, covering 70% of the planet.

“Water, water, everywhere, nor any drop to drink” from the poem “The Rime of the Ancient Mariner,” is true not just for a sailor any more. 97% of the total water available on earth’s surface is undrinkable because it’s salt water. Of the other 3% 77% is frozen (Figure 1.1).
Among the various environmental resources water is one of the most important commodities which require special attention. The Gandhian Quote says, “There is enough on earth for everyone’s need and not for everyone’s greed”. This is true about the water resources. Water is not only a liquid but elixir of life. Water covers 70% of the planet surface, mainly in the form of salty water in oceans. It is a vital substance for supporting life on Earth. A tree contains 60% water; most animals are composed of about 65% water, while our body contains around 55% water. Every year 111,000 km$^3$ of water falls on land and 70,000 km$^3$ returns to the atmosphere via evaporation from wet surfaces and transpiration from plants, these two processes are collectively called as evapotranspiration. The remainder, 41,000 km$^3$, is the runoff, which eventually reaches the oceans. If the runoff were divided evenly, it could provide each person with 6,760 m$^3$ a year of freshwater (2000 population). But of course it is not divided evenly. The amount of water withdrawn for human uses is much less than the total runoff. Averaging about 8% worldwide; but in some countries the fraction is considerably higher.

The burgeoning population is exhausting the available fresh water resources as a result of which the world is heading towards a water crisis. It is predicted that
in future most of the social conflicts are going to be water based and pure water will be a heavily priced commodity.

So the real challenges before the society are as follows:

» Water conversation and management.
» Consideration of water as an endangered resource.
» Protection of all surface water bodies from pollution.
» Treatment of available water by cost effective methods.
» Development of new environmental friendly technologies.

Water is used for many purposes: drinking, cooking, washing, carrying wastes, cooling machines, irrigating crops and many more. Per capita water utilization varies widely; the continental averages range from 1,374 m$^3$ per year in North America to 181 m$^3$ per year in Africa. In Canada and Poland, three-quarters of the water utilization is for industry and power generation, while about one-tenth is for agriculture. In most of the developing countries, these percentages are reversed. Interestingly, the European per capita utilization 626 m$^3$ per year, is less than half of that of North America, despite similar economic conditions. India receives about 1400 – 1800 mm of rainfall annually. It is estimated that 96% of this water is used for agriculture, 3% for domestic use and 1% for industrial activity. An analysis conducted in 1982 revealed that about 70% of all the available water in our country is polluted. In appreciation of this situation, several steps are being taken to control water pollution.

Everyone needs fresh water everyday to cover the daily demand in food, domestic use, etc. Fresh water is used in agriculture, construction, transport, chemical industries and numerous other human activities. Many people around the world are chronically short of water for personal needs. In many places, freshwater aquifers are being drained faster than they can be replenished. Local reservoirs might be insufficient, especially in times of drought. It has to be noted that in many regions on Earth, where the struggle for existence of population is continuous, it is the lack of fresh and clean water that limits the production of food. The quality of water is of vital concern for mankind since it is directly linked with human welfare.
Environmental pollution is the unfavorable alteration of our surrounding. It is the introduction of contaminants into the environment that causes harm or discomfort to humans or other living organisms, or that damage the environment. The word ‘pollution’ has been taken from the Latin word “pollutionem” meaning ‘to make dirty’. Pollution can be in the form of chemical substances, or energy such as noise, heat, or light. Pollutants can be naturally occurring substances or energies, but considered contaminants when in excess of natural levels. It is mainly linked with human activities, discharge of domestic, industrial and agricultural wastes, application of pesticides by farmers, leaks of radioactive materials, gas emissions into the atmosphere etc.

Few decades back, water was considered to be pure and unpolluted if it was odorless, free from turbidity and good from aesthetic point of view. But now, the whole concept of water pollution has changed. Even if the water is clear, it may be polluted, it may contain dissolved impurities like toxic metals, organic pollutants, radioactive nuclides etc. water pollution may be defined as any change in physical, chemical or biological properties of water [1]. It is the contamination of water by foreign matter that deteriorates the quality of the water.

Almost all Indian cities face chronic water shortage during summer months. Government agencies are increasingly failing to meet the demands of a raising urban population. The water table is falling all the time due to over extraction from ground aquifers, and rivers and other water bodies are increasingly getting polluted, encroached, built upon, and commonly used as defecation grounds or simply outlets for sewage. Even the groundwater quality in many parts of the country has become suspicious. Agricultural, urban and industrial wastes pose a never-ending threat to groundwater. Only 0.06 – 0.07% of the fresh water is readily available as lakes and rivers [2] yet human beings pollute water in all possible ways. As the term applies, water pollution occurs in the oceans, lakes, streams, rivers, underground water and bays, in short water containing areas. It involves the release of toxic substances, pathogenic germs, substances that require much oxygen to decompose, easily soluble substances, radioactive substances etc which deposits at the bottom and their accumulations interferes with the condition of aquatic
ecosystems. One of such interference is eutrophication, lack of oxygen in a water body, caused due to excessive algae growth, which is due to enrichment of pollutants.

Water in the earth’s biosphere is used and reused again and again. This is called water cycle or continuous movement of water between the earth and the atmosphere. It involves the following mechanisms (Figure 1.2):

» **Evaporation:** Changing of water from liquid to gas

» **Transpiration:** Release of water vapor from plant leaves

» **Condensation:** Changing of vapor to liquid (cooled down)

» **Precipitation:** Water that returns to the earth (water droplets in clouds become large enough and then it rains).

Figure 1.2 Sources of groundwater contamination
HARMFUL EFFECTS OF WATER POLLUTION

According to the water cycle, water around us gets absorbed to the land (soil) and rivers move from upstream to downstream and released to the sea. Normally, organic pollutants are biodegraded by microbes and are converted to a form that brings benefits to the aquatic life. And the inorganic pollutants, in the same situation, don’t bring too much hazards because they are widely dispersed and have almost no effect to the environment to which they are released. In a small scale, both inorganic and organic pollutants safely decompose throughout the stream, their concentration decrease in the sea, and they don’t harm the sea ecosystem and its distribution. But in an excessive scale, communities in beach and estuary will be affected by the pollutants, and can heavily harm them.

Pathogenic microorganism may enter the water body along with sewage and other wastes and may cause tremendous damage to public health. Disease-causing (pathogenic) microorganisms, like bacteria, viruses and protozoa can cause swimmers to get sick. Fish and shellfish can become contaminated and people who eat them can get ill. These microbes, comprising mainly of viruses and bacteria, can cause dangerous water-borne diseases such as cholera, typhoid, dysentery, polio and infectious hepatitis in humans.

Chemical such as synthetic pesticides, synthetic detergents, food additives, pharmaceuticals, insecticides, paints, synthetic fibers, elastomers, solvents, plasticizers, plastics, and other industrial chemicals may enter the hydrosphere either by spillage during transport and use or by intentional or accidental release of waste from their manufacturing establishments. Most of these chemicals are potentially toxic to plants, animals and humans. Some bio refractory (i.e., resistant to microbial degradation) organics such as aromatic chlorinated hydrocarbons may cause offensive colors, odors and taste in water, even when present in traces and make the water unacceptable from aesthetic point of view. Non-degradable chemicals, such as alkyl benzene sulphonate from synthetic detergents often lead to persistent foams. Volatile substances such as alcohols, aldehydes, ethers and gasoline may cause explosion in sewers. The Niagara River, between the US and
Canada, even caught fire at one time because of flammable chemicals wastes discharged into the water [3]. Pesticides used in agriculture and around the home insecticides for controlling insects and herbicides for controlling weeds are another type of toxic chemical. Some of these can accumulate in fish, shellfish and other aquatic animals and enter the food chain.

The presences of toxic organic and inorganic substances are gradually increasing in water and waste water, as the result of its wide spread use in diversified area. Owing to indiscriminate abuse, many water bodies have become sewers because municipal and industrial waste is dumped in them with little or hardly any treatment. Thus the water resource needs to be conserved and the industrial effluent needs to be recycled. Therefore, the concept of reuse, recycle, and reduce have been very well conceived by industries, efforts in this direction need to be accelerated.

CLASSIFICATION OF WATER POLLUTANTS

‘Pollutant’ may be defined as a physical, chemical or biological component that changes the natural quality of environment in such a way that it tends to be injurious to the whole living biota. As this thesis deals with the characterization and removal of pollutants from the wastewater, only the pollutants generally present in the wastewater are described. As a result of industrial, agricultural and domestic activities, a number of inorganic and organic chemicals, biological active agents and heat may be thrown out into the water. All these additions cause pollution and the nature of pollutants in wastewater varies from place to place depending upon the type of activity that has produced the wastewater.

It is essential to understand the sources, interactions and effect of water pollutants for controlling them in an environmentally safe and economically acceptable manner. Water pollutants can be divided among general classifications, as summarized in Table 1.1.


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### Table 1.1 General types of water pollutants

<table>
<thead>
<tr>
<th>Class of Pollutants</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trace elements</td>
<td>Health, aquatic biota</td>
</tr>
<tr>
<td>Heavy metals</td>
<td>Health, aquatic biota</td>
</tr>
<tr>
<td>Organically bound metals</td>
<td>Metal transport</td>
</tr>
<tr>
<td>Radio nuclides</td>
<td>Toxicity</td>
</tr>
<tr>
<td>Inorganic pollutants</td>
<td>Toxicity, aquatic biota</td>
</tr>
<tr>
<td>Asbestos</td>
<td>Human health</td>
</tr>
<tr>
<td>Algal nutrients</td>
<td>Eutrophication</td>
</tr>
<tr>
<td>Acidity, alkalinity, salinity (in excess)</td>
<td>Water quality, aquatic life</td>
</tr>
<tr>
<td>Trace organic pollutants</td>
<td>Toxicity</td>
</tr>
<tr>
<td>Polychlorinated biphenyls</td>
<td>possible biological effects</td>
</tr>
<tr>
<td>Pesticides</td>
<td>Toxicity, aq. biota, wildlife</td>
</tr>
<tr>
<td>Petroleum wastes</td>
<td>Effect on wildlife, esthetics</td>
</tr>
<tr>
<td>Sewage, human, and animal waste</td>
<td>Water quality, oxygen levels</td>
</tr>
<tr>
<td>Biochemical oxygen demand</td>
<td>Water quality, oxygen levels</td>
</tr>
<tr>
<td>Pathogens</td>
<td>Health effects</td>
</tr>
<tr>
<td>Detergents</td>
<td>Eutrophication, wildlife, esthetics</td>
</tr>
<tr>
<td>Chemical carcinogens</td>
<td>Incidence of cancer</td>
</tr>
<tr>
<td>Sediments</td>
<td>Water quality, aq. biota, wildlife</td>
</tr>
<tr>
<td>Taste, odor, color</td>
<td>Esthetics</td>
</tr>
</tbody>
</table>

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**ELEMENTAL POLLUTANTS**

Elements that occur at very low levels of a few parts per million or less in a given system are known as Trace elements. The term trace substance is a more general one applied to both elements and chemical compounds [4]. Some of these are recognized as nutrients required for animal and plant life. Of these, many are essential at low levels, but toxic at higher levels. This is typical behavior of many substances in aquatic environment. Thus it is a point that must be kept in mind in judging whether a particular element is beneficial or detrimental. Some of these elements, such as lead or mercury, have such toxicological and environmental significance.

Some of the heavy metals are among the most harmful of the elemental pollutants. These heavy metals in concentration higher than permissible limits are introduced into the surface water by the wastewater from many industries and show significant toxic effects [5] and therefore, needs to be removed. These elements in
general are the transition metals and some of the representative elements, such as lead and tin, in the lower right hand corner of the periodic table. Heavy metals include essential elements like iron as well as toxic metals like cadmium and mercury.

Some of the metalloids, elements on the borderline between metals and non-metals, are significant water pollutants. Arsenic, selenium, and antimony are of particular interest. Inorganic chemical manufacturing units contaminate water with trace elements.

ORGANIC POLLUTANTS

Organic pollutants include dyes, phenols, detergents, pesticides, aromatic hydrocarbons, polychlorinated biphenyls and other organic chemicals [6]. These organic compounds enter into the water streams and undergo degradation and putrefaction by bacterial activity. They consume dissolved oxygen and cause marked decrease in its content. The decrease in dissolved oxygen content is an indication of water pollution, generally caused by organic chemicals. Some of the common organic pollutants are discussed in brief here.

*Dyes*

Dyes are widely used for both domestic and industrial purposes. The use of natural dyes dates back to much before the signs of first civilization. However, with the invention of synthetic dyes [7], various forms of dyes are manufactured and consequently used for specific purposes. Dyes are important water pollutants which are generally present in the effluents of textile, leather, food processing, dyeing, cosmetics, paper and dye manufacturing industries. They are synthetic aromatic compounds which are embodied with various functional groups. The worldwide high level of production and extensive use of dyes generates coloured wastewaters which give cause of environmental pollution. The coloured dye effluents are generally considered to be highly toxic to the aquatic biota and affect the symbiotic
process by disturbing the natural equilibrium through reducing photosynthetic activity due to the colouration of the water in streams. Dyes are considered obnoxious type of pollutants because (i) they impart color to water which is not acceptable due to aesthetic consideration and (ii) adversely affect life due to toxic effects. The nonbiodegradable, toxic and inhibitory nature of the spent dye bath has considerable deleterious effect on the environmental matrix (water and soil). Some dyes are reported to cause allergy, dermatitis, skin irritation, cancer and mutation in humans \[8\]. Thus, the removal of dyes from effluents is important \[9, 10\] before they are mixed up with unpolluted natural water bodies.

**Phenols**

Among the various aqueous pollutants generally present in wastewaters, phenols and substituted phenols are considered priority pollutants, as they impart bad taste and odour to water and are also toxic even at low concentrations. Phenol is a basic structural unit for variety of synthetic organic compounds and therefore, wastewater originating from many chemical plants, pesticide and dye manufacturing industries contain phenol. Besides this, wastewater originating from other industries like pulp and paper, resin manufacturing, gas and coke manufacturing, tanning, textile, plastics, rubber, pharmaceutical and petroleum also contain different types of phenols. Wastewaters also contain phenols formed as a result of decay of vegetation. The removal of phenols from effluents is considered essential before they are discharged due to their toxicity, taste and odour imparted to water \[11, 12\].

**Pesticides**

It was realized in the early period of human civilization, that pests harm crops and transmit diseases both to men and animals. The use of chemicals to kill pests dates back to 70 A.D., when arsenic was utilized to kill insects. Arsenic compounds were continued to be used as lead-arsenate on a large scale during
The introduction of DDT during World War II marked a very rapid growth in the use of pesticides. The era of synthetic organic pesticides started around 1940. At present, there are more than 10,000 different pesticides. Depending on their functions, pesticides are available with different names, such as insecticides, molluscicides, nematicides, rodenticides, avicides, piscicides, fungicides, bactericides, slimicides, algicides, and herbicides. Amongst these, insecticides and fungicides are important pesticides with respect to human food exposure because they are applied shortly before or even at harvesting of the crops. Herbicide production has increased significantly as these chemicals are being increasingly used during cultivation of land for controlling weeds, and now account for majority of agricultural pesticides. Subsequent research showed that there were appreciable quantities of pesticide residues in the biota and moreover, in certain birds, mammals and human beings. Pesticides are very harmful and dangerous because of their toxic and carcinogenic nature. The removal of pesticides has been studied by sorption processes [13, 14]. The long-term ecological hazards of the persistent pesticides led to restrictions or ban on their use in many countries of the world. Though DDT has been banned, its various substitutes like toxaphene, lindane, parathion, malathion, heptachlor, endrin etc. are still in use and cause environmental pollution.

**Soaps and Detergents**

Soaps, detergents, and associated chemicals are potential sources of organic pollutants. Soaps are salts of higher fatty acids, such as sodium stearate. The cleaning action of soap results largely from its emulsifying power and its ability to lower the surface tension of water. The primary disadvantage of soap as a cleaning agent comes from its reaction with divalent cations to form insoluble salts of fatty acids. As soon as soap gets into sewage or an aquatic system, it generally precipitates as calcium and magnesium salts. Hence, any effects that soap might have in solution are eliminated. With eventual biodegradation, the soap is completely eliminated from the environment. Therefore, aside from the occasional
formation of unsightly scum, soap does not cause any substantial pollution problems.

Synthetic detergents have good cleaning properties and do not form insoluble salts with “hardness ions” such as calcium and magnesium. The key ingredient of detergents is the surfactant, which acts in effect to make water ‘wetter’ and a better cleaning agent. Until 1960s, the most common surfactant used was an alkyl benzene sulphonate, ABS, which suffered the distinct disadvantage of being only very slowly biodegradable because of its branched-chain structure. ABS was replaced by a biodegradable surfactant known as linear alkyl sulphonate, LAS. A commercial solid detergent contains only 10-30% surfactant. In addition, some detergents still contain polyphosphates added to complex calcium and to function as a builder. Other ingredients include ion exchanger, alkalies, anticorrosive sodium silicates, amide foam stabilizers, soil dyes and diluent sodium sulphate. Of these materials, the polyphosphates have caused the most concern as environmental pollutants, although these problems have largely been resolved. Many techniques have been used and developed to remove surfactants from wastewater. Removal of surfactants by sorption has been studied by various researchers [15, 16]. Wastewater contaminated with detergents carries a huge cap of foam. This visible foam is not acceptable on aesthetic considerations.

Polychlorinated Biphenyls

Polychlorinated biphenyls (PCB compounds) have been found throughout the world in water, sediments, bird tissue and fish tissue. These compounds constitute an important class of special wastes. Polychlorinated biphenyls have high chemical, thermal and biological stability; low vapour pressure; and high dielectric constants. These properties led to the use of PCBs as coolant-insulation fluids in transformers and capacitors; for the impregnation of cotton and asbestos; as plasticizers; and as additives to some epoxy paints. They do not cause biochemical oxygen demand problem in aquatic ecosystem, but are extremely toxic [17].
THERMAL POLLUTANTS

Thermal pollution of water may be defined as “Heated effluents, either from natural or man-made sources, contaminated with water supplies may be harmful to life because of their toxicity, reduction of normal oxygen level of water, aesthetically unsuitable and spread diseases”. The term thermal pollution has been used to indicate the detrimental effects of heated effluents discharged by various power plants. It denotes the impairment of quality and deterioration of aquatic and terrestrial environment. Various industrial plants like thermal, atomic, nuclear, coal fired plants, oil field generators, factories, and mills utilize water for cooling purposes.

The heated effluents are discharged at a temperature 8°C to 10°C higher than the temperature of intake waters. About 80% of the total water withdrawn for industrial operations is used for cooling only. The water drawn is discharged substantially unchanged except for an increase in temperature. The heated water discharged in rivers, lakes, streams and ponds etc. have reduced concentration of dissolved oxygen which produces distinct changes in aquatic biota, bacteria, protozoa, micro-organisms, organic matter production and has over all deleterious effects on the ecosystem.

RADIOACTIVE POLLUTANTS

The massive production of radioactive isotopes by weapons and nuclear reactors has been accompanied by increasing concern about the effects of radioactivity upon health and environment. Radionuclides are produced as fission products of heavy nuclei of such elements as uranium or plutonium. They are also produced by the reaction of neutrons with stable nuclei. Artificially produced radionuclides are also widely used in industrial and medical applications, particularly as ‘tracers’. With so many possible sources of radionuclides, it is impossible to entirely eliminate radioactive contamination of aquatic systems. Furthermore, radionuclides may enter aquatic systems from natural sources.
Therefore, the transport, reactions and biological concentration of radionuclides in aquatic ecosystems are of great importance to the environmental chemist.

Radio-nuclides once present in water bodies disrupt the eco-cycling process, enter into food chain and affect metabolic pathways. Radiation damages living organisms by initiating of harmful chemical reactions in tissues. For example, bonds are broken in the macromolecules that carry out life processes. As the use of nuclear power has increased, the possible contamination of water by fission-product radioisotopes has become more of a cause for concern.

BIOLOGICAL POLLUTANTS

The biological pollutants (pathogenic bacteria, viruses, etc.) transmit several diseases to man through contaminated water supplies [19]. The common and severe diseases are dysentery, typhoid, cholera, gastroenteritis, jaundice, leptospirosis, etc. The dangerous pathogenic disease spreading bacteria are Salmonella typhosa, Leptospira, Vibrio comma, Escherichia coli, Tuberculosis, etc. The common viruses present in polluted waters and sewage are Adenoviruses, Enteroviruses, Polioviruses and Hepatitis viruses. Most dreadful virus disease is poliomyelitis, in which body parts get paralyzed due to the destruction of certain nerve cells controlling the muscles.

METHODS FOR WATER POLLUTION CONTROL

Water treatment process selection is complex task involving the consideration of many factors which include available space for the treatment facilities, reliability of process equipment, waste disposal constraints, desired finished water quality and capital and operating cost. Wastewater to be treated must be characterized fully, particularly with a thorough chemical analysis of possible waste constituents and their chemical and metabolic products.

The treatment of wastewaters to make them suitable for subsequent use requires physical, chemical, and biological processes. A number of methodologies
are available with varying degree of success to control water pollution. Some of these physio-chemical processes have been developed, such as coagulation [20], reverse osmosis [21], electrochemical oxidation and membrane filtration [22], ion exchange [23], biological methods [24], solvent extraction [25], sorption [26], foam flotation [27], advanced oxidation processes [28], electro dialysis [29], etc. A particular treatment may not be effective sometimes in removing all pollutants and in such cases; a number of processes may be used in conjunction, so that all type of pollutants can be tackled.

Effluents with sturdy color and high COD are common in chemical process industries such as textile, paper, leather and mineral processing industries. In textile industries, dyeing and finishing are the two most important process operations which consumes large amount of water and generates considerable amount of wastewater which contains strong color, suspended particles, high pH and high COD and BOD. The textile effluent cannot be treated by chemical methods as these techniques generate considerable amount of sludge, which itself requires further treatment. While the biological methods are cheap and simple to apply, but cannot be applied to textile wastewaters since most of the commercial dyes are non-biodegradable and toxic to the organisms resulting in sludge bulking. On the other hand the advanced techniques such as reverse osmosis/ultra-filtration have the disadvantages of high cost and low throughput.

Among physio-chemical processes, sorption technology is considered to be the most effective and proven technology having wide potential applications in both water and wastewater treatment [30]. Sorption process is considered better because of convenience, easy operation and simplicity of design. Sorption is now widely accepted as an effective purification method for the treatment of wastewater. Further, this process can remove/minimize different type of pollutants and thus it has a wider applicability in pollution control. As the present thesis deals with removal of pesticides from aqueous solution by sorption, the literature on sorption methodology has been surveyed.
ADSORPTION PROCESS

The term adsorption was proposed by Bios-Reymond but introduced into the literature by Kayser [31]. Ever since then, the adsorption process has been widely used for the removal of solutes from solutions and harmful gases from atmosphere. Adsorption process is efficient for the removal of organic matter from waste effluents. Adsorption is the physical and/or chemical process in which a substance is accumulated at an interface between two phases. For the purposes of water or wastewater treatment, adsorption from solution occurs when impurities in the water accumulate at a solid-liquid interface. The substance which is being removed from the liquid phase to the interface is called as sorbate and solid phase in the process is known to be sorbent.

The use of term ‘sorption’ instead of adsorption became common in 19th century, for the surface activities. Sorption is defined as being the attraction of an aqueous species to the surface of a solid. Sorption is a rapid phenomenon of passive sequestration of sorbate from an aqueous/gaseous phase onto a solid phase. Sorption occurs between two phases in transporting pollutants from one phase to another. It is considered to be a complex phenomenon and depends mostly on the surface chemistry or nature of the sorbent, sorbate and the system conditions in between the two phases. Sorption processes offer the most economical and effective treatment method for removal of pollutants. The process is often carried out in a batch mode, by adding sorbent to a vessel containing contaminated water, stirring the mixture for a sufficient time, then letting the sorbent settle and drawing off the cleansed water.

At the surface of the most solids, there are unbalanced forces of attraction which are responsible for sorption. In cases where the sorption is due to weak Van der Waals forces, it is called physical sorption which is reversible in nature with low enthalpy values. On the other hand, in many systems there may be a chemical bonding between sorbate and sorbent molecule. Such type of sorption is chemisorption. As a result of chemical bonding, the sorption is irreversible in nature and has high enthalpy of sorption.

Sorption phenomenon is operative in most natural physical, biological and
chemical systems. Sorption operations employing solids such as activated carbon and synthetic resins are used widely in industrial applications and for purification of waters and wastewaters.

Physical sorption (physisorption) is relatively non-specific and is due to the operation of weak forces between molecules. In this process, the sorbed molecule is not affixed to a particular site on the solid surface; it is free to move over the surface. The physical interactions among molecules, based on electrostatic forces, include dipole-dipole interactions, hydrogen bonding and dispersion interactions. When there is a net separation of positive and negative charges within a molecule, it is said to have a dipole moment. Molecules such as H₂O and N₂ have permanent dipoles because of the configuration of atoms and electrons within them. Hydrogen bonding is a special case of dipole-dipole interaction and hydrogen atom in a molecule has a partial positive charge. Positively charged hydrogen atom attracts an atom on another molecule which has a partial negative charge. When two neutral molecules which have no permanent dipoles approach each other, a weak polarization is induced because of interactions between the molecules, known as the dispersion interaction [32].

In water treatment, sorption of an organic sorbate from polar solvent (water) onto a nonpolar sorbent (carbonaceous material) has an often interest. In general, attraction between sorbate and polar solvent is weaker for sorbates of a less polar nature; a nonpolar sorbate is less stabilized by dipole-dipole or hydrogen bonding to water. Nonpolar compounds are sorbed more strongly to nonpolar sorbents. This is known as hydrophobic bonding. Hydrophobic compounds sorb on to carbon more strongly. Longer hydrocarbon chain is more nonpolar, so, degree of this type of sorption increases with increasing molecular length [32].

Additionally, branched chains are usually more sorbable than straight chains, an increasing length of the chain decreases solubility. An increasing solubility of the solute in the liquid decreases its sorbability. For example, a hydroxyl group generally reduces sorption efficiency. Carboxyl groups have variable effects according to the host molecule. Double bonds affect sorbability of organic compounds depending on the carboxyl groups. The other effective factor
on sorption is molecular size [33]. Aromatic and substituted aromatic compounds are more sorbable than aliphatic hydrocarbons [34].

Chemical sorption (chemisorption) is also based on electrostatic forces, but much stronger forces act a major role on this process [35]. In chemisorption, the attraction between sorbent and sorbate is a covalent or electrostatic chemical bond between atoms, with shorter bond length and higher bond energy [32].

The enthalpy of chemisorption is very much greater than that for physisorption and typical values are in the region of 200 kJ/mol, whereas this value for physisorption is about 20 kJ/mol. Except in the special cases, chemisorption must be exothermic. A spontaneous process requires a negative free energy (ΔG) value. Because, the translational freedom of the sorbate is reduced when it is sorbed, entropy (ΔS) is negative. Therefore, in order for ΔG to be negative, ΔH must be negative and the process exothermic. If the enthalpy values less negative than -25 kJ/mol, system is physisorption and if the values more negative than -40 kJ/mol it is signified as chemisorption [36].

**Table 1.2 The bond energies of various mechanisms for the sorption**

<table>
<thead>
<tr>
<th>Interaction between sorbent and sorbate</th>
<th>Enthalpy (kJ/mol)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- ΔH</td>
<td>+ ΔH</td>
</tr>
<tr>
<td>Electrostatic chemical bonding</td>
<td>&gt; 40</td>
<td>&gt; 200 chemisorption</td>
</tr>
<tr>
<td>Dispersion interactions and hydrogen bonding</td>
<td>8 -40</td>
<td>physisorption</td>
</tr>
<tr>
<td>Dipole-dipole interaction</td>
<td>&lt; 8</td>
<td>&lt; 20 physisorption</td>
</tr>
</tbody>
</table>

** ADSORPTION VERSUS ABSORPTION**

Adsorption is a process that occurs when a gas or liquid or solute (called adsorbate) accumulates on the surface of a solid or more rarely a liquid (adsorbent), forming a molecular or atomic film (adsorbate) layer. It is different from absorption, where a substance diffuses into a liquid or solid to form a solution.
Absorption is the process by which atoms/molecules or ions enter a bulk phase of the whole volume of the absorber. Figure 1.3 shows the primary differences between the absorption and adsorption. The main difference being that, in adsorption, contaminant particles are attracted to the outer surface of the particle, while in absorption they are actually incorporated into the particle's structure.

**Figure 1.3** Differences between Adsorption and Absorption

Absorption at the microscopic scale commonly involves adsorption at the nanoscopic scale. For example, a molecule of water adsorbed on the surface of a single crystal/grain is part of the water absorbed in a mass of those crystals/grains (Figure 1.4).

**Figure 1.4** Sorption: Adsorption and Absorption
To design a sorption system, it is essential to understand the process of sorption mechanism, so that optimization can be achieved. It is also important to understand the sorption mechanism for effective activation and regeneration of the sorbents.

**MECHANISM OF SORPTION**

The mechanism of sorption on the sorbent in removal process involves the following three steps: (1) diffusion of sorbate molecules through the solution onto the surface of the sorbents, (2) sorption of sorbate molecules on the surface of the sorbents through molecular interactions and (3 and 4) diffusion of sorbate molecules from the surface into the interior of the sorbent materials either monolayer or multi layer. The concentration of sorbate and agitation may affect the first step of sorption. The second step is dependent on the nature of the sorbate molecules, such as anionic and cationic structures. The third step is usually considered as the rate determining stage in the sorption process, which certainly should affect the sorption of sorbate on the substrates.

Resistance to mass transfer in sorption processes can be described by two processes, resistance due to external mass transfer through the particle boundary layer and resistance due to intraparticle diffusion. The external mass transfer has been described by two methods using linear and nonlinear isotherms [37]. The major differences in the two resistance models are due to the mechanism of intraparticle diffusion proposed, namely pore diffusion, solid diffusion or a combination of both. Solid phase diffusion is the dominant effect in intraparticle mass transfer. The film homogeneous solid diffusion model assumes external mass transfer dominance in the initial stages of sorption.

Sorption phenomena are dependent on experimental conditions like pH, temperature, sorbent dose, sorbent particle size, surface morphology of sorbent, sorbate concentration and type and structures of the sorbates.
Figure 1.5 Mechanism of sorption process
LITERATURE REVIEW

SORBENTS FOR POLLUTION CONTROL OF WASTEWATER

The extent of sorption depends on the nature of sorbent especially porosity and surface area [38]. As such, various sorbents showing higher and sometimes selective sorption capacity have been developed. Most sorbents which have been used in pollution control tend to have porous structure. The porous structure not only increases surface area and consequently sorption, but also affects the kinetics of the sorption. A better sorbent is considered the one which has high surface area and time for sorption equilibrium is small enough, so that the pollutants can be removed in lesser time. Thus, for the removal of pollutants, one generally looks to sorbents with high surface area and faster kinetics. The most common industrial sorbents are activated carbon, silica gel and alumina, because they present enormous surface area per unit weight. Some of the important sorbents used in pollution control and various industrial operations are discussed herein.

SILICA GEL

Silica gel, prepared by the coagulation of colloidal silicic acid results in the formation of porous and noncrystalline granules of different sizes. Silica gel is a coherent, rigid, continuous three dimensional network of spherical particles of colloidal silica. Both siloxane, \(-\text{Si-O-Si}\) and silanol, \(-\text{Si-O-H}\), bonds are present in the gel structure. Silica gels are classified into three types – regular density, intermediate density, and low density gels. Regular density silica gel is prepared in an acidic media and show high surface area (750 m\(^2\)/g). Intermediate and low density silica gels have low surface areas (300-350 m\(^2\)/g and 100-200 m\(^2\)/g respectively). The gel is considered good to be a sorbent [39]. Alexander and McKay [40] investigated the sorption of basic dyes onto silica. Although the sorption capacities were high but the drawback was that silica is expensive sorbent.
ACTIVATED ALUMINA AND BAUXITE

Activated alumina comprises of partially hydroxylated alumina oxide, $\text{Al}_2\text{O}_3$. They are porous solids made by the thermal treatment of aluminum hydroxide precursors and find applications mainly as sorbent, catalyst and catalyst supports. In general, as a hydrous alumina precursor is heated, hydroxyl groups are driven off leaving a porous solid structure of activated alumina. One of the earliest uses for activated alumina was removal of water vapor from gases and this remains as an important application. Activated alumina having the surface area ranging from 200-300 $\text{m}^2/\text{g}$, is a versatile sorbent. It is also used to remove water from organic liquids including gasoline, kerosene, oils, aromatic hydrocarbons, and many chlorinated hydrocarbons. Activated alumina is receiving renowned attention as a sorbent [41]. Alumina has been studied by Haung et al. for the removal of dyes [42].

On the other hand, bauxite consists of mainly aluminum hydroxide minerals but also contains small and variable amounts of silica, iron oxides- hematite, $\text{Fe}_2\text{O}_3$ and magnetite, $\text{Fe}_3\text{O}_4$, rutile or titanium oxide and alumina silicate clays. It is widely used in place of alumina [43]. Its surface area ranges from 25-250 $\text{m}^2/\text{g}$.

ION EXCHANGE RESINS

Organic ion exchange resins having cross linked hydrocarbon matrix and derivatized with inorganic group are the most common ion exchange materials used in industrial applications. The majority of the commercial resins are based on the styrene-divinylbenzene structure because of its good resistance against chemical and physical stress. The nature of ionogenic groups can vary from strong acidic cation exchangers [$\text{R-SO}_3^-$] to strong basic anion exchangers [$\text{R-N}^+(\text{CH}_3)_3$] and to chelate forming exchangers. There are also active groups which have no electric charge but donor atoms attract cations by donating free electron pairs to form coordination bonds. Ionogenic, chelating, and complex forming active groups may be called functional groups.
Chapter-1 Introduction and Literature Review

The main object of the most of the research on chelating resins is preparation of insoluble functionalized polymers which can provide more flexible working conditions together with good stability and high capacity for certain metal ions [44, 45]. A number of ion-exchange resins have been used for the removal of specific compounds. The primary applications of ion exchange resins are the softening and deionization of water. Other applications are wastewater treatment, catalysis, purification of chemicals and pharmaceuticals etc. Recently, anion exchange resins have been used by Karcher et al. [46] for removal of dyes.

Chelating ion exchange resins have ionogenic groups, which can form coordination bonds with metals, their donor atoms are usually sulfur, nitrogen or both in the same group. The bonds formed in this kind of metal sorption usually have both covalent and ionic characteristics. The sorption properties of chelating resins are well known and documented [47]. Probably, the best property of the chelating resins is their selectivity towards transition metals and the weakly acidic nature of chelating groups makes the regeneration step with mineral acid quite easy. Sengupta recommends such complex forming resins for removing trace amounts of metal cations from the background of very high concentrations of competing alkaline and alkaline earth metal ions at acidic pH [48]. Resins seem to have several favorable properties, but there are some important reasons why the resins are not used. Firstly, the resins are expensive. Secondly, the resins are prone to fouling by organics which are predominant in wastewater.

ACTIVATED CARBON

Activated carbon is an amorphous carbon in which a high degree of porosity has been developed during its manufacture. It is this porosity, which governs the way in which activated carbon performs its purifying role, the very large surface area provides many sites upon which the sorption of impurity molecule can take place. Activated carbon has become the water industry’s standard sorbent for the reclamation of municipal and industrial wastewaters to a potable water quality.
Activated carbon is produced by a process consisting of raw material dehydration and carbonization followed by activation. The activated carbon used in wastewater treatment is generally prepared from coconut shells [49], peat [50], sawdust, wood char, lignin, petroleum coke [51], bone char, anthracite coal [52] etc.

Based on its size and shape, there are four types of activated carbon: powdered activated carbon (PAC), granular activated carbon (GAC), activated carbon fibrous (ACF) and activated carbon cloth (ACC). PAC offers some practical problems because of separation requirement of the sorbent from the fluid. However, in spite of these problems, PAC is also used for wastewater treatment due to low cost and lesser time requirements [53].

The activated carbons which are used as sorbents, not only remove different types of dyes [54, 55] but also other organic and inorganic pollutants such as metal ions [56], phenols [57], detergents [58], pesticides [59], humic substances, chlorinated hydrocarbons and many other chemicals and organisms.

Amongst all the sorbent materials proposed, activated carbon is the most popular for the removal of pollutants from wastewater [60, 61]. In particular, the effectiveness of sorption on commercial activated carbons (CAC) for removal of a wide variety of dyes from wastewaters has made it an ideal alternative to other expensive treatment options [61]. Ozacar et al. [54] investigated calcined alunite’s performance against that of granular activated carbon for the sorption of acid dyes from aqueous solutions. The results indicated that for the removal of acid dye, calcined alunite was most effective sorbent, although comparable dye removals were exhibited by granular activated carbon.

Regeneration is the most significant aspect in the use of granular activated carbon and other low cost sorbents. The most common technique practiced in regeneration is thermal decomposition and steam carbon reaction [62]. Besides this, chemical regeneration has also been tried. Srivastava et al. [63] observed that 5% NaOH can be used to remove 96% of phenol loaded on the carbon column and a treatment with 1M HNO₃ reactivates the sorbent particles which can be used for 6-10 cycles.
Chapter-1 Introduction and Literature Review

However, activated carbon presents several disadvantages [58]. It is quite expensive, the higher the quality, the greater the cost, non-selective, and ineffective against disperse and vat dyes. The regeneration of saturated carbon is also expensive, not straightforward and results in loss of the sorbent. The use of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications [64]. This has led many workers to search for more economic sorbents.

LOW COST SORBENTS

Natural materials or the wastes/by-products of industries or synthetically prepared materials, which cost less and can be used as such or after some minor treatment as sorbents are generally called low-cost sorbents. Conversion of these materials into activated carbon, which can be used as a sorbent for water purification, would improve economic value, helping industries to reduce the cost of waste disposal and providing a potential alternative to activated carbon. A wide variety of materials have been investigated for this purpose and they can be classified into three categories; (i) natural materials (ii) agricultural wastes and (iii) industrial wastes. The materials are generally available free of cost or cost little as compared to activated carbons.

NATURALLY OCCURRING MATERIALS AS SORBENTS

Various naturally occurring materials are available in large quantities having characteristics of a sorbent. The abundance of these materials in most continents in the world and their low cost make them strong candidate as sorbents for the removal of many pollutants from the wastewaters. Among the various naturally occurring sorbents, zeolite, siliceous materials, and clay are widely used.
Zeolite

Zeolites are important microporous sorbents, which are found naturally and are prepared synthetically too. The classical definition of a zeolite is a crystalline, porous aluminosilicate. However, some relatively recent discoveries of materials virtually identical to the classical zeolite, but consisting of oxide structures with elements other than silicon and aluminum have stretched the definition. In their definition of zeolite, most researchers now include virtually all types of porous oxide structures that have well-defined pore structures due to a high degree of crystallinity.

In these crystalline materials we call as zeolites, the metal atoms (classically, silicon or aluminum) are surrounded by four oxygen anions to form an approximate tetrahedron consisting of a metal cation at the center and oxygen anions at the four apexes. The tetrahedral metals are called T-atoms for short, and these tetrahedra then stack in beautiful, regular arrays in such a way that channels will form. The possible ways for the stacking to occur is virtually limitless and hundreds of unique structures are known. The size and shape of the channels have extraordinary effects on the properties of these materials for sorption processes and this property leads to their use in separation processes. Molecules can be separated via shape and size effects related to their possible orientation in the pore or by differences in strength of sorption.

Zeolites consist of a wide variety of species. There are about 40 natural and more than 140 synthetic species of zeolites. The characteristics and applications of zeolites have been reviewed by Ghobarkar et al. [65]. High ion-exchange capacity and relatively high specific surface areas and more importantly their relatively cheap prices, make zeolites attractive sorbents. Their price is about US$ 0.03–0.12/kg, depending on the quality of the mineral [60]. Another advantage of zeolites over resins is their ion selectivities generated by their rigid porous structures. Zeolites are becoming widely used as alternative materials in areas where sorptive applications are required. They have been intensively studied recently because of their applicability in removing trace quantities of pollutants.
such as heavy metal ions and phenols, due to their cage-like structures suitable for ion exchange.

Zeolites also appear as suitable sorbents for dyes. Several studies have been conducted on the sorbent behavior of natural zeolites [65-69]. However, raw clinoptilolite was not suitable for the removal of reactive dyes due to extremely low sorption capacities [69, 70]. Similar conclusions have been found by Ozdemir et al. and Benkli et al. [66, 71]. These authors suggested chemical modification with quaternary amines as a means of increasing sorption.

In spite of the promising results, the real applicability of these natural materials to purify dye waste waters is still quite unknown. The sorption mechanism on zeolite particles is complex because of their porous structure, inner and outer charged surfaces, mineralogical heterogeneity, and other imperfections on the surface [67, 72]. However, it is recognized that the sorption properties of zeolites result mainly from their ion-exchange capabilities. Although the removal efficiency of natural zeolites for dyes may not be as good as that of clay materials, their easy availability and low cost may compensate for the associated drawbacks.

Clay

Among natural materials, clay occupies a prominent position being low cost, available in abundance and having good sorption properties. Clay materials possess a layered structure and are considered as host materials. They are classified by the differences in their layered structures. There are several classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pyrophyllite (talc), vermiculite and sepiolite [73]. The sorption capabilities result from a net negative charge on the structure of minerals. This negative charge gives clay the capability to sorb positively charged species. Their sorption properties also come from their high surface area and high porosity [74]. Montmorillonite clay has the largest surface area and the highest cation exchange capacity. Its current market price (about US$ 0.04–0.12/kg) is considered to be 20 times cheaper than that of activated carbon [60]. In recent years, there has been an increasing interest in
utilizing clay minerals such as bentonite, kaolinite, diatomite, and Fuller’s earth for their capacity to sorb not only inorganic but also organic molecules. In particular, interactions between dyes and clay particles have been extensively studied [75-80].

Clay minerals exhibit a strong affinity for both heteroatomic cationic and anionic dyes. However, the sorption capacity for basic dye is much higher than for acid dye because of the ionic charges on the dyes and character of the clay. The sorption of dyes on clay minerals is mainly dominated by ion-exchange processes. This means that the sorption capacity can vary strongly with pH. Al-Ghouti et al. [81] showed that the mechanism of sorption of dye onto diatomite is due to physical sorption (depending on the particle size) and the presence of electrostatic interactions (depending on the pH used). High capability of clay materials to take up dye has been demonstrated. Espantaleon et al. [82] reported that a sorption capacity of 360.5 mg of dye/g was achieved by bentonite. Due to its high surface area, it was suggested that bentonite is a good sorbent for (basic) dye removal. Similar results have been published by Bagane and Guiza [83]. It was found that 1 g bentonite could sorb 300 mg of basic blue 9. The sorption of dyes on kaolinite was also studied. The sorption to kaolinite was about 20 times greater than to alumina [84]. The removal performances for basic blue 9 on Fuller’s earth and CAC were compared by Atun et al. [85]. They showed that the sorption capacity is greater on Fuller’s earth than on CAC. Moreover, Fuller’s earth is an interesting sorbent since its average price is US$ 0.04/kg whereas cost of CAC is US$ 20/kg. Shawabkeh and Tutunji [86] studied the sorption of basic blue 9 onto diatomaceous earth (diatomite). They showed that this naturally occurring material could substitute for activated carbon as a sorbent due to its availability and low cost, and its good sorption properties. The feasibility of using diatomite for the removal of the problematic reactive dyes was also investigated by Al-Ghouti et al. [81]. The sorption of acid blue 9 onto mixed sorbent (activated clay and activated carbon 12:1) has been studied by Ho and Chiang [87]. As with other materials, clay materials can be modified to improve their sorption capacity. Ozdemir et al. [66] investigated modified sepiolite as a sorbent for a variety of azo-reactive dyes. They showed that the sorption capacities are substantially improved upon modifying their
surfaces with quaternary amines. The sorption capacity of kaolinite can be improved by purification and by treatment with NaOH solution [79]. The acid-treated bentonite showed a higher sorption capacity than non-modified bentonite [82]. Similar results have been published by Ozcan et al. [78]. The results presented above show that clay materials may be promising sorbents for environmental and purification purposes.

Various other naturally occurring biosorbent materials are available in large quantities having characteristics of a sorbent. Some of these biosorbents are chitin and chitosan [88, 89], peat [50, 90], biomass [91], etc. The abundance of these materials in most continents in the world and their low cost make them strong candidate as sorbents for the removal of many pollutants from the wastewaters.

AGRICULTURAL WASTES AS SORBENTS

Raw agricultural solid wastes and waste materials from forest industries such as sawdust and bark have been used as sorbents. These materials are available in large quantities and may have potential as sorbents due to their physico-chemical characteristics and low cost. Sawdust is an abundant by-product of the wood industry that is either used as cooking fuel or as packing material. Sawdust is easily available in the countryside at zero or negligible price [92]. It contains various organic compounds (lignin, cellulose and hemicellulose) with polyphenolic groups that might be useful for binding dyes through different mechanisms. The role of sawdust materials in the removal of pollutants from aqueous solutions has been reviewed by Shukla et al. [93]. Sawdust has proven to be a promising effective material for the removal of dyes from wastewaters [92, 94]. The sorption mechanisms can be explained by the presence of several interactions, such as complexation, ion-exchange due to a surface ionization and hydrogen bonds. One problem with sawdust materials is that the sorption results are strongly pH-dependent [94, 95]. There is a neutral pH beyond which the sawdust will be either positively or negatively charged. Ho and McKay [94] showed that the sorption capacity of basic dye is much higher than that of acid dye because of the ionic
charges on the dyes and the ionic character of sawdust. Khattri and Singh [95] noted that the sorption capacity of Neem sawdust was highly dependent on concentration. Chemical pretreatment of sawdust has been shown to improve the sorption capacity and to enhance the efficiency of sawdust sorption [92].

Another waste product from the timber industry is bark, a polyphenol-rich material. Bark is an abundant forest residue which has been found to be effective in removing dyes from water solutions. Because of its low cost and high availability, bark is very attractive as a sorbent. Morais et al. [96] studied sorption of Remazol BB onto eucalyptus bark from Eucalyptus globulus. Bark is an effective sorbent because of its high tannin content. The polyhydroxy polyphenol groups of tannin are thought to be the active species in the sorption process. The sorption capacity at pH 2.5 and 18°C was found to be 90 mg of dye/g of dry bark. Parallel sorption tests, under similar conditions, carried out with a commercial activated carbon and with bark, showed a half sorption capacity for bark than that of the commercial activated carbon.

Hirata et al. [97] investigated the feasibility of carbonaceous material produced from coffee grounds for the removal of two basic dyes, Methylene blue and gentian violet, and found that the sorption of dyes depended upon the surface polar groups on the carbonaceous material. Pearl millet husk was studied as a sorbent by Inbaraj et al., who reported a sorption capacity 82.37 mg/g for Methylene blue at pH 6.0 [98]. They also reported that Methylene blue sorption is a chemisorption process and formic acid could be used to remove the sorbed dye. Tree fern, an agricultural by-product, has been recently investigated to remove pollutants from aqueous solutions [99]. Tree fern is a complex material containing lignin and cellulose as major constituents. Maximum sorption capacity of tree fern for basic red 13 was 408 mg/g. The capacity increased as the sorbent particle size decreased. The sorption mechanism involves chemical bonding and ion-exchange. Other agricultural solid wastes from cheap and readily available resources such as date pits [100], pith [101], corncob and barley husk [102], wheat straw, wood chips and orange peel [103] have also been successfully employed for the removal of dyes from aqueous solution.
Overall, waste from agricultural sources has demonstrated its ability for dye removal. Chemical modification with an oxidizing agent can enlarge its surface area, thus improving its sorptive capacity. This process requires extra operational cost due to the consumption of chemicals. However, improved sorption capacities of the sorbents may compensate for the cost of additional processing. Compared to sorbents from other sources, those from agricultural waste possess unique characteristics such as ease of regeneration and desorption with basic or acid solutions.

INDUSTRIAL BY-PRODUCTS AS SORBENTS

Widespread industrial activities are producing huge amount of solid waste materials. Some of these materials are being put to use while others find no proper utilization and are dumped elsewhere. Industrial wastes are available almost free of cost and causes major disposal problem. Thus, a number of industrial wastes have been investigated with or without treatment as sorbents for the removal of pollutants from the wastewater. Because of their low cost and local availability, industrial solid wastes such as metal hydroxide sludge, fly ash, and red mud are classified as low-cost materials and can be used as sorbents for dye removal [104, 105]. The major solid waste byproduct of thermal power plants based on coal/bagasse burning is fly ash. The high percentage of silica and alumina in fly ash makes it a good candidate for utilization as inexpensive sorbent and such studies have been carried out. Fly ash is utilized by many researchers for the sorption of dyes [104, 106]. Although fly ash contains some hazardous substances, such as heavy metals, it is widely utilized in industry in many countries [107].

However, bagasse fly ash generated in the sugar industry does not contain large amounts of toxic metals and has been widely used for sorption of dyes [106]. Its properties are extremely variable and depend strongly on its origin [107]. Mall et al. [108] investigated the use of fly ash for the removal of dyes and found the process to be endothermic with pseudo second order kinetics. Akgerman et al. [109] investigated the removal of phenolic compounds by using fly ash and found
Chapter-1 Introduction and Literature Review

the capacity of 67 mg/g, 20 mg/g and 22 mg/g for phenol, 3-chlorophenol and 2,4-
dichlorophenol respectively. Weng et al. [110] examined the sorption
characteristics of Zn (II) on fly ash and found the sorption to be physical in nature
following Langmuir sorption isotherm.

Another abundant industrial by-product is red mud. Waste red mud is a
bauxite processing residue discarded in alumina production. Namasivayam and
Arasi [97] proposed red mud as sorbent for the removal of congo red. The
maximum capacity was 4.05 mg/g. Wang et al. [111] showed that physical and
chemical treatment can significantly change the sorption capacity. Recently,
Netpradit et al. [112] studied the capacity and mechanisms of metal hydroxide
sludge in removing azo reactive dyes. The sludge is a dried waste from the
electroplating industry, which is produced by precipitation of metal ions in
wastewater with calcium hydroxide. The authors demonstrated that metal
hydroxide sludge was an effective positively charged sorbent with a high maximum
sorption capacity for azo reactive (anionic) dyes. The charge of the dyes is an
important factor for the sorption due to the ion-exchange mechanism.

Gupta et al. [113] had utilized solid waste materials generated in some prime
industries. They converted waste generated in fertilizer plants in India into a cheap
carbonaceous sorbent material and investigated the column operations for the
treatment of pesticides. Chrome sludge, a solid waste material from an
electroplating industry was used as a sorbent for the removal of color by Lee et al.
[114] and positive results were found. Buffing dust, a leather industry waste was
used by Sekaran et al. [115] for the removal of dyes. The sorption capacity was
found to be 6.24 mg/g at pH 3.5 and temperature 30 °C for acid brown dye.

Chareonpanich et al. [116] were successful in synthesis of ZSM-5 zeolite
from fly ash and rice husk in presence of tetrapropyl ammonium bromide. Inada et
al. [117] studied the conversion of coal fly ash into zeolite by conventional
treatment and microwave assisted treatment by alkaline hydrothermal process.
They found that when microwave was applied in the course of hydrothermal
treatment, zeolitization was promoted by the early stage irradiation, while in the
middle and later stage irradiation retarded the crystallization of zeolite.
MICROWAVE TECHNIQUE

In the past few decades, many significant advances in organic chemistry, such as the novel synthetic reagents and methods, as well as the advent of an array of analytical apparatus and techniques, have made the organic synthesis more dynamic and effective than ever before. However, the practical aspects for carrying out laboratory-scale reactions have changed little during this period. Especially when heating is necessary, oil baths and heating jackets are the main equipment used. These traditional heating techniques are slow and time-consuming and sometimes can lead to overheating and decomposition of the substrate and product. To this end, microwaves have been employed in organic chemistry to reduce the reaction times from hours to minutes, to increase yields and selectivity [118].

Microwave irradiation is becoming an increasingly popular method of heating samples in the laboratory. It offers a clean, cheap and convenient method of heating which often results in higher yields and shorter reaction times. Despite this popularity and an increasing number of literature on the subject, microwaves remain an area of mystery and magic for many people. Myths abound about the capabilities and properties of microwaves, which unfortunately leads to unwarranted scorn. Microwaves are not a panacea, but used correctly and with understanding, they can be colossal benefit to the chemist, saving both time and money.

Although microwave technology has been used in inorganic chemistry since 1970s, Giguere [119] and Gedye [120] first implemented it to accelerate the organic reactions in 1986. The slow development of the technique in organic synthesis was principally attributed to the lack of controllability and reproducibility due to use of poorly designed domestic microwave ovens as reactors. Safety is another consideration since explosions have been reported [120]. However, with the availability of commercial microwave equipment intended for organic synthesis and the development of the solvent free techniques, microwave assisted organic chemistry has experienced exponential growth since the mid-1990s.
Figure 1.6 The growth publications describing microwave-assisted organic synthesis over the past 20 years. Major technical developments of the hardware during this period are indicated.

MICROWAVE REGION

In the electromagnetic spectrum, microwave region is located between infrared radiation, which has shorter wavelengths and radio frequencies. The wavelength of microwaves ranges from 1 cm to 1 m, corresponding to the frequencies from 30GHz to 0.3GHz. However, some wavelengths in this region are employed for radar and telecommunication. In order to avoid disruption, only limited wavelengths have been allocated for industrial and domestic microwave ovens intended for heating and drying by international convention. The most commonly used frequency for microwave heating is 2.45GHz, corresponding to a wavelength of 12.2 cm.

MICROWAVE HEATING MECHANISM

The easiest way to visualize the true mechanism of microwave heating is to picture microwaves as a high frequency oscillating electric and magnetic field.
There are two mechanisms associated with microwave heating: dipolar polarization (dipole rotation) and conduction mechanism (ionic conduction). A molecule is irradiated with microwaves [121] it will attempt to align itself with the electric field by rotation (Figure 1.7) [122]. If the frequency of molecular rotation is similar to the frequency of microwave radiation (2.45GHz), the molecule will continually align and realign itself with the oscillating field, therefore, the electric energy is absorbed by the molecule. It is obvious that solvents with large dielectric constants (DMSO, DMF) tend to absorb energy readily under microwave irradiation, while less polar solvents with no net dipole moment (hexane, dioxane) are microwave inactive.

![Dipolar molecules and ions, which try to move with an oscillating electric field.](image)

Figure 1.7 Dipolar molecules and ions, which try to move with an oscillating electric field.

However, when solvents with comparable dielectric constants, such as acetone ($\varepsilon = 20.6$D) and ethanol ($\varepsilon = 24.6$D) are heated at the same radiation power and same period of time, the final temperature will be much higher in ethanol than in acetone. In order to compare the abilities of different solvents to generate heat from microwave irradiation, their capabilities to absorb microwave energy and to convert the absorbed energy into heat must be taken into account. The equation (1) is usually used to calculate the ability of a solvent to convert microwave energy into heat at a given frequency and temperature.
\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad \text{...(1)}
\]

\[
\begin{align*}
\delta &= \text{Dissipation Factor} \\
\varepsilon' &= \text{Dielectric loss which measures the efficiency with which heat generated from electromagnetic radiation.} \\
\varepsilon'' &= \text{Dielectric constant i.e. the ability of the molecule to be polarized by an electric field.}
\end{align*}
\]

The ionic conduction mechanism also contributes to microwave heating effect, if ions are involved in the sample. When the ions move through the solution under the applied field, heat is generated by frictional losses, which depend on the size, charge and conductivity of the ions, converting the kinetic energy to heat (Figure 1.8).

Any solvent having high dielectric constant and high boiling point is excellent transfer media for a variety of microwave induced organic reactions. Polar solvents such as DMF (\(\varepsilon = 3.67\) and b.p = 160 °C), ethanol is good microwave absorbers and will get heated efficiently. On the other hand, less polar or non-polar solvents such as toluene, dioxane and THF are more or less transparent to the microwave irradiation (possess low tan\(\delta\)) and will not get heated in the pure form. Fluid salts or ionic liquids, consisting entirely of ions, absorb microwave radiation in a highly efficient manner. They are particularly attractive additives because they are relatively inert and stable at temperatures up to 200 °C, have a negligible vapour pressure [123, 124] and dissolve to an appreciable extent in a wide range of organic solvents. Energy transfer between the polar molecules that couple with the microwave radiation and the non-polar solvent bulk is rapid and often provides an efficient means of using non-polar solvents for synthesis using microwave irradiation.
WHY DOES MICROWAVE IRRADIATION SPEED UP CHEMICAL REACTIONS?

Chemical reactions, performed using MAOS technique, are rapid mainly because the reactions are performed at higher temperature than their conventional counterparts. The modern microwave based synthesizers can achieve temperature of up to 250 °C and pressures of up to 20 bars allowing reactions to be carried out at higher temperature than their reflux counterparts. In early literature there have been many claims of a specific 'microwave effect' responsible for the observed rate accelerations [125]. An attempt to rationalize a possible specific microwave effect has been published by Perreux et al. [126]. Even in today's specialized equipments it is very difficult to capture the true temperature of a reaction performed on a dry solid support or in a continuous flow system. Under microwave irradiation at atmospheric pressure the boiling point of solvents can be raised up to 26 °C above their conventional values. The enhanced boiling point can be maintained in pure solvents as long as the microwave radiation is applied.

Figure 1.8 Microwave-assisted organic chemistry can be used to speed up the chemistry development by allowing more reactions to be conducted per time unit.
NOTE ON ORGANOPHOSPHORUS PESTICIDES

The United States Environmental Protection Agency (U.S. EPA) defines pesticide as any substance or mixture of substance intended for preventing, destroying, repelling, or mitigating any pest. Pesticides may also be described as any physical, chemical, or biological agent that will kill an undesirable plant or animal pest. The term pest includes harmful, destructive, or troublesome animals, plants, or microorganisms.

The organophosphorus ester insecticides were first synthesized in 1937 by a group of German chemists led by Gerhard Schrader at Farbenfabriken bayer AG [127]. Many of their trial compounds proved to be exceedingly toxic and, even under the management of the Nazis in World War II, some were developed as potential chemical warfare agents. Although it is true that all of the organophosphorus esters were derived from “nerve gases” (chemicals such as soman, sarin and tabun), a fact that the media continually emphasizes, the insecticides used today are at least four generations of development away from those highly toxic chemicals [128]. The first organophosphorus ester insecticide to be used commercially was tetraethylpyrophosphate (TEPP) and, although effective, it was extremely toxic to all forms of life and chemical stability was a major problem. Further development was directed toward the synthesis of more stable chemicals having moderate environmental persistence, giving rise to organophosphorus insecticides.

Agricultural development continues to remain the most important objective of Indian planning and policy. In the process of development of agriculture, pesticides have become an important tool as a plant protection agent for boosting food production. Further, pesticides play a significant role for plant by keeping away many dreadful diseases.

Cotton provides a livelihood to more than 60 million people in India by way of support in agriculture, processing, and use of cotton in textiles. Cotton contributes 29.8% of the Indian agricultural gross domestic product, and nearly nine million hectares of land in India is used to produce 14.2 million bales of cotton.
lint. Indian cotton production is third in the world in quantity, although the productivity is substantially low. However, exposure to pesticides both occupationally and environmentally causes a range of human health problems. It has been observed that the pesticides exposures are increasingly linked to immune suppression, hormone disruption, diminished intelligence, reproductive abnormalities and cancer. Currently, India is the largest producer of pesticides in Asia and ranks twelfth in the world for the use of pesticides.

Among different pollutants of aquatic ecosystems, especially organophosphorus pesticides are considered as priority pollutants since they are harmful to organisms even at µg l\(^{-1}\) levels [129]. Organophosphorus pesticides are used in agriculture, in home-gardens and in veterinary practice. All apparently share a common mechanism of cholinesterase inhibition and can cause poisoning symptoms. Organophosphorus pesticides constitute a diverse group of chemical structures exhibiting a wide range of physicochemical properties.

One of the most terrifying effects of pesticide contamination of groundwater came to light when pesticide residues were found in bottled water. Between July and December 2002, the Pollution Monitoring Laboratory of the New Delhi-based Center for Science and Environment (CSE) analyzed 17 brands of bottled water, both packaged drinking water and packaged natural mineral water, commonly sold in areas that fall within the national capital region of Delhi. Pesticide residues of organochlorine and organophosphorus pesticides, which are most commonly used in India, were found in all the samples. All these were present above the permissible limits specified by the European Economic Community (EEC), which is the norm, used all over Europe.

One may wonder as to how these pesticide residues get into bottled water that is manufactured by several big companies. This can be traced to several facts. Currently, the manufacturing plants of most brands are situated in the dirtiest industrial estates or in the midst of agricultural fields. Most companies use bore-wells to pump out water from the ground from depths varying from 24-152 m below the ground. The raw water samples collected from the plants also revealed the presence of pesticide residues. This clearly indicated that the sources of
pesticide residues in the polluted groundwater are used to manufacture the bottled water. This is despite the fact that all bottled water plants use a range of purification methods. Thus, the fault obviously lies in the treatment methods used. Similarly, six months after CSE reported pesticide residues in bottled water it also found these pesticides in popular cold drink brands sold across the country. This is because the main ingredient in a cold drink or a carbonated non-alcoholic beverage is water and there are no standards specified for water to be used in these beverages in India. There were no standards for bottled water in India till September 29, 2000, when the Union Ministry of Health and Family Welfare issued a notification (no. 759(E)) amending the Prevention of Food Adulteration Rules, 1954. The BIS (Bureau of Indian Standards) certification mark became mandatory for bottled water from March 29, 2001. However, the parameters for pesticide residues remained ambiguous. Following the report published by CSE in Down to Earth (Vol 11, no. 18), a series of Committees were established and eventually on 18th July 2003, amendments were made in the Prevention of Food Adulteration Rules stating that pesticide residues considered individually should not exceed 0.0001 mg/L and that the total pesticide residues should not be more than 0.0005 mg/L and that the analysis shall be conducted by using internationally established test methods meeting the residue limits specified herein.

Today, there are some 200 different organophosphorus ester insecticides in the marketplace, formulated into literally thousands of products. One among the top ten organophosphate insecticides sold throughout the world is Acephate. The increased use of agricultural pesticides has meant that the mechanisms and magnitude of pesticide movement after their application continue to be an active area of research. Furthermore, their removal from contaminated lands is of paramount interest. Many pesticides which have been introduced to replace organophosphorus pesticides are so designed that they tend to break down fairly quickly in water. Thus their relatively high solubility in water makes them quite mobile in the environment [130]. When the potential level of exposure to contaminants at a given site is unacceptable from the human health or ecological standpoints, remediation strategies become necessary.
Chapter-1 Introduction and Literature Review

Poison information center in National School of Occupational Health (NIOH), Ahmedabad, India, has reported that organophosphorus compounds are responsible for maximum number of poisoning (73%) among all agricultural pesticides [131]. Patients of acute organophosphorus poisoning have been reported to suffer from problems like vomiting, nausea, miosis, excessive salivation, blurred vision, headache, giddiness, and disturbance in consciousness [132].

A vast majority of the population in India is engaged in agriculture and is therefore exposed to the pesticides used in agriculture. Although Indian average consumption of pesticide is far lower than many other developed economies, the problem of pesticide residue is very high in India. Pesticide residue in several crops has also affected the export of agricultural commodities in the last few years. There is a dearth of studies related to these issues in India. Therefore, the thrust of this research was to improve the removal methods for organophosphorus pesticides and minimizing the problems related to health and environment.
AIM AND OBJECTIVE OF PRESENT WORK

The literature review has revealed that recently many methods have been used for removing pollutants from the wastewater. Application of traditional treatment techniques needs enormous cost and continuous input of chemicals, which becomes impracticable and uneconomical and causes further environment damage. Hence, easy effective, economical and ecofriendly techniques are required for fine tuning of effluent/wastewater treatment. Among all the techniques, sorption is found to be the most extensively used procedure because of its versatility and easy operation. The activated carbons are the most preferred sorbents in wastewater treatment plants, where sorption methodology is adopted. The activated carbons are costly material and therefore, regeneration of spent carbon is resorted too. However, chemical regeneration may create additional pollution and regenerated carbon also exhibits lower sorption capacity. Attempts have therefore been made to utilize low cost natural materials or industrial wastes as alternative sorbents of activated carbons. The search for a low cost and easily available sorbent has led to the investigation of materials of agricultural and biological origin along with industrial by products, as sorbent.

There is a growing interest in the preparation of low cost sorbents for wastewater treatments, so the usage of natural (untreated) and synthesized zeolitic abundant materials are important for the cost-cutting of the processes. Various techniques have been investigated for sorption of organic and inorganic pollutants from water by different fly ashes over the past years. Several research studies had been reported on the characterization of fly ashes and sorption of organic and inorganic pollutants using them [133-137]. But from the survey of the literature, no information for the adsorptive removal of Acephate, Phosphamidon and Monocrotophos organophosphorus pesticides by bagasse fly ash and modified bagasse fly ash (zeolitic bagasse fly ash) is available. Hence, it was decided to embark on this investigation. Thus, the present study is envisaged to develop low cost zeolitic material using abundantly available sugar industry solid waste, Bagasse Fly Ash (BFA), which is facing solid waste disposal problem of sugar
industries for the removal of organophosphorus pesticides from water. *Suitably treated BFA can be effectively and efficiently converted into Zeolite by microwave assisted alkaline hydrothermal treatment (MZBFA). It has been successfully converted into zeolitic products and utilized to study their potential for the removal of organophosphorus pesticides from simulated water system*. The results of investigation incorporated in this thesis show that zeolitic material prepared from BFA remove pesticides satisfactorily and can therefore, be looked forward as low cost alternative as compared to activated carbons. The aim behind this study is to minimize the cost of wastewater treatment so that the small scale industries in developing countries could get advantage of it. This would provide basic probability of obtaining a successful treatment method of industrial effluents containing organophosphorus pesticides.

The scope of this study was to:

» Characterize the bagasse fly ash and zeolitic material (MZBFA).

» Investigate the effectiveness of the BFA and MZBFA to sorb Acephate, Phasphamidon and Monocrotophos from aqueous systems (simulated wastewater) during batch processes.

» Investigate the effects of pH, contact time, initial pesticide concentration, sorbent dosage and temperature during batch experiments.

» Determine the applicability of Freundlich, Langmuir, Temkin, Dubinin Reduskwich isotherms.

» Determine the sorption kinetics of the various organophosphorus pesticides onto BFA and MZBFA.

» Examine the mechanism of pesticide sorption on sorbents.