CHAPTER 1

INTRODUCTION
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Environmental pollution:

Today the cry of "pollution" is heard from all the nooks and corners of the globe, and the pollution has become a major threat to the very existence of mankind on this earth. It is the major challenge of our times. The pollution of various forms has gone to such an extent that we are unable to breath fresh air and drink fresh water. On one hand the industrial developments have increased the human comforts by giving automobiles, electrical appliances, better medicines, better chemicals to control harmful insects, fertilizers for more productivity, new synthetic fibers, textiles, fine chemicals etc., on the other hand they have given us an alarming problem to face: Pollution. In fact it is not a new problem, except in dimension which we see today. When man and other animals began their life on this earth, there was absolutely no sign of pollution. The problem of pollution arose with the very civilization of man. The rapid population growth and the unplanned industrial progress added to the problem of pollution[1]. This has resulted in a major public health hazard as well as in a general deterioration of natural water resources in many parts of the world[2].

The word "pollution" has originated from the Latin word "Pollutionem" which means to make dirty[3]. It can be defined as an undesirable change in the physical, chemical and biological characteristics of air, water or land that can harmfully affect health, survival or activities of human or other living organisms. Thus pollution is a phenomenon which upsets, the equilibrium of the system.

Pollution causes health problems, economical problems and ecological problems. It is a threat to many of the endangered species[4,5]. Many chemicals which are considered to be pollutants are present in earth as a part of the natural core. Heavy metals and radio active materials are examples for this. They are considered as pollutants only when their level increases to a certain limit, i.e., a substance is
Chemical abstract lists more than five million chemicals of which a significant part are man made. Along with the enormous benefit to the society brought by these chemicals, new dangers have also come up largely through the pollution generated during their manufacture[6].

Depending upon the medium it affects the pollution can be broadly classified into four categories:

- Water pollution
- Air pollution
- Soil pollution
- Noise pollution

WATER POLLUTION:

Water is a vital resource. It is a prime need for human survival, domestic uses, industry, irrigation etc. [7-11]. With out water neither an individual nor an organized community can survive. Modern industrial development would not have been possible without an adequate supply of water [12].

Water is more prone to pollution than air. The unequal distribution of water on the earth and the fast declining availability of fresh usable water per capita per year due to increasing population are the major causes for concern in terms of the quantity and quality of water.
All natural fresh water contain microorganisms which require organic matter for growth and oxygen for respiration. Normally 9 mg/l of oxygen at 15°C is dissolved in water which is the source of oxygen to these microorganisms [13, 14]. These microorganisms are responsible for the self purification capacity of the water. This self cleaning capacity of water is being affected by waste generated by increasing population. The national concern over the increasing pollution is clearly reflected in the water (prevention and control of pollution) act of 1974 [10].

Water pollution is defined as the introduction by man into environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structure or amenity or interference with legitimate uses of environment [15,16]. There are two main sources of water pollution.

- **Industrial water pollution**
- **Domestic sewage pollution**

**Industrial water pollution:**

Water pollution is the immediate result of industrial development. Many of the industries produce waste, some of them are toxic even in small quantities [17]. Depending on the raw materials used and the various production processes involved, the characteristic of the wastewater varies from one industrial sector to the other [18,19]. The diversity in the industrial waste have intensified the problem of water pollution. Industrial discharges are strictly prohibited in many developed countries, but in developing countries these discharges are largely ignored [17].
The industrial activities produce a large number of waste products which are generally discharged into rivers and other water bodies. Indian rivers and fresh water streams are seriously polluted by effluents from petrochemical, pharmaceutical, fertilizer, oil refinery, textile, pulp, paper, tannery, mining, thermal power production, dye stuff making industries etc. Pollutants from these industries include metals, detergents, oil and grease, acids, alkalis, phenols, cyanides, dyes, non-degradable and bio-degradable materials and many other organic and inorganic toxic pollutants. Depending upon the nature, these pollution may be 1) inorganic 2) organic and 3) physical pollution.

Acidity, alkalinity, pH, heavy metals and soluble salts are the main sources of inorganic pollution. These pollutants cause the corrosion of metals and also are responsible for the toxicity of streams to which the liquid effluents are thrown. Many of these heavy metals when present above certain limit becomes toxic to man and aquatic life. It is known that anaerobic bacteria in the bottom mud convert inorganic mercury to methyl mercury which can be concentrated in living organisms and lead to mercury poisoning [13]. Acid and alkali concentration in polluted water can be critical in receiving streams. It is generally a measure of the toxicity of the polluted water. Wide fluctuation in the pH of the stream is a threat to the aquatic life.

Physical pollution is mainly due to the presence of turbidity, suspended solids, colour, odour, radioactivity and temperature of the effluent [3, 19, 20]. The colloidal matters which do not settle readily are mainly responsible for the turbidity of the water. Turbidity occurs from the fine clay particles, milk waste and also from sewage. Turbidity reduces the penetration of sunlight, reduces the photosynthesis by microorganisms which in turn affects the oxygenation of stream water. The suspended solids, floating solids like oil and grease and coloured wastewater from textiles and dye stuff industries also reduce the penetration of sunlight and thus affects the photosynthesis [21, 22]. Moreover, the oil and grease destroys marine and inland fisheries [23]. The surfactants present in the effluent give rise to foams and stabilizes the colloidal
particles. These foams have a capacity to carry suspended solids and pathogenic bacteria. This stable foams makes the treatment of wastewater a difficult task [24].

Another form of physical pollution is thermal pollution, in which cooling water discharged from power generating station is the main source. They discharge hot effluent into the river. This increase the temperature of the water, thereby reducing the density and the dissolved oxygen content of the water. Rapid change in temperature also perturb the life of the fish and microorganisms which move to another locations or die [21, 25].

Settleable solids present in the polluted water form a sludge blanket, which decompose to produce odour, gases and floating mats on the surface of the water body. Fish hatching is also hindered by settleable solids [25]. Odour pollution is caused by chemicals like hydrogen sulfide, ammonia, phenols etc. and biological agents like algae. The hydrogen sulfide odour will be high if the effluent is highly acidic.

Organic pollution is due to the high molecular compounds such as sugars, oil, fats etc. present in the water. They impart high BOD values for the liquid effluent. Using the dissolved oxygen, the microorganisms generally degrade the organic pollutant present in the water. This process reduces the dissolved oxygen level, below a certain limit which affect the aquatic life adversely [14, 22, 26]. Heavy organic pollution affects the whole taxonomic group of macro-invertebrates, rather than individual sensitive species [27, 28]. Effluent generated from sugar, distillery, tannery, paper and pulp mill, oil refineries, textile industries etc. are generally accompanied by very high organic load with BOD values 2500 to 1, 2200 mg/l. The waste from oil refinery and the other industries which contain the most objectionable pollutant known as phenols, causing high odour and toxicological problems in the receiving water body. The effect of oil pollution in water are manifold, and generally only the acute effects are understood [29]. Petrol, white spirit and similar volatile products are generally regarded as the
most toxic pollutants from oil industry. It is found that 75 percentage of the suspended solids and 40 percentage of the filterable solids are organic in nature. Fats and oils, carbohydrates, proteins, urea, pesticides and large number of different synthetic organic compounds also causes organic pollution in water. Further the number of such compounds are growing yearly as more and more organic molecules are being synthesized. In recent years, the presence of these organic substances in waste waters complicated the treatment process because many of them can not be decomposed biologically. Because of this a renewed interest in the use of chemical treatment is seen among the environmental engineers.

The organic pollution from a biological point of view can be recognized into two major types: bio-degradable and non-biodegradable. A biodegradable pollutant can be decomposed or recovered and thus reduced to acceptable level either by natural process or by human engineered systems. Non-biodegradable pollutants are not broken down by natural process. If non-biodegradable pollutants are present in the effluent the pollution problem will become more complicated.

INDUSTRIAL WATER POLLUTION IN GUJARAT:

The alarming population growth, rapid industrialization and deforestation have seriously affected the water resources. Every day the cities and industries are pouring millions of tonnes of effluent to rivers and lakes [19]. Water pollution due to discharge of industrial wastes has already become a serious problem in many areas of the country [30]. The practice adopted for disposal of industrial wastewater in India was to discharge the effluent into public sewers, rivers or into sea and also on land with little or no treatment. Because of this most of the regions with high industrial activity have been the foci of pollution [18].
Gujarat has the biggest industrial estate in India. The North Gujarat is suffering from water scarcity. Low rain fall made most parts of this region desert or semi-desert. Every drop of water is important in this area. Rapid industrialization in Gujarat has proved a boon to states economy, but it has posed a serious threat to environment with air and water pollution becoming uncontrollable. More than half of the industrial units in the state are chemical units which have directly or indirectly contributed to the pollution problem. The situation is very bad in the entire industrial belt, described as "Dangerous zone" stretching from Mehsana in North Gujarat to Vapi in South Gujarat, including Ahmedbad, Baroda, Ankaleshwar, Surat and Bulsar, where state's most prestigious projects have come up. The pollution is severe because of the huge industries viz., petrochemicals, refineries as well as the mushrooming of the small scale industries mainly of dye stuff and textiles which collectively dumping the untreated and partially treated effluents to nearby water bodies. According to the industrial association at Ankaleshwar, more than 270 million litters of hazardous effluent water per day are produced [31]. More than five treatment plants are needed to treat all these effluent.

Death of more than nine tones of fish in Aji river near Rajkot area of Gujarat was reported because of the acidic pollutants from sari printing and silver industries flowing in to it. These acidic pollutants decreased the dissolved oxygen content to less than 3 mg/L level which caused the death of the fish [32].

Multi coloured effluents flowing into the ponds and then overflowing to roads is a common scene at Nandesary industrial estate near Baroda. Mini river flowing through this area has no sign of aquatic life. The iron poles of electricity and telephone departments are corroded and often fall down. Many of the industries discharge their effluent into small streams which flows into Mini river without any treatment. These waters are destroying the vegetation at banks and also are polluting the well of near by
villages [33, 34]. In many areas the chemical wastes are found piled on open land. During monsoon, these wastes leak into ground water or nearby streams.

The most important factor for this poor implementation of pollution control programme is the limited availability of funds [35]. The estimated cost of treatment 15 paise/litre is considered to be too high by most of the industries [31]. Recently the pollution control board has made the rules more strict and the industries started thinking about treating their effluent before discharging in to the streams.

**Industrial wastewater treatment:**

The most challenging field in environmental engineering practice is the treatment and disposal of the industrial wastes. Because of the great variety of waste from established industries and the introduction of waste from new process, a knowledge of chemistry is essential for solution of most of the problems[36].

According to the US Environmental Protection Agency (EPA) treatment is defined as any practice other than recycling designed to alter the physical, chemical, or biological character or composition of the hazardous substance, pollution or contaminant or render it non hazardous through a process or activity separate from the production of a product or providing of a service [37]. There are numerous treatment methods for the industrial effluent. The selection of treatment process depends upon the nature of the industry, pollution control board regulations for the discharge and the economical feasibility of treatment for that particular industry[19,38]. Depending on the mode, the treatment can be generally classified in to 1) Chemical 2) Biological and 3) Physical [39]. Usually a combination of these treatments is employed depending on the nature of the pollutant in the waste and the degree to which they are to be removed.
Chemical treatment method is used to convert the waste into other less hazardous forms. Biological treatment also involves chemical reaction but occurs in and around microorganisms whereas physical treatment is used to concentrate and reduce the waste volume [37]. Several standards have been laid down for the discharge of effluents into streams, municipal severs and on land [40].

**Chemical Treatment:**

Neutralization [41]: Effluent generally contain acids and alkalis and should be neutralized before discharging into rivers. Lime is generally used for neutralisation of acid waste. When lime is used for neutralizing hydrochloric acid waste water, gives soluble calcium chloride salt which is again an undesirable component and has to be treated further with sodium carbonate to precipitate calcium carbonate. This increases the sludge problem. In order to avoid this known amount of acids and alkalis are used for neutralization.

Floatation and precipitation can be effectively used to reduce the organic and inorganic load by settling the sludge or by precipitation. Dispersed polymers and oil emulsion can be broken by flocculation [40, 42, 43]. Oxidation with chlorine is used for killing pathogenic organisms. Cyanide gets oxidized to cyanate by chlorine[40]. Oxidation can also aid in the precipitation of certain metal ions by changing its oxidation state [37, 40]. Chlorine is a less expensive and most often used chemical for this purpose. But unfortunately chlorine has a tendency to combine with organic compounds in water to form chlorinated organic compound which are highly carcinogenic.

Sedimentation is used to remove suspended solids from waste-water by gravitational settling [41]. Colloidal particles are usually subjected to coagulation in order to increase the particle size to make it suitable for sedimentation [38]. Chemical
Coagulants are added which reduce the electrical field around the colloidal particles. This process destabilizes the colloid and makes it possible for the particles to come together and flocculate during mechanical agitation [41]. The inorganic coagulants generally used for this purpose are alum, aluminium sulfate, ferric and ferrous salts [44-46]. Synthetic polyelectrolytes are also being used for this purpose [47-51].

Organic compounds in the wastewater are the energy source for the microbial growth. In the presence of dissolved oxygen present in the water, the microorganisms convert the organic pollutants to CO$_2$ and H$_2$O. This is the basic principle of biological treatment. The microorganism may be aerobic (requiring free oxygen) or anaerobic (not requiring free oxygen). Process in which microorganism use bound oxygen is called anoxic.

Aerobic treatment methods include activated sludge process, trickling filter and stabilization ponds [40, 52]. The design of the activated sludge basin is determined by the biodegradability and the amount of organic material present in the effluent. The anaerobic process takes place in total absence of oxygen and it is a slow process [52-54]. But highly concentrated effluent can be handled by this process. Anaerobic filtration, digestion and lagooning are the main steps in this treatment.

Physical methods are used to remove the solids or liquid pollutants based on their density difference from that of water. Coarse materials are removed by screening plant. The specific method under physical treatment is thermal process, i.e., incineration and vaporization of wastewater or sludge. Other physical treatment processes are reverse osmosis, electrodialysis, filtration, adsorption etc. They help to remove the fine organic particles and inorganic dissolved materials resulting in a better quality for reuse or disposal.
Sand is a good medium for filtration of final traces of suspended particles [38]. Two types of sand filtrations are common slow sand filtration and rapid sand filtration. In slow sand filtration the effluent is passed through the filter very slowly where the suspended particles will be trapped on the surface of the filter medium which can be easily removed. In rapid sand filtration the chances of entering the suspended particles inside the filter medium is more. This can be removed by proper washing.

**Advantages of chemical treatment over biological treatment**[55]:

There are some advantages of chemical treatment over biological treatment. The results are quickly seen in case of chemical treatment and the amount of reagent can be adjusted to minimize the cost. Chemical treatment plants always take less space than biological plants. Automatic control can more easily applied to chemical treatment than biological treatment and they adapt more quickly with the changes in the quantity. Sudden variations of temperature or dissolved solids concentration may not effect the chemical dosing stage, but are likely to affect the performance of the biological settling tank. For the repair of the compressed air aeration in aerobic treatment plant the basin has to be emptied. Large amount of undesirable odors are present when strongly smelling waste are processed.

**Objectives of the present work:**

Wastewater from petrochemical industries, refineries and oil well drilling are the main oil pollution in Gujarat state. The Oil and Natural Gas Corporation of India, Mehsana project, in North Gujarat is producing more than 5000 m³/day of oil wastewater containing 9000-12000 mg/l of total dissolved salts(TDS) and 200 mg/L emulsified oil and grease. The Pollution Control Board do not allow this effluent to be discharged into rivers and they are being pumped back in to the dead wells. This
interfere the yield of oil production and also increased the proportion of water in oil emulsion. Hence it was desired to reduce the traces of oil in water using different treatment techniques and utilize it for increasing the agricultural productivity of this semi-arid area.

Since the effluent contain high amount of salinity, the biological treatment is difficult as very few bacteria can tolerate the salinity [56, 57]. So chemical treatment is suggested for the treatment. Emulsified oil requires special type chemical treatment to break the emulsion so that the oil will be free and can be separated by gravity or coagulation. Generally used flocculants for this purpose are Al₂(SO₄)₃ and FeCl₃. But the COD of the wastewater is found to be very high which necessitate further treatment [58]. Moreover, the sludge formed during the treatment with these flocculants create the sludge disposal problems. In order to achieve the maximum oil removal and minimum sludge formation a combination of inorganic electrolytes, FeSO₄ and Na₂SO₄ is used. The oil removal efficiency of this combined inorganic electrolytes was compared with the effect of FeCl₃, FeSO₄ and Na₂SO₄ when they were used individually. Results of these experiment are given and discussed in Chapter- 2 of this thesis. The effect of pH and concentration of electrolytes is also discussed.

Chapter- 3 describes the effect of this treated oil effluent containing high amount of TDS on the exchange composition of the soil at Mehsana region. The effect of pH and different calcium salts on the exchange composition is also discussed here.

Field experiments were conducted using the treated effluent. Different trees and crops were planted and irrigated with this effluent. The growth rate, fresh weight of trees and crops as well as the pH of the soil were noted. The results of this field study are presented in the Chapter- 4 of this thesis.
Dye stuff making industries and textile industries are the main sources of colour and organic pollution in the state. There are at present more than 300 dye stuff making and textile industries in Gujarat. Because of the discharge of untreated and partially treated effluent from these industries, the river water has become coloured. In Rajkot area of Gujarat the colour pollution is so severe that even drinking water has become coloured.

Chemical coagulation, oxidation of organic matter by aeration, chemical or biological method or a combination of these are generally used for the treatment of dye stuff making and textile mill effluent [59]. The efficiency of these method depends completely on the type of dye wastewater[61]. Among the chemical oxidants ozone is most widely used because of its high reactivity with majority of the dyes. Hydrogen peroxide in presence of Fe$^{+2}$ as the oxidation agent is also used for the colour removal [62]. Adsorbents like activated carbon is used for the colour removal, but it is an expensive process [63]. But very little work has been done on the sunlight photo-oxidation method to remove the soluble dyes in waste-water. Chapter- 5 deals with the removal of the water soluble vat dye from the dye stuff making industry effluent using sunlight photo-oxidation method. The effect of pH and the TDS present in the effluent on the removal efficiency is discussed in detail in this chapter.
REFERENCES


32. A. Borkar. Toxic effluents from dyeing units choke fish to death in Rajkot, Indian Express, Baroda, August-6, 1995.


