Wastes have a potential for recycling if separated well. It is said that waste is gold if it is properly managed.

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CHAPTER 1

ENVIRONMENTAL DAMAGES THROUGH INDUSTRIAL EFFLUENTS

- INTRODUCTION
- INDUSTRIAL EFFLUENTS: THEIR SOURCES, GENESIS, IMPORTANT CHARACTERISTICS AND TREATMENTS.
- THEIR POLLUTIONAL CHARACTERISTICS AND REMOVAL METHODOLOGIES
- THEIR ADVERSE EFFECTS ON ENVIRONMENT
- THEIR CHEMICAL REACTIVITY AND INTERACTABILITY

- SCOPE AND METHODOLOGY
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1.1 INTRODUCTION

The genesis and the discharge of waste fluids commenced with the commencement of life on the earth planet. However, this genesis and the discharge of the waste fluids, was never an environmental concern on account of the biodegradable nature of the fluids the small size of discharged fluids, and their almost uniform distribution over the entire earth surface. With the turn of this century, however, the mankind discovered and acquired gigantic sources of energy, power and raw materials, and diverted all of the them to generate new products for attaining materialistic happiness. The other name of this development was 'industralisation' and the other name of the waste fluids was effluents.

The impact of the effluents on the earth planet was found to be different from that of the earlier waste fluids on accounts of the non-biodegradable contents of the effluents and their massive discharge at localized spots far beyond the capacities of the natural factors to assimilate the damaging effects and strains of the discharged effluents. The results of the massive discharge of the effluents soon become noticeable in one or the other forms which compelled some actions and some thinking on the part of the mankind to bring the ever worsening situation within some control. The studies and the treatments of the effluents for improving their nature, prior to their discharge into the environment, are the outcome of the above stated thinking of the mankind.

Wastes are not necessarily pollutants in themselves, but all have the capacities to be so. According to the definition of effluent given by Werner, "a substance is normally considered to be a pollutant if it adversely alters the environment by changing the growth rate of a species, interferes with
the food chain, is toxic, or interferes with health, comfort, amenities or property values of people). A polluting substance can be a solid, semi-solid, liquid, gas or sub-molecular particle (1). Pollution is the result of the action or presence of the pollutant in a part of the environment where it is considered to have deleterious effects (1).

Once an effluent is formed, it is discharged in one or more of the following manners:

**Disposal on Land**: The disposal of effluents on land is a common practice. A well designed disposal of effluents on land helps to achieve economic crop irrigation, depending on the water holding capacity of the soil, land topography, general climate, and the particular crop in question. The industrial effluents discharged on land should not result in any adverse effect on the crop, soil and ground water (1).

**Disposal into Public Sewers**: The presence of certain constituents in industrial effluents may choke or damage sewers, impair the proper working of the sewage treatment plant, and where land irrigation is adapted for final disposal of sewage, the vegetation and the soil may be adversely affected. Large amounts of sulphur compounds in effluents may tend to form sulphuric acid under certain conditions which would corrode the sewer. Toxic elements such as chromium, or others with a high acidity or alkalinity level, and the high temperature of the effluents are inimical to biological activity in the treatment plant. The presence of flammable and toxic volatile matters may cause explosions in sewers or in the sewage treatment plants. Oils, tar and grease may stick to the sides of sewers, and reduce their hydraulic capacity. It is, therefore, necessary to limit the
concentrations of such constituents in industrial effluents discharged into public sewers (1).

**Disposal into inland, surface water**: As per definition laid down by the Bureau of Indian Standards (BIS), inland surface water meant rivers, estuaries, streams, lakes and reservoirs, including rivers liable to seasonal drying. The water polluting, contaminants of industrial effluents discharged into inland surface water may be an acid, alkali, oil or grease, suspended or dissolved matter, a toxic substance or a colour.

For the prevention and control of water pollution, the Bureau of Indian Standards has prescribed certain standards so that the receiving water courses or the receiving surface soils could be safely used for various purposes. The tolerance limits of selected characteristics for industrial effluents prescribed by Bureau of Indian Standards as reported in literature (2) have been shown in Table 1-1. These limits have been used as guidelines during the studies of the effluents described in the subsequent chapters.

### 1.2 INDUSTRIAL EFFLUENTS: THEIR SOURCES, GENESIS, IMPORTANT CHARACTERISTICS AND TREATMENTS

With the advancement of industrialization, more and more of new types of industrial units are getting added to the older lists of industries. Out of the vast list, it was found more useful to select those industries which are associated with the common needs of the general public. For the purpose of the studies being described here, a score of industries of the above-stated nature have been identified here. It will be relevant to get acquainted with the genesis, important characteristics and treatments of
such industries. The details in the cases of selected industries are as follows:

**Acid manufacture**: In most cases of acid manufacture, cooling water is the only effluent produced. The effluents have low pH and are treated by neutralisation (3,4).

**Bakery**: The effluents are generated through washing of pans, and floors. These have high BOD, oil and grease, sugar and detergents. These are normally treated by biological oxidation (3).

**TABLE 1-1 TOLERANCE LIMITS (BIS) FOR INDUSTRIAL EFFLUENTS**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Characteristics of effluents</th>
<th>Tolerance limits prescribed for industrial effluents discharged</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Into inland water</td>
<td>Into public sewers</td>
</tr>
<tr>
<td>1.</td>
<td>Colour and Odour</td>
<td>preferable by absence</td>
<td>--</td>
</tr>
<tr>
<td>2.</td>
<td>Total Suspended Solids (mg/L)</td>
<td>100</td>
<td>600</td>
</tr>
<tr>
<td>3.</td>
<td>Dissolved Solids (mg/L)</td>
<td>2100</td>
<td>2100</td>
</tr>
<tr>
<td>4.</td>
<td>pH</td>
<td>5.5 - 9.0</td>
<td>5.5 - 9.0</td>
</tr>
<tr>
<td>5.</td>
<td>Temperature</td>
<td>Not above 40°C</td>
<td>Not above 45°C</td>
</tr>
<tr>
<td>6.</td>
<td>Oils and Grease (mg/L)</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>7.</td>
<td>Total Kjeldahl Nitrogen (as N) (mg/L)</td>
<td>100</td>
<td>--</td>
</tr>
<tr>
<td>8.</td>
<td>BOD (5 days at 20°C) (mg/L)</td>
<td>30</td>
<td>350</td>
</tr>
<tr>
<td>9.</td>
<td>COD (mg/L)</td>
<td>250</td>
<td>--</td>
</tr>
<tr>
<td>10.</td>
<td>Chlorides (mg/L)</td>
<td>1000</td>
<td>--</td>
</tr>
<tr>
<td>11.</td>
<td>Sulphates (mg/L)</td>
<td>1000</td>
<td>--</td>
</tr>
<tr>
<td>12.</td>
<td>Sulphates (mg/L)</td>
<td>20</td>
<td>--</td>
</tr>
<tr>
<td>13.</td>
<td>Phenolic compound (mg/L)</td>
<td>10</td>
<td>--</td>
</tr>
<tr>
<td>14.</td>
<td>Fluorides (mg/L)</td>
<td>10</td>
<td>--</td>
</tr>
</tbody>
</table>

*CONT'D*
TABLE 1-1 (contd)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Characteristics of effluents</th>
<th>Tolerance Limits prescribed for industrial effluents discharged</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Into inland surface water</td>
</tr>
<tr>
<td>15.</td>
<td>Phosphates (as P) (mg/L)</td>
<td>5.0</td>
</tr>
<tr>
<td>16.</td>
<td>Cyanide (mg/L)</td>
<td>0.2</td>
</tr>
<tr>
<td>17.</td>
<td>Pesticides</td>
<td>Absent</td>
</tr>
<tr>
<td>18.</td>
<td>Arsenic (mg/L)</td>
<td>0.2</td>
</tr>
<tr>
<td>19.</td>
<td>Mercury (mg/L)</td>
<td>0.01</td>
</tr>
<tr>
<td>20.</td>
<td>Lead (mg/L)</td>
<td>0.1</td>
</tr>
<tr>
<td>21.</td>
<td>Cadmium (mg/L)</td>
<td>2.0</td>
</tr>
<tr>
<td>22.</td>
<td>a) Hexavalent Chromium (mg/L)</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>b) Total Chromium (mg/L)</td>
<td>2.0</td>
</tr>
<tr>
<td>23.</td>
<td>Copper (mg/L)</td>
<td>3.0</td>
</tr>
<tr>
<td>24.</td>
<td>Zinc (mg/L)</td>
<td>5.0</td>
</tr>
<tr>
<td>25.</td>
<td>Selenium (mg/L)</td>
<td>0.05</td>
</tr>
<tr>
<td>26.</td>
<td>Nickel (mg/L)</td>
<td>3.0</td>
</tr>
<tr>
<td>27.</td>
<td>Boron (mg/L)</td>
<td>2.0</td>
</tr>
</tbody>
</table>


**Cement manufacture**: The effluents result from the wet scrubbing of gases. These are hot and have high suspended solids. These are treated by neutralisation followed by sedimentation (3).

**Coal washery**: The effluents are produced during the washing of coals with water. The effluents have high suspended load, and low pH. These are treated by neutralisation followed by settling (3).

**Coke manufacture**: The effluents are generated during the cooling of hot coke using water. These have high suspended load, contain tar, ammonia, cyanide, H₂S, and aromatics. Treatment involves settling, neutralisation, coagulation, recoveries and reuse (1,3,5).
**Dairy**: The effluents are produced by washing of cans, tankers, equipments and floors. The effluents have high BOD, and contain dissolved organic matters such as fats, proteins and lactose. The methods applied are biological treatments and oxidation with aeration. The effluents can also be disposed off economically as irrigants (1,3,4,).

**Detergent manufacture**: The effluent contains spill overs and floor washing. These contain alkyl benzenesulphonate alongwith phosphates and borax. These are usually alkaline. These are treated by floatation, skimming and precipitation with CaCl₂. These effluents do not respond to biological treatments (3).

**Distillery**: The effluents contains spent wash and water from heat exchangers. The effluents have abnormally high BOD, suspended solids and dissolved solids. These have dark brown colour and disagreeable odour. The treatment involves anaerobic digestion, biogas production and evaporation (1,3,4,6).

**Edible oil refinery**: The effluents contain salts of fatty acids and spill overs. These have high BOD, COD and oil contents. The treatment involves neutralisation, coagulation, settling, aerobic or anaerobic digestion (3,4,6).

**Electroplating**: These contain pickling liquors, plating wastes and rinse waters. These are highly acidic, have high COD and contain heavy metals and cyanide. The treatments involve electrochemical precipitation using steel slag, neutralization followed by precipitation (3).

**Explosives**: The effluents contain TNT, gunpowder, washings and pickling of cartridges. The effluents have low pH, and contain oils and
soaps. The treatment involves precipitation, chlorination, neutralisation, absorption and biological treatment (3,5). The water hyacinth is also reported to absorb nitrogenous contents of the effluents (8).

**Fertilizer manufacture**: The effluents contain spill over from acid manufacture, boiler blow down, and cooling waters. These have low pH, high phosphate and fluoride, and also ammonia and nitrates. The treatment involves sedimentation, neutralisation and removal of fluorides and phosphates by lime treatment (1,3,9-11).

**Lamps and tubes manufacture**: The combined effluent is slightly acidic. The effluent from coiling section contains high load of sulphates, nitrates and Mo, that from glass blowing section has high load of oil and grease. The treatment involves settling, skimming, followed by the chemical treatment using alum and calcium chloride (3,5).

**Steel foundary**: Effluents are slightly alkaline, and contain high load of suspended solids. Treatment mainly involves settling (3,12).

**Electric fan manufacture**: The combined effluent is acidic and has high load of dissolved solids. Sulphate content is high, and it contains Zn, Cr, Fe, oil, grease and cyanide (5).

**Ball bearing industry**: The combined effluent is alkaline, has high load of dissolved and suspended solids, emulsified oil, total oil and grease. The treatment involved settling and skimming, followed by chemical treatment using lime and ferrous sulphate (13).
Steel plants: Effluents are slightly alkaline, contain high volatile solids and traces of cyanides, oil and grease. Chemical treatment involves neutralisation and coagulation (3,5).

Oil refinery: The effluents are generated through pumping, de salting and refining processes. The effluents contain mud, saline water, oil, and sulphur compounds. The effluents are generally discharged into sea, after removal of oils, phenols etc (3).

Paints manufacture: The effluents originate from washing, and contain resins, solvents, pigments, lacquers, varnishes and heavy metals such, as Pb, Cr etc. These have high COD. The treatment involves settling,(3) chemical reduction and adsorption (29).

Pesticides manufacture: The effluents are generated during washing and purification. The effluents are highly acidic, and contain residues of pesticides. The treatment involves neutralisation, adsorption, chlorination and dilution (3).

Synthetic drugs manufacture: The effluents are formed by process and wash waters. These are acidic in nature and contain lot of dissolved compounds. The treatment involves neutralisation, chlorination and biological oxidation (3).

Photographic processing: The effluents contain spent hypo, fixing solution and wash waters. The effluents contain silver (1%) and various organic and inorganic reducing agents. Their nature is alkaline. The effluents are discharged into sewers after the recovery of silver (3).
Brass and copper pickling: The effluents contain pickle liquors and wash waters. They are highly acidic, and contain mineral acids and dissolved copper. The treatment involves recovery of copper, followed by neutralisation with lime and treatment with acid-charred waste (11) or steel plant slag (7).

Iron and steel pickling: These effluents are spent pickle liquors, and wash waters. These contain mineral acids and dissolved iron. The dissolved iron is recovered as pigment (14). The treatment involves neutralisation using lime (14,15).

Foam industry: The effluents are formed during processing and washing. The effluents are milky, pungent and slightly alkaline, have high suspended and dissolved loads and COD. Contain zinc and fluorides. The treatment involves acidification and removal of fluoride using acid-charred waste (11).

Pulp and paper manufacture: The effluents are formed during digestion of wood and washing of fibres. The effluents are acidic, brown in colour and have high suspended and dissolved loads. The treatment involves recovery of bye-products, coagulation, clarification and biological treatment (3).

Rice mills: The effluents are formed during soaking, cooking and washing of parboiled rice. The effluents are turbid, have foul smell, acidity, high dissolved solids, COD and BOD. The effluents are treated using bleaching powder, ferric alum and lime (16).
**Tread rubber plant**: The combined effluent contain process effluents and resin regeneration effluents. The combined effluents are alkaline, have high dissolved loads and oil and grease. The treatment involves the use of lime and ferrous sulphate (17).

**Slaughter house**: The effluents contain bones, fats and residues of killed animals. The effluents have high BOD, dissolved and suspended loads, oils and fats. The treatment involves removal of fats and grease, sedimentation, chemical precipitation, activated sludge process, anaerobic digestion and aerobic biological process (3).

**Soap manufacture**: The effluent contains spill-overs and process waters. These contain unsaponified oil, alkali and suspended solids. The treatment involves skimming of fatty acids, recovery of glycerol, and neutralisation (3,4).

**Tannery**: The effluents are formed during soaking, liming, de-liming, and contain spent liquors. These have foul odour, high suspended and dissolved loads, BOD, COD, oils, grease, chromium, chlorides and sulphides of sodium. The treatment involves settling, chemical coagulation, activated sludge process, uses of oxidation ponds and lagooning (3,10,18).

**Textile mills**: The effluents are generated by the processes of sizing, desizing, mercerizing, bleaching, dyeing, printing, and finishing. The nature of the effluents differs from one process to the other. The combined effluents are alkaline, have high loads of dissolved and suspended solids, high BOD, COD, phenolic substances, Zn and Cr (19). The treatment involves equalization, neutralisation, chemical coagulation, aeration or
biological treatment (3,10). Treatments using acid-charred waste (20), and fly ash (21,36) have also been found to be effective.

**Thermal power plant**: The effluents are mostly those from the ash pond of the thermal power station. The effluents are slightly acidic, and have high loads of suspended and dissolved solids, and traces of Pb, Hg and As (20,23). The treatment involves settling (3).

**Alumina plant**: The effluents are discharged from the alumina plant and smelter plant, and contain dissolved Al, Fe, Cr, Zn, Mn etc. The smelter plant effluents are mostly alkaline, and contain dissolved metal ions and anions including fluorides (24). Treatment involves settling, neutralisation and coagulation (3).

**Iron ore screening plant**: The effluents are generated during the screening of the crushed iron ore using water stream. The colour of the effluent is reddish. The effluent has high suspended load (25). The effluents are discharged after settling in tailing dams.

**Alum manufacture**: The liquor after the removal of alum crystals forms the effluent. The liquor is highly acidic, contains free acid and dissolved aluminium and iron (19).

**Chlor-alkali plant**: The effluents are generated during the electrolysis of brine. The effluents are alkaline. If hydrochloric acid is also manufactured at the same plant, the combined effluents may be acidic. The effluents have high load of dissolved solids, and traces of dissolved mercury (4). The treatments involve settling, neutralisation, and mercury removal by chemical or electro-chemical methods (26,48).
**Copper ore-concentrate plant**: The effluents are generated during wet grinding of ores in ball mills, and during floatation of the fine ore. The effluents are yellowish, pungent in smell, alkaline, and contain high suspended loads, sulphur compounds and fluorides (27). The treatment involves settling, neutralisation and chemical treatment.

**Automobile service station**: The effluents are generated during the washing of the automobiles. The effluents have high suspended loads, and high amounts of hydrocarbon oils, greases and lead (23). The treatment involves settling and skimming.

**Lead-zinc smelter plant**: The effluents are generated in the sinter plant, copper recovery plant, boiler blow-down, wash down from acid plant and gas washing system. The effluents are treated for the removal of cyanide, and heavy metals, and the treated effluents are subjected to evaporation. The combined effluents are turbid, alkaline, have high dissolved load, alkali metals, sulphates, chlorides, and a number of toxic metals (4).

The description of a wide range of industrial effluents has provided an insight with regard to the genesis, characteristics and the treatment methodologies of the effluents. It is out of these effluents that selections have been made for the studies of effluent-effluent interactions which have been described in subsequent chapters.
1.3 THE POLLUTIONAL CHARACTERISTICS OF THE EFFLUENTS AND THEIR REMOVAL METHODOLOGIES

The total pollutional nuisance of waste waters or industrial effluents is the sum of the contributions of each of the pollutional parameters of the respective fluid systems. The details of such parameters are being given below:

**Colour**: The colour of a waste water or effluent is the first signal detectable by human eye for caution against the intake of such waters or effluents. Colours may be imparted to the waters through man made sources such as dyes contained in textile mill effluents, and coloured salts contained in galvanising or electroplating waste waters. The water may also acquire colours due to the occurrence of natural products, such as humic acids or humates present in soils, or dissolved iron or its complexes present in soils. Colour is measured in Hazen Units on platinum-cobalt standard, in which the solution is compared with a mixture of chloroplatinic acid and cobalt chloride. As the organic compounds present in an effluent are broken down by bacteria, the dissolved oxygen is reduced to zero, and the colour of the fluid changes to black. In this condition; colour of the waste water is said to be septic (18,28,31). The methods adapted for colour removal involved aeration, adsorption, chemical coagulation and biological treatment (1,3,18). Khageshan and co-workers (32) have reported the use of activated carbons and bleaching powder for the colour removal of textile dye waste. Murthy et al (33) have reported the use of activated charcoal, fuller earth and bottom ash for the removal of the colour from paper mill waste waters. Sastry et al (34) have reported the use of alum along with poly-electrolytes for colour removal from combined waste waters of pulp and paper mill. Singhal and co-worker (35) have reported the use of fly
ash for the colour removal of the same effluent, whereas Pervez and co-worker (36) have used fly ash for the colour removal of textile mill effluent and distillery effluent. Upadhyay and co-worker (37) used calcium hypochlorite for the decolourisation of pulp and paper effluent. Shukla and co-worker (38) have used sewage sludge for colour removal of selected acid dyes.

**Odour**: The odours have an adverse effect on environmental qualities only when they cause a nuisance to those who are exposed to the odours. It has been found by one survey that in over one half of cases of odour nuisance complaints do not occur beyond 400m of the source, and only in one in eight cases do complaints occur beyond 2 kms (28). Distilleries are known for odour nuisance all over India. Other odour sources are manure spreading, sewage treatment plants, animal bye-product manufacture, foundries, paint spraying, sewage, sludge disposal, restaurants, kitchen, poultry houses, pig houses, tanning, abattoir and maggot farms (28). Odour can be detected by the human nose at levels below that of most instruments, hence it is necessary to employ the human nose for odour detection. The measured numbers of dilutions with clean air required for an odourous species to render it undetectable by 50% of a panel of persons is referred to as the dilution factors, and is used in a way equivalent to concentration (28,39). The methods adopted for odour removal involve absorption, adsorption, incineration, chemical coagulation, scrubbing and chemical oxidation (1,3,10,18,28).

**Suspended Solids**: The suspended matter has a larger particle size than the colloidal materials, that gives rise to turbidity, and can be separated by settling in lagoons or sedimentation tanks. If they are allowed into a water course, the particles will settle on a river bed and interfere
with the self-purification by smothering the benthic organisms. Excessive solids can harm fish, and interfere with photosynthesis by preventing the sunlight being transmitted through the water. The treatment method involved settling, clarification, filtration and chemical treatment \((1,3,40-45)\). When water contains fine clay particles and colloidal matter, it becomes necessary to apply sedimentation with coagulation which is the process of removing fine suspended and colloidal impurities by the addition of requisite amount of chemicals (called coagulants) to water before sedimentation. There are two major types of coagulants used in water treatment processes: inorganic metal salts and organic polymers. The metal salts most commonly used are aluminium sulphate, sodium aluminate, ferrous sulphate, ferric sulphate, ferric chloride and chlorinated copperas \([\text{iron (III) Chlorosulphate}]\). The most common of those listed is aluminium sulphate \((1,3,40-45)\).

**Dissolved Solids** - The filterable solid fraction consists of colloidal and dissolved solids. The dissolved solids consist both organic and inorganic molecules and ions that are present in true solution in water. Chlorides, sulphates, nitrates, bicarbonates and phosphates of sodium, potassium, calcium, magnesium, iron and manganese, and some of the fluorides are soluble in water. Water softening plants and drainage from salt works contribute many of these salts to river and streams. Fluorides and nitrates are considered to be toxic to man above certain levels.

When waters containing excessive salts are discharged into rivers the river course becomes brackish which affects fish life and certain vegetation. Many of the fresh water fish varieties die in salt water, and this is entirely due to osmotic change. Not only these soluble salts affect biological organisms, but they also cause severe effects to pipelines, pumps
and other metallic or concrete structures. Sulphates are converted either to sulphuric acid which aids corrosion, or to sulphides which produce odour nuisance. The conversion to sulphides is brought about by sulphate reducing bacteria.

Certain soluble salts of iron and aluminium react with the natural bicarbonate alkalinity to form insoluble hydroxides. When the river or stream is depleted of dissolved oxygen due to sewage or other contaminants, the water may turn black due to the formation of ferrous sulphide. Iron can react with phenols to form various coloured compounds and make the streams coloured.

The removal methods include coagulation, sedimentation and filtration. Loomba and co-worker have used steel plant granulated slag for the removal of toxic metal ions. Pervez and co-worker (46) have used lepidocrocite and pyrolusite for the removal of dissolved iron in ground water (47). Loomba and co-worker also used granulated slag of steel plant for the removal of dissolved mercury from chlor-alkali plant effluent (48). Shukla and co-worker used charred waste from an oxalic acid plant for the treatment of textile mill effluent (49). Jallan and co-worker used alum plant waste for the removal of fluoride (50). Moitra and co-worker used water hyacinth for the removal of dissolved nitrates from slurry explosive plant waster waters (51). Jallan and co-worker also reported the use of sewage sludge for the removal of dissolved metals ions such as Pb(II) and Zn(II) (52). Loomba and co-worker also used steel plant slag for the removal of cyanide (53).

**Acidity and alkalinity**: The industries which discharge effluents containing free mineral acids are: chemical, fertilizer, pesticide, battery
manufacture, electroplating, viscose, rayon processing, mining, iron and copper pickling etc. Organic acids are discharged from the manufacture of rayon, fermentation plant, distilleries, rice mills, dyeing industries etc. Neutralisation using lime is the usual method for the treatment of acidic waste waters. The use of lime stone grit is the most economical method for the removal of acidity. The removal of acidity from effluents is desired on account of their corrosive effects on steel and concrete structures, adverse effect on aquatic life (54) and surface soils (55).

Effluents from textile mills, tanning, soap and detergents, edible oil refining, and boiler blow down are highly alkaline in nature. Most of the effluents possess caustic alkalinity (hydroxide alkalinity) only. Quantities of carbonates and bicarbonates are much less. Effluents containing caustic alkalinity should not be discharged into water courses without treatment. The alkalinity of waste waters is removed by neutralisation using appropriate acids.

**BOD and COD**: BOD is the quantity of oxygen required by bacteria and other micro-organisms during the biochemical degradation and transformation of organic matter present in waste-waters under aerobic conditions. It is the only test that gives a measure of the amount of biologically oxidisable organic matter. It is highly useful in studies of measuring the purification capacity of streams, and serves regulatory authorities as a means of checking the quality of effluents discharged to such water.

Chemical Oxygen Demand (COD) is the oxygen requirement of a sample for oxidation of organic and inorganic matter. In COD test, the sample is subjected to a chemical oxidation induced by chemical reagents.
and it is an artificial oxidation by which both biologically oxidisable and biologically inert organic matter are oxidised. Hence the COD value for a sample is always higher than BOD value. As the inert organic materials are also oxidised, the COD test is of great value, particularly in evaluating the pollutional potential of effluents such as from pulp and paper industries, rayon industries and chemical industries. Though these effluents contain enough organic matter, the BOD of them is much less as the materials are not biodegradable, and may lead to wrong conclusion. In these cases COD reveals the real pollution potential (3).

In the interactability studies of effluents being described in subsequent chapters, due emphasis has been placed on COD determination.

The maximum permissible values of BOD and COD for the discharge of waste waters have been shown in Table 1-1. The control of BOD and COD prior to their discharge into natural water streams is desired on account of the depletion of dissolved oxygen caused in the waters of natural streams due to the inflow of high BOD and COD effluents. The depletion of the dissolved oxygen is injurious to aquatic life.

**Oil and grease**: Determination of oil and grease is useful to overcome the difficulty during treatment. The presence of oil and grease in trade effluents is quite common. The sources of oil and grease are natural raw materials used in the process and/or from the lubricants applied to the machinery. The oil and grease fractions may contain hydrocarbons, lipids, fatty acids, soaps, fats, waxes and oils (3). Oil can kill stream flora and fauna at the surface and below if it becomes attached to particles of materials which can settle on the river bed. The gills of fish become fouled, and the flesh can be tainted by oil, while fish eggs and fry may be directly
damaged (31). Moitra and co-worker have used lime and ferrous sulphate in the removal of oil from ball bearing industry effluents (56). Their treatment also included skimming in the beginning, and adsorption using rice husk in the last phase of the treatment.

**Toxic metals**: A large number of heavy metals (Pb, Cr, Cu, Cd, Ni, Hg, Zn, U, As, Ag, Se, Mn, Sn, Bi, Sb etc) have toxicities associated with them (29). The removal methodologies have been found to depend on the nature of the metal ions present in the waste waters. The general principles in the removal of the toxic metals are based on precipitation as sulphide and hydroxide, adsorption in columns packed with appropriate materials (58,59), and ion exchange processes using polymeric resins (29,30). A large number of toxic metals have been removed from industrial effluents by electrochemical precipitation methods (60).

In the preceding paragraphs, the essential description of most commonly observed parameters related to the characteristics of industrial effluents has been given. An appraisal of treatment methodologies for the correction or removal of these parameters has also been given. A flow sheet chart showing the possible choices for effluent treatment (61) has been shown in Fig. 1.1.
Figure 1-1: Possible choices for wastewater treatment and their sequence.
1.4 INDUSTRIAL EFFLUENTS: THEIR ADVERSE EFFECTS ON ENVIRONMENT

Pollution of Surface and Ground Waters: When massive volumes of industrial effluents are led into natural water streams, the natural characteristics of the water streams are altered. The self-purification mechanism of the water streams is disrupted due to the excessively high loads of unwanted species in the effluents. Pervez and co-worker have reported the changes in the water quality and sediment composition of Hasdeo river arising through the discharge of thermal power ash pond effluent (62). The same authors have also reported the solubilizing effect of sulphuric acid plant effluent on limestone and the evolution of $\text{H}_2\text{S}$ on interaction of sulphide bearing materials by this effluent (63).

The natural characteristics of ground water have also been reported to be altered by the effluents of industries such as textile mill, thermal power ash pond and distilleries (64,65). The cadmium spillage through galvanising effluents has also been reported (63). The pollution of Pandu river near Kanpur by the effluent of a urea plant (66), and that of natural water streams by the iron ore slime discharge at Bailadila (67) have been reported. At Minamata Bay in Japan, more than hundred people lost their lives, and many thousands were permanently paralysed by eating fish which were contaminated by mercury that was present in the effluent discharged by a vinyl chloride plant (68). Another episode was that of "itai-itai" disease in North Japan which was attributed to cadmium which was present in the mining waste which polluted the water supply resulting in the contamination of rice growing areas (29). The examples cited are only few out of a large number which have been reported, and these may be sufficient to convey the adverse effects of effluents on surface and ground waters.
Pollution of Soils: The permeation of toxic metals in surface soils through iron ore slime discharge has been reported (69). Agrawal and co-worker have reported the distortion of de-nitrification of soil by spent wash discharge (70). The same authors have also reported depletion of Mn in soils, and the impairment of its oxidation as a result of spent wash discharge on soils (71). Agrawal and co-worker (55) have reported a damage assessment of soils polluted by some high acidity effluents. These authors have also reported extractability of soil iron by the spent wash (72). Shukla and co-worker have reported the methylation of inorganic mercury in normal soils (73). The same authors have described the leaching of ferrous ions from laterite near the storage pond of textile mill effluents where the soil was contaminated with the effluents. The reports cited here show that the natural characteristics, composition and functions of soils are adversely affected on their coming in contact with the discharged effluents.

Pollution of Air: The effect of effluents on air quality can be easily noticed in areas situated close to industries such as distilleries, rice mills, tannery etc. The air pollution arises due to the continual entry of sulphur-containing odourous and volatile molecules from the liquid phase to the atmospheric air. Pervez and co-worker have described the release of H₂S gas when sulphuric acid plant effluent is released on open lands (63). Agrawal and co-worker have reported the release of methylmercury when mercury contaminated effluent is discharged on paddy soils (4).

Impact on Human Health, Aquatic Life, Vegetation and Croips: A number of adverse effects on human health resulting from the presence of toxic elements in water have been reported. Shukla and co-worker have reported fluoride presence in lenses of cataracts in a selected urban area.
resulting from the presence of fluoride in drinking water (75). The same authors have reported the presence of lead in teeth and its uptake rate from drinking water (11). The episode of Minamata disease resulting from the mercury contamination of water, and "itai-itai", disease resulting from the cadmium contamination of water have already been described (29,68). The adverse effect on the growth parameters of selected cereals by oxalic acid manufacturing plant waste waters (76), and the toxicity of steel plant waste waters for a variety of fish (77) have also been reported. Reports about the adverse effects of distillery effluents on the growth of cane plants and uptake of toxic metals (Hg, Zn, Cu, Pb, As, Cd and Mn) by rice plant (78) have also been found. The distillery effluent has also been reported to have adverse effects on the growth parameters of wheat, paddy, gram, mung and maize (78). Haniffa and co-worker have reported adverse effect of textile mill effluent on a variety of fresh water fish (79). Rao and Reddy have described mortality of arthropods resulting from the effluents of dye factory (80). Pramod Kumar and co-worker have described retardation in the growth of mustard plant, resulting from the effluent of pharmaceutical factory (81). The bio-accumulation of heavy metals by wheat plants fed by textile effluents has also been reported (82). The growth parameters of groundnut by dyeing factory effluents has been reported (83). Sewage water paper and dye industry effluents have been reported to have adverse effect on the growth parameters of gram and maize seeds (84). The growth of some variety of trees has also been reported to be adversely affected by pulp and paper mill effluents (85). The textile mill effluent has been found to adversely affect the growth of green gram seedling (86). The adverse effects of the effluents have been found to be quite clear and obvious from the illustrative examples cited here.
An effluent is a system containing a number of components in dissolved or undissolved states which have attained a sort of equilibrium amongst themselves in the water medium in which they are present. If, the undissolved fraction is removed, the clear liquid may be considered as a true solution of a number of chemical species which may have high, moderate or low chemical reactivity, or may be even inert at the temperature of the effluent. Effluent systems, therefore, need to be looked in terms of their capabilities for inducing chemical reactions. It is this inherent property of the effluents which has been tapped in the studies undertaken here. The tapping of this inherent property of an effluent should also quench the chemical reactivities of the components of the effluent, and the result expected should be the cooling down of the offensive nature of the effluent, which should render the effluent acceptable to the environment. For the illustration of this phenomenon, an example of textile mill effluent may be taken. The highly alkaline nature (pH-11.0) of this effluent suggests the presence of highly reactive hydroxyl ions equivalent to $40 \text{ g NaOH/m}^3$. For destroying the harmful effects of this amount of caustic alkalinity of the textile mill effluent, it shall be required to add $49 \text{ g. of H}_2\text{SO}_4$ or $36.5 \text{ g of HCl}$ for $1 \text{ m}^3$ volume of the textile mill effluent. We may obtain the same result if we mix $1 \text{ m}^3$ of the textile mill effluent with $1\text{ m}^3$ of any other effluent of acidic nature having a pH 3.0 e.g. sulphuric acid plant effluent (having pH 3.0). While arranging an interaction of this nature, we are saving a consumption of $49.0 \text{ g of H}_2\text{SO}_4$ per $\text{ m}^3$ of textile mill effluent, and $40.0 \text{ g of NaOH per m}^3$ of sulphuric acid plant effluent, and are thus removing the undesired acidity and alkalinity from a total of $2\text{ m}^3$ of effluents. Thus if an effluent-stream
of a textile mill flowing at a rate of 1000 m$^3$/day is able to join another effluent stream of sulphuric plant at the same flow rate, a consumption of 40 kg. of NaOH/day and 49 kg. H$_2$SO$_4$/day is saved from the simple process of intermixing the two effluents. This comes to a saving on annual basis of 14.6 tonnes of caustic soda and 17.9 tonnes of sulphuric acid for the pH corrections of the two industrial effluents.

We may take another example of effluent which may have more than one reactive species present in it. The oxalic acid manufacturing plant effluent (pH 3.0) contains dissolved oxalates at a level of about 473 mg/l. If 1 m$^3$ volume of this effluent is made to interact with 1 m$^3$ volume of textile mill effluent (pH 11.0), not only the entire acidity and alkalinity of the two effluents will be destroyed, but the metal ions (Ca, Mg, Cr, Zn etc) present in the textile effluents shall also be removed as their insoluble oxalates. Similarly galvanising liquor and the alum plant waste liquor both are highly acidic and contain dissolved iron and aluminium respectively. On interaction with alkaline waste waters (such as those from soap plant, dairy, textile mill etc), not only the acidity and alkalinity of the interacting effluents will be destroyed, but the dissolved iron and aluminium salts which both are known as excellent coagulants (44,87) shall contribute additional corrective effect in the removal of dissolved species present in the alkaline waste waters.

Taking into consideration the compatibility of the effluents for chemical reactions between themselves, the entire range of commonly available industrial effluents can be divided into two main groups (A and B) on the basis of their known characteristics. The division of the effluents into two main groups here is mainly based on the acidic or alkaline nature of the effluents. The division of the respective effluents in
two groups (A and B) on this basis has been shown in Table 1-2, along with the average pH values associated with them.

From the details given in Table 1-2 it can be seen that on interaction at optimum volume ratios one or more effluents shown under Group A with one or more effluents shown under Group B, one or more of the effects described below may be observed.

1. The excess acidity or alkalinity of the interacting effluents shall be removed.

2. The cations present in one effluent may react with anions present in another effluent, and both types of the ions may be removed as insoluble products. The coloured and pH-sensitive complex ions or molecules present in the interacting effluents may lose their colour intensities completely or partially.

3. The metal ions present in the effluents of acidic nature (Group A) may get hydrolysed on interaction with effluents of alkaline nature (Group B), and may be transformed into colloidal or precipitate forms.

4. The colloids formed as above, due to their surface active forces, may adsorb a variety of dissolved species and suspended solids and settle down resulting in the lowering of TDS and COD values of the interacting effluents.
### TABLE 1-2 CATEGORIZATION OF EFFLUENTS ON THE BASIS OF THEIR ACIDIC OR ALKALINE NATURE

<table>
<thead>
<tr>
<th>GROUP - A (Acidic Effluent)</th>
<th>Source of Effluents</th>
<th>pH</th>
<th>Prominent Characteristics</th>
<th>GROUP - B (Alkaline Effluents)</th>
<th>pH</th>
<th>Prominent Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphuric Acid Plant</td>
<td>2.3</td>
<td>High Sulphates Mill</td>
<td>Cotton Textile</td>
<td>10.5</td>
<td>High BOD,COD,TSS</td>
<td></td>
</tr>
<tr>
<td>Chlor-Alkali</td>
<td>1.7</td>
<td>Dissolved Hg</td>
<td>Dairy</td>
<td>8.2</td>
<td>High COD,BOD</td>
<td></td>
</tr>
<tr>
<td>Galvanising</td>
<td>2.3</td>
<td>Dissolved iron</td>
<td>Tannery</td>
<td>8.5</td>
<td>High TSS,TDS,Cl</td>
<td></td>
</tr>
<tr>
<td>Distillery</td>
<td>4.4</td>
<td>High TDS,COD,BOD</td>
<td>Pulp &amp; Paper</td>
<td>8.2</td>
<td>High TDS,COD</td>
<td></td>
</tr>
<tr>
<td>Rice Mill</td>
<td>5.5</td>
<td>High TDS,COD</td>
<td>Oil Refinery</td>
<td>6.5 - 9.0</td>
<td>High oil and fats</td>
<td></td>
</tr>
<tr>
<td>Electric Fan Manufacture</td>
<td>5.2</td>
<td>Cr,Zn,CN [Coke Oven]</td>
<td>Steel Plant</td>
<td>9.1</td>
<td>High phenol,cyanide</td>
<td></td>
</tr>
<tr>
<td>Oxalic Acid Manufacture</td>
<td>2.9</td>
<td>High TDS,Oxalates</td>
<td>Poultry</td>
<td>6.5 - 9.0</td>
<td>High total solids</td>
<td></td>
</tr>
<tr>
<td>Ahum Plant</td>
<td>3.2</td>
<td>Dissolved Al</td>
<td>Soap Plant</td>
<td>11.0</td>
<td>High TDS,COD</td>
<td></td>
</tr>
<tr>
<td>Phosphatic Fertilizer Plant</td>
<td>2.0</td>
<td>Fluorides</td>
<td>Ball Bearing Manufacture</td>
<td>10.5</td>
<td>High TDS,COD</td>
<td></td>
</tr>
<tr>
<td>Lamp &amp; Tubes Industry</td>
<td>6.1</td>
<td>High TDS,dissolved Mo</td>
<td>Aluminium Plant</td>
<td>10.5</td>
<td>High TDS,Dissolved Al,Cr,Zn,Mn</td>
<td></td>
</tr>
<tr>
<td>Metal Pickling [Brass&amp;Copper]</td>
<td>3.0</td>
<td>Free acid,dissolved toxic</td>
<td>b)Smelter Plant</td>
<td>7.5</td>
<td>High TDS,Zn,Mg</td>
<td></td>
</tr>
<tr>
<td>Coal Mining</td>
<td>3.7</td>
<td>High free acid, sulphates</td>
<td>c)Red Mud Pond Plant</td>
<td>1.5</td>
<td>Zn,Mg</td>
<td></td>
</tr>
<tr>
<td>Synthetic Resin</td>
<td>6.5</td>
<td>High TSS,TDS Chlorides</td>
<td>Automobile Service Station</td>
<td>7.5</td>
<td>Oil and grease, dissolved Pb</td>
<td></td>
</tr>
<tr>
<td>Explosive Manufacture</td>
<td>6.0</td>
<td>High TSS,TDS,Gr,Al,TNT and Ni-</td>
<td>Foam Industry</td>
<td>8.12</td>
<td>Milky suspension, High TDS</td>
<td></td>
</tr>
<tr>
<td>Plastic Resin Manufacture</td>
<td>4.5</td>
<td>Dissolved organic matter</td>
<td>Copper Ore-Concentrate Plant</td>
<td>8.5</td>
<td>High TSS,Fluoride and Xanthate</td>
<td></td>
</tr>
</tbody>
</table>

* Average Values
In the subsequent chapters, the anticipated behaviours of the effluents under Group A on interaction with effluents under Group B have been experimentally verified and described.

1.6 SCOPe AND METHOdOLOGY

The preservation of the natural characteristics of the environment is becoming more and more challenging job with the rapid growth of industrialisation in India and elsewhere resulting in the discharge of waste waters of strange natures and compositions into the environment.

The effluents discharged are required to be treated suitably under statutory regulations prior to their discharge for the minimisation of the injury to the environment. The treatments of the effluents in one or the other manners are in practice in the developed and also in the developing countries. Effluent treatment is always investment-oriented. The investment factor is quite significant for developing countries such as India. The expensive methodologies of effluent treatment being followed in advanced countries have limited scope in India due to the economic constraints. It was felt desirable to think about such methodologies for use in the country which may attract wide applicability due to the cost-effectiveness involved in the methodologies. The above stated observation has remained the central point in undertaking the type of studies being described in the subsequent chapters.

The prime objective of the study is to create an awareness where two or more industries located in close proximities could identify the nature of the effluent produced by their respective units, and examine how the damaging features of their effluents could be quenched or greatly reduced
by the simple act of pooling the discharged effluents together at some predetermined flow rate or ratio. For obtaining an acceptability for the proposed line of approach, a number of interactions of effluents have been experimentally studied, and their beneficial results described in the subsequent chapters.

It is hoped that during the planning stage of new industries, the criterion of site-selectivity based on the mutual advantage of the effluent interactability shall also be a point of due consideration.

An attempt has been made to base the treatment methodology studied and described here on sound scientific principles. As with every other research studies, the methodology studied and presented here is open for further improvements and perfections.

While undertaking the studies, a spectrum of effluents as wide as could practically be possible was used. The described work involved field visits to a total of fifteen industrial places. A total number of thirty five samples of industrial effluents were collected and analysed. A total of thirty one chemical species, in the collected samples of effluents, were determined by conventional and instrumental methods of analysis.

The Work carried out is being presented in chapters as detailed below


CHAPTER - 4 : Effluent - Effluent Interactions : Study of some Quarternary Cases.


CHAPTER - 6 : Industrial Effluents : Some specific studies.

It is believed that the inferences drawn out of the conducted studies shall achieve some degree of acceptability in the years to come, resulting in relief of the strain on environment caused by the discharge of the industrial effluents.
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