CHAPTER-II

LITERATURE REVIEW
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In modern society proper management of wastewater is a necessity, not an option. Wastewater generated from a community or industries if untreated and is allowed to accumulate, the decomposition of an organic matter it contain can lead to production of large quantities of malodorous gases. In addition, untreated wastewater usually contains numerous pathogenic microorganisms. It also contain nutrient, which can stimulate the growth of aquatic plants, and it may contain toxic compounds. For these reasons the immediate and nuisance-free removal of wastewater from its sources of generation, followed by treatment and disposal is not only desirable to adopt but also necessary in an industrialized society. The characterization and quantification of wastewater is a must to decide line and degree of treatment. Various treatment options are available, both conventional and non-conventional which are in practice. However there is a need to exercise of great care in selecting the line and degree of treatment option.

In this chapter an attempt has been made to throw light on characterization of wastewaters, treatment options available and their suitability and investigations carried out by various researchers in this field.

2.1 CHARACTERISTICS OF WASTEWATER

To decide line, degree of treatment and disposal of wastewater it is essential to know its composition, quality and characteristics. Though the characteristic of sewage depends on the source, in general contain organic matter, inorganic matter and living organisms. The domestic wastewaters may be classified as strong, medium and weak depending upon the constituents of wastewaters. A typical composition of domestic wastewater is shown in the Table 2.1.
Table 2.1: Typical Composition of Domestic Wastewater
(Punmia and Ashok Jain: 1998)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Strong</td>
<td>Medium</td>
<td>Weak</td>
</tr>
<tr>
<td>1. Solids: Total</td>
<td>(mg/l)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dissolved, total</td>
<td>1200</td>
<td>750</td>
<td>350</td>
</tr>
<tr>
<td>Fixed</td>
<td>850</td>
<td>500</td>
<td>250</td>
</tr>
<tr>
<td>Volatile</td>
<td>525</td>
<td>300</td>
<td>145</td>
</tr>
<tr>
<td>Suspended, total</td>
<td>325</td>
<td>200</td>
<td>105</td>
</tr>
<tr>
<td>Fixed</td>
<td>350</td>
<td>220</td>
<td>100</td>
</tr>
<tr>
<td>Volatile</td>
<td>75</td>
<td>55</td>
<td>20</td>
</tr>
<tr>
<td>2. Settleable solids</td>
<td>(mg/l)</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>3. Biochemical oxygen demand</td>
<td>(mg/l)</td>
<td></td>
<td>400</td>
</tr>
<tr>
<td>(BOD\textsubscript{5}, 20°C)</td>
<td>(mg/l)</td>
<td>290</td>
<td>160</td>
</tr>
<tr>
<td>4. Total organic carbon</td>
<td>(mg/l)</td>
<td>1000</td>
<td>500</td>
</tr>
<tr>
<td>(TOC)</td>
<td>85</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>5. Chemical oxygen demand</td>
<td>(mg/l)</td>
<td>35</td>
<td>15</td>
</tr>
<tr>
<td>(COD)</td>
<td>50</td>
<td>25</td>
<td>12</td>
</tr>
<tr>
<td>6. Nitrogen (total as N)</td>
<td>(mg/l)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Organic</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>free ammonia</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nitrites</td>
<td>15</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Nitrates</td>
<td>5</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>7. Phosphorus (Total as P)</td>
<td>10</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Organic</td>
<td>100</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>Inorganic</td>
<td>200</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>8. Chlorides</td>
<td>(mg/l)</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>9. Alkalinity (as CaCO\textsubscript{3})*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10. Grease</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Depends upon its amount in domestic water supply.
Characteristics of industrial wastewater vary greatly from industry to industry and also on the technology adopted, process raw materials, unit production, housekeeping practice etc. Characteristics of industrial wastewaters have been quoted by the authors and are widely available in the literature. But with reference to the present research work, the characteristics of electroplating industry and wastewaters from the sugar mills are discussed in the further sub sections.

2.1.1 Wastewater from Electroplating Industry

After metals have been fabricated into the appropriate sizes and shapes to meet customers’ specifications, they are finished to final product requirements. Finishing usually involves stripping, removal of undesirable oxides, cleaning, and plating. In plating metal in solution serves as the anode. The total liquid wastes are not voluminous, but are extremely dangerous because of their toxic content. The most important toxic contaminants are acids and metals, such as chromium, Zinc, copper, Nickel, tin, and cyanides. Alkaline cleaners, grease, and oil are also found in the wastes.

2.1.2 Characteristic of Metal-Plating Wastes.

Most stripping baths are acidic in nature and consist of solutions of sulfuric, nitric and hydrochloric acid, but alkaline baths containing sodium sulfide, cyanide and hydroxide may also be used. Usually the chemicals in the stripping solution are present in concentrations of less than 10 percent. Cleaning is carried out by organic solvents, pickling, or alkaline cleaning compounds. The organics-emulsion cleaners are petroleum or coal-tar solvents coupled with an emulsifier. Alkaline cleaners consist of sodium hydroxide, orthophosphate, complex phosphates, silicates, carbonates, some organic emulsifiers and synthetic wetting agents.

The character and strength of plating wastes vary considerably, depending on plating requirements and type of rinsing used. The total plant waste may be either acidic or alkaline, depending on the type and quantity of baths used. A preponderance of cyanide or alkaline cleaning baths is likely to result in a highly alkaline pH, while the opposite may be true for chromate baths. The amount of stripping done is also important, since this operation contributes a highly acid waste to the plant mixture.
Table 2.2 presents typical plating-waste concentrations obtained from seven different plants.

Table 2.2: Plating-Waste Concentrations. (Nelson L. Nemerow: 1971)

<table>
<thead>
<tr>
<th>Plant</th>
<th>pH</th>
<th>Cu, ppm</th>
<th>Fe, ppm</th>
<th>Ni, ppm</th>
<th>Zn, ppm</th>
<th>Chromium, ppm</th>
<th>Cn, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.2</td>
<td>16</td>
<td>11</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>A</td>
<td>10.4</td>
<td>19</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>B</td>
<td>4.1</td>
<td>58</td>
<td>1.2</td>
<td>0</td>
<td>0</td>
<td>204</td>
<td>246</td>
</tr>
<tr>
<td>C</td>
<td>2.8</td>
<td>11</td>
<td>0.2</td>
<td>0</td>
<td>82</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>D</td>
<td>2.0</td>
<td>300</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.7</td>
</tr>
<tr>
<td>E</td>
<td>2.4</td>
<td>35</td>
<td>8</td>
<td>0</td>
<td>82</td>
<td>555</td>
<td>612</td>
</tr>
<tr>
<td>E</td>
<td>10.7</td>
<td>14</td>
<td>4</td>
<td>19</td>
<td>39</td>
<td>32</td>
<td>39</td>
</tr>
<tr>
<td>F</td>
<td>10.5</td>
<td>6</td>
<td>2</td>
<td>25</td>
<td>39</td>
<td>36</td>
<td>10</td>
</tr>
<tr>
<td>G</td>
<td>11.3</td>
<td>18</td>
<td>18</td>
<td>26</td>
<td>39</td>
<td>95</td>
<td>13</td>
</tr>
<tr>
<td>G</td>
<td>11.9</td>
<td>23</td>
<td>21</td>
<td>32</td>
<td>39</td>
<td>36</td>
<td>15</td>
</tr>
</tbody>
</table>

2.1.3 Wastewater from Sugar Mills

At the factory, the sugar cane is cut into pieces and crushed in mills to release the juice. The fibrous residue, known as bagasse, is burned in boilers. Lime is added to the juice to prevent the inversion of sucrose into glucose and fructose, and to clarify it. Usually bentonite or other auxiliary coagulants are also added. Next the juice is pumped through preheaters into clarifiers, from where the clarified juice passes to multi-effect evaporators. The sludge retained in the clarifiers, is filtered on vacuum filters and the juice extracted is passed to the main manufacturing cycle. The solid residue is used as a fertilizer.

The juice is concentrated in evaporators to a water content of 30-40%. The syrup is passed into vacuum pans where the sugar is crystallized. Centrifuges are used to separate the crystallized sugar from the residual components of the syrup, i.e. the molasses. A second crop of sugar is crystallized from the molasses.
Cane-sugar wastes can be divided into two groups. The first includes cooling and condenser wasters, while the other group comprises concentrated wastes from spillage, scum leaks, the washing of equipment and production rooms, effluents from the boiler house and wastes containing lubricants and oil from machinery.

Characteristics of wastes from the different sections of common sugar mill and that of the combined waste, are given in Table 2.3.

Table 2.3: Characteristics of Sugar Mill Wastes (Rao and Datta: 1987)

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Mill-house waste</th>
<th>Filter cloth washings</th>
<th>Condenser water</th>
<th>Boiler house and floor washings</th>
<th>Combined waste (excluding condenser water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate of flow, liters per tonne of cane Crushed</td>
<td>730</td>
<td>360</td>
<td>1640</td>
<td>230</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>6.7</td>
<td>9.5</td>
<td>-</td>
<td>7.2</td>
<td>4.6-7.1</td>
</tr>
<tr>
<td>COD, mg/l</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>600-4380</td>
</tr>
<tr>
<td>BOD, mg/l (5 day 20°C)</td>
<td>210</td>
<td>1765</td>
<td>-</td>
<td>5150</td>
<td>300-2000</td>
</tr>
<tr>
<td>Total solids, mg/l</td>
<td>1760</td>
<td>6970</td>
<td>-</td>
<td>5130</td>
<td>870-3500</td>
</tr>
<tr>
<td>Total volatile solids, mg/l</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>400-2200</td>
</tr>
<tr>
<td>Total suspended solids, mg/l</td>
<td>910</td>
<td>4000</td>
<td>-</td>
<td>120</td>
<td>220-800</td>
</tr>
<tr>
<td>Total nitrogen mg/l</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10-40</td>
</tr>
<tr>
<td>COD/BOD ratio</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.3-2.0*</td>
</tr>
</tbody>
</table>

*Average value

2.2 TREATMENT OPTIONS

A wastewater treatment system is composed of a combination of unit operation and unit process designed to reduce constituents of wastewater to an acceptable level. Many different combination are possible. Although practically all wastewater treatment systems are unique in some respect, a general grouping of unit operations and unit
process according to target contaminant has evolved over the years. Unit operations and process commonly used in wastewater treatment and their arrangement according to conventional grouping available elsewhere in the literature. The merits and demerits of the process in treating wastewaters are also discussed elsewhere in the literature.

The land treatment of wastewater involves the use of soil surface and soil matrix for wastewater treatment although land treatment of wastewater is in practice for centuries, its full potential as only recently being recognized. The principle reason for this is the wide spread research and development activity on water reuse, nutrient recycling and the use of wastewater for crop production. Further more systematic method of treatment of wastewater by application on land and thereby recharging of groundwater in arid zone has lead to the development of soil aquifer treatment system for effective disposal of wastewater.

2.3 TREATMENT OF WASTEWATERS

Wastewater which if not properly disposed off, can create problems of hygiene and health. Most of our cities and towns face these problems. Further since large number of our cities are located on banks of rivers, unhygienic wastewater disposal practices cause pollution of river water. Several conventional and innovative technologies are available for treatment and disposal of municipal wastewater. Conventional primary and secondary treatment techniques have mostly aimed at disposal of treated effluent either into public sewers, for irrigation, into marine coastal area and or inland water bodies, without much consideration for conservation and renovation. The practice of disposing of even the secondary treated wastewater into inland water bodies may result in hazardous consequences particularly in less developed countries where sizeable population consume stream/river water, after a minimal filtration. It is therefore, desirable that alternative technology for wastewater disposal that result in conservation of natural water sources in their pristine condition and renovation of wastewater for reuse are devised. Reuse of wastewater is more economical alternative to desalination of seawater. Wastewater reuses in irrigation also permits a convenient and inexpensive utilization of nutrients (nitrogen and phosphorous) present in water for their fertilizer value.
One of the major requirements of wastewater reuse is that it be treated to a level suitable for the intended use at an acceptable cost to the community. Conventional wastewater treatment plants usually have three stages of treatment, namely, primary, secondary and tertiary levels of treatment. In primary treatment, physical operations such as screening and sedimentation are used to remove the floating and settleable solids present in the wastewater. In secondary treatment, biological and chemical processes are used to remove most of the organic matter. In tertiary treatment, an additional combination of unit operations and processes are used to remove constituents such as nitrogen and phosphorous. The cost of conventional treatment of wastewater varies considerably and depends on the size of the plant (Bouwer: 1993).

Furthermore, major problems impede the reuse of treated wastewater produced by conventional wastewater treatment plants. These are: (1) the high cost of treatment, (2) the lack of buffer storage and (3) the psychological disadvantage of the term wastewater. It is expensive to produce high quality, treated wastewater that can be used for irrigation or landscaping without restriction. Production of wastewater is normally constant, irrespective of seasons. The demand for treated wastewater varies with the seasons, and hence, a buffer storage is required for the storage of treated wastewater produced when the supply exceeds demand. The quality of wastewater treated in conventional plants can be very high, but it is still called wastewater and hence, is disliked by many for psychological reasons. As a consequence of the accelerating threat of pollution to the environment and our incomplete knowledge of ways to stabilize pollutant movement throughout the environment, land treatment technology is being actively sought.

2.4 LAND TREATMENT

The land is a gigantic biodigetion system developed over millions of years. This natural system digests the animal and plant wastes to become part of the soil. The soil continues to be the primary means of mass disposal. The role of the land (soil) for recycling wastes, particularly organic wastes and wastewaters, receives increasing attention because of the quantity and variety of wastes and variations in methods of
disposal. Land disposal sites, however, present a serious potential threat to the quality of surface and underground waters as well as to the soil itself.

Land treatment of hazardous wastes is characterized as spreading the waste on the soil surface or incorporating it into the upper few centimeters by mechanical manipulation such as tilling or soil injection. The method of application and extent of soil manipulation depends on the physical, chemical and toxic nature of the waste and the rate of biodegradation desired.

The major benefit of land treatment is to engage the natural assimilative capacity of the land for disposal. Once the wastes have been destroyed, the land may be used for other beneficial purposes. In some instances, the land is more fertile following land treatment as a result of the accumulation of organic matter or humus as by-products of the decomposition reactions and incidental release of certain plant nutrients.

Land treatment must be understood, planned, and managed with the same degree of attention provided any other process operation. The complexities of waste-soil and natural process interactions, must be understood if land treatment is to be an acceptable practice and develop on a sound technical basis. An appreciation and knowledge of suitable land treatment site locations is the first step in adequate pollution control and protection of the surrounding environment.

2.5 SOIL AQUIFER TREATMENT (SAT)

Soil Aquifer Treatment represents a wastewater reclamation/reuse technology that can renovate wastewater effluent to drinking water levels and hence can be an important component in an indirect potable reuse system.

SAT, an advanced wastewater treatment system, consist of controlled passage of effluents through unsaturated zone and the aquifer, mainly for purification purposes, as well as for seasonal and multiannual storage. The vadose zone in soil acts as natural filter and is capable of removing all the suspended solids, biodegradable material, bacteria, viruses and other significant organisms from wastewater. As the water percolates downward, biological and chemical actions that takes place in the first few feet of soil and sandy substrates breakdown organic compounds and other pollutants.
Rapid infiltration achieves an excellent reduction of biochemical oxygen demand, suspended solids, and fecal coliform. Significant reductions in phosphorous, nitrogen and heavy metal concentration have also been achieved. SAT adds to purification of effluents by process of slow sand filtration, chemical precipitation, adsorption, ion exchange, biological degradation, nitrification and de-nitrification.

2.5.1 Risks Associated with SAT

SAT systems are very efficient systems for renovation of wastewater but certain risks involved with these systems are as follows: (Samanpreet Kaure and Mandeep Singh: 2002)

- The life span of these SAT systems is shorter as compared with some other natural systems.

- There is increase in the concentration of calcium, magnesium, potassium, and cation exchange capacity of the soils used at the sites.

- If ground water is shallow (i.e. less than 1 m), use of SAT system can cause mixing of renovated wastewater with ground water, consequently deteriorating the quality of ground water.
• As system is less effective in removing heavy metals and nutrients so it can’t be used at places where industrial effluent enters wastewater.

• Human consuming crops grown at such places contain toxic chemicals that can cause health hazard.

• Systems are adoptable if there is no land constraint.

• Soil compaction may occur with passage of time.

• In winter climates filter failure may occur due to pore clogging.

2.6 SPECIFIC REVIEWS ON SAT

A large number of research projects have been undertaken to study the effectiveness of SAT. The review study has shown some significant results in the wastewater treatment processes that were found economical in the third world countries, having economical and technological constraints.

Study conducted at the Northwest water reclamation plant, Mesa (Arizona), evaluated MF/RO and SAT (> 6 months residence time) treated tertiary effluent with respect to organics removal. Jorg et al. (2003). The study revealed that final TOC (Total Organic Carbon) concentrations of MF/RO and SAT are 0.3 and 1.0 mg/l, respectively. Based on the characterization techniques used, the character of bulk organics present in final SAT water resembles the character of natural organic matter present in drinking water. Depending on the molecular weight cut-off, RO (reverse osmosis) membranes can efficiently reject high molecular weight organic matter (characterized as humic and fulvic acids). However, approximately 40-50 percent of the remaining TOC in permeates consists of low molecular weight acids and neutrals representing a molecular weight range of ~ 500 Da and less. In the SAT treated effluent, EDTA and APEC’s were removed to approximately 4.3 and 0.54 µg/l, respectively, but were below the detection limit in the MF/RO treated effluent.

A 5-year program of study was conducted at the Sweetwater Recharge Facilities (SRF) to assess the performance of surface spreading operation for organics attenuation
during field-scale SAT of municipal wastewater (David et al.: 2003). Studies were conducted utilizing both mature (~10 yr old) and new infiltration basins. Removals of dissolved organic carbon (DOC) were robust, averaging > 90 percent during percolation through the local 37 m vadose zone. The hydrophilic (most polar) fraction of DOC was preferentially removed during SAT; removals were attributed primarily to biodegradation. Reductions in trihalomethane formation potential (THMFP) averaged 91 percent across the vadose zone profile. Variations in the duration of wetting/drying periods did not significantly impact organic removal efficiencies.

A new methodology for determining optimal operation of SAT systems considering parameter uncertainty was conducted by Liang xu et al. (2001). The problem of optimal operation of SAT systems is formulated and solved in discrete-time optimal control framework by interfacing the SALQR (Successive Approximation Linear Quadratic Regulator) optimizer with the MSTS (Multiphase Subsurface Transport Simulator) model. Both deterministic and stochastic programming formulations have been solved. Through the use of first order-analysis of uncertainties, the uncertainty of the water content due to the uncertainties of the simulation parameters are evaluated. A chance constrained formulation of the optimization is utilized to account for the uncertainties of water content in the SAT operation. This approach enables one to quantify the uncertainty of the parameter estimates, and automatically account for the parameter uncertainty in the decision-making process through SAT management model.

Vishwanathan et al. (1999) carried out field studies to access the feasibility of SAT in treating wastewater treated to tertiary level. An experimental pond and ground water monitoring well adjacent to pond were constructed and utilized for studies. The wastewater was allowed to infiltrate in the experimental pond for 112 days. The overall loading rate for the entire period was about 0.76 m/day. The results showed 70, 81, 80 and 100 % removal of COD, BOD, phosphates and fecal coliform respectively. The authors concluded that the wastewater produced after SAT is suitable for unrestricted irrigation and cost of treatment by SAT is considerably less than that of conventional methods.
Houston et al. (1999) studied that infiltration rates of SAT were influenced by soil type and profile characteristics, surface clogging material, pond depth and wetting/drying cycle times. Primary effluent may be more desirable than secondary effluent for SAT system because higher OC content enhances denitrification beneath infiltration basins.

Mays et al. (1998) conducted pilot scale column studies from two proposed SAT sites and two existing SAT sites. Sets of columns were operated to simulate five different soils and six different effluent qualities. Results stated that chlorinated denitrified effluents with sandy soil provided high infiltration rates. Persistent organic carbon concentrations of 4-6 mg/l were observed for all wastewater effluents evaluated. Virus removal was found to be inversely proportioned to infiltration rate. Removals ranged from 50-99 % for one meter of soil.

Gupta and Nema (1997) conducted a pilot study on SAT in Sabarmathi bed at Ahmedabad and found 90 % reduction in organic pollutants (COD, BOD and SS), 70 % reduction in NH4-N, 90 % reduction in PO4-T, and 95 % reduction in PO4-O. NO3-N showed an increase of 40 %, metals concentration also increased by 50-450 %. Bacteria and viruses were efficiently removed. TDS on other hand showed an increase of about 2 %.

Zinc adsorption was studied in four soils (two alfisols and two inceptisols) under three different moisture regiments, viz., flooded-drying(FD), alternate wetting and drying (AWD), and preflooding(PF), each with and without added organic matter (0.50 and 0 %). (Biswapati Mandal and Hazra: 1997). Results showed that FD and AWD moisture treatment caused a marked decrease, whereas the PF treatment caused a marked increase, in the magnitude of Zn adsorption by the soils compared with controls (no moisture and no organic matter treatment). However, there was a significant increase in Zn adsorption compared with no organic matter control when organic matter was combined with all three moisture regime treatments. Other adsorption related parameters of the soils, such as adsorption maxima, bonding energy constant, free energy change for Zn and Zn-hydroxide potential, affirmed the pattern of changes in Zn adsorption following such treatments. All such changes have been explained on the basis of the changes in soil physico-chemical properties, viz., pH, CaCO3 equivalent and
Fe oxides as a result of treatments. Amorphous Fe oxides and soil pH were, however, found to play a major role in this regard. Results indicated the need for split application of Zn under AWD and FD regimes, but the reverse is true under PF treatments.

Bench-scale soil column experiments were performed at the University of Arizona by David et al. (1996) to examine the effects of soil type and infiltration rate on the removal of wastewater organics during SAT. SAT was simulated in 1-meter soil columns containing repacked homogenized soils ranging from poorly graded sands to Silty sands. Treatment efficiencies in biologically active and inhibited columns were compared to determine the mechanism of water quality improvements and the sustainability of SAT. Differences in through-column removal of non-purgable dissolved organic carbon were significant for columns containing sandy loam (56 %), sand (48 %) and Silty sand (44 %). Removal of UV-absorbing organics was not significantly different for columns containing sand and sandy loam (22 and 20 %, respectively). There was no significant correlation between infiltration rate and removal efficiency of either organic parameter for both soils.

Wilson et al. (1995) summarized the results of field studies in Tucson, Arizona, to estimate the SAT effectiveness of 5.7 ha water spreading facility. Results showed 92 % and 85 % removal of dissolved organic carbon and total organic carbon respectively. Enetroviruses were completely removed during 37 m travel through vadose zone.

Amy et al. (1993) found the average dissolved organic carbon and total organic carbon removal was 50 % and 40 % respectively from secondary effluent through SAT system.

The competitive adsorption of Cd, Cu, Pb and Zn from 0.025M NaClO₄ solutions onto four soils with differing chemical properties was investigated with batch adsorption experiments by Elliott et al. (1986). For two mineral soils, adsorption under acidic conditions (pH 5.0) followed the sequence Pb > Cu > Zn > Cd, which corresponds to the order of increasing pK for the first hydrolysis product (e.g., pbOH⁺) of the metal ions. In contrast, the order of selectivity for two soils containing 20 to 40 g/kg organic C was Pb > Cu > Cd > Zn, suggesting that organic matter (OM) increased Cd retention preferentially over that of Zn. When accompanied by a sizable reduction in
cat-ion exchange capacity (CEC), extraction of soil OM markedly reduced adsorption of all four metals. However, only Cd and Cu adsorption were appreciably smaller for a soil that maintained a sizeable CEC following OM removal. Lead and possibly Zn, adsorption by soils with substantial inorganic exchange sites may be unresponsive to organic waste amendments. For Cd and Cu, increased soil OM should restrict mobility and bioavailability, at least under acidic conditions were soluble metal complex formation is limited.

David et al. (1996) carried out soil column experiments to differentiate between abiotic and biological mechanisms for removal of residual organics from chlorinated municipal effluent during SAT and to relate SAT efficiency to degree of wastewater treatment. Three water quality parameters were examined: dissolved organic carbon (DOC), ultraviolet (UV) absorbance at 254 nm (UVA$_{254}$) and adsorbable organic halide (AOX). DOC was removed primarily by biological activity during SAT. Through-column removal using chlorinated secondary effluent averaged 48 %. UVA$_{254}$ reductions were dependent on biological and abiotic removal mechanisms. Aerobic biological activity did not contribute significantly to AOX removal. Through-column reductions for UVA$_{254}$ and AOX from secondary effluent averaged 30 % and 17 %, respectively. Forty-four percent of the through-column DOC removal and 57 % of UVA$_{254}$ attenuation occurred in the top 8 cm of soil. The post-SAT organic quality of secondary and tertiary effluents was essentially equivalent.

Effect of wastewater loading rate and soil amendments proposed to help overcome the detrimental effect of soil smearing on wastewater treatment by a soil absorption system was evaluated by Uebler (1984). Three loading rates 7.5, 11.3 and 15.0 L/m$^2$/d, were tested and two soil amendments, cement and lime, were compared with a control. The amendments were added to the soil on a 5 % by-weight basis. Three absorption trenches, 3.0 m in length, were dug for each loading rate-soil amendment combination. Soil water samples were obtained monthly for 12 months from ceramic cups placed 15 and 30 cm below the trenches. Water samples were analyzed for NH$_4^+$-N, NO$_3^-$-N, soluble P, chloride and pH. Concentrations of NH$_4^+$-N, NO$_3^-$-N, and soluble P varied significantly with the time of sampling. Transformation of NH$_4^+$-N to NO$_3^-$-N was enhanced by the soil amendments, indicating that the aeration status of the soil near
the trenches was improved by the amendments. The effect of the amendment was most noticeable during the spring recovery period as aeration status was increasing from winter minimums. Higher NO$_3^-$-N levels for the cement as compared with the lime in spring suggest that cement may be a more effective amendment than lime. The lowest loading rate had significantly higher concentration of NO$_3^-$-N during the spring months. Soluble P levels increased linearly from 0.1 to 0.9 mg/l over the first year operation of the system.

Bouwer and Rice (1984) reported 40 % reduction in infiltration rates during first few months of operation due to soil compaction and pore clogging.

Carlson et al. (1982) studied rapid infiltration system located on the site of 75$^{th}$ street wastewater treatment plant in Boulder, colo. He found that all the nitrogen was oxidized by nitrification and discharged as nitrate nitrogen. Phosphorous removal was 60-90 %. All the fecal coliform was removed from secondary effluent.

Gerba (1992) studied fate of viruses in treated sewage effluents during SAT. A minibasin (3.6 m x 3.6 m) was constructed at Arizona, USA. The results indicated that 90 % removal of bacteriophage MS-2 (a virus that infects and lyses certain bacteria) and 99 % removal of PRD-1 (Drug Resistance Plasmid Dependent Host Range of PRD-1), after movement of sewage through 4.5 m of soil at high infiltration rates (up to 15 m/day).

Bouwer et al., (1980) studied flushing meadows project. It consisted of six parallel, horizontal basins 6.1 m x 213 m each, each 6.1 m apart. Infiltration rate ranged from 0.3 m/day to 1 m/day. Soil consists of top 1 m of loamy sand followed by coarse sand. They found that maximum hydraulic loading was observed with flooding periods of 2-3 weeks in summer and 20 days in winter. Also after 10 year of project operation, there were no signs of reduction of hydraulic loading or hydraulic conductivity of underlying aquifer. The suspended solids content was less than 1 mg/l after renovation. Total organic carbon (TOC) removal was 50-75 % through SAT. Nitrogen removal was 30 % at maximum hydraulic loading and 65 % at reduced hydraulic loading. Phosphate removal was 40 % at high hydraulic loading and 80 % at reduced hydraulic loading. Boron showed no removal. Zinc was reduced from 193 g/l to 35 g/l. Copper was
reduced from 123 g/l to 16 g/l. Fecal coliform removal occurred within top meter of vadose zone and 3-6 m movement through aquifer. Total removal of BOD$_5$ was observed through SAT. However, some residual organic carbon (OC) was present in the incoming effluent.

Levine (1980) reported that even after 30 years of SAT system operation nitrogen accumulation within the soil profile was only 2 % of nitrogen applied. However, there was increase in conductivity, cation exchange capacity, exchangeable calcium, magnesium and potassium of soil. Soil maintained its ability to absorb phosphorous. pH of soil decreased. There was 30 % reduction in infiltration rates during second 34 weeks of flooding indicating that some cultivation is necessary for long term maintenance of infiltration rates.

Lance (1980) in another study found that nitrogen removal through soil columns was 45.6 % from primary effluent, 28.5 % from secondary effluent both using bare soils and 81.8 % from primary effluent and 48.1 % from secondary effluent using vegetated columns. Fecal coliform reduced sharply during first 8 cm travel and then decrease in their count was linear. In addition, presence or absence of vegetation did not affect coliform removal.

Lance et al. (1978) further studied, using same setup that nitrogen removal was increased by 10-18.5 % when vegetation was used.

The relationship between the total solids load and the hydraulic properties of the restricting layer as affected by different gradients and SS concentrations on two soils is studied by Robert (1974). The authors reported that the maximum infiltration of secondary wastewater effluent can be obtained by efficient management of recharge facilities. Physical clogging caused by deposition of SS on the soil surface was the predominant cause of infiltration reduction. Little evidence of surface biological clogging was found. Maintaining low SS concentrations in the wastewater was the most important factor in optimizing infiltration. Concentrations below 10 mg/l should be maintained. Low solids concentration can usually be obtained by sedimentation. During long periods of intermittent inundation, clogging developed below the surface because entrapped gasses blocked the soil pores. This clogging was probably caused by
microbial activity. High hydraulic gradient should be maintained in the soil system even though infiltration rates decreased faster than at low gradients. At high gradients, the higher initial infiltration rates yielded greater total volumes of water than the low gradients.

Lance (1977) used soil columns consisting of loamy sand soil and wetting/drying schedule of 9 days flooding and 5 days drying to determine phosphate removal from sewage. The results showed that phosphate removal from secondary sewage effluents by calcareous sand columns was proportional to infiltration rates. 75-80 % phosphate removal from secondary sewage effluents continued when infiltration rate was maintained below 15 cm/day.

Vries (1972) reported that physical condition of sand filters did not deteriorate as a result of daily application of secondary effluent for 240 days at a rate of 20 cm/d, 5 days/wk with daily application period of 2 hr and providing rest period of 22 hr between application, but if temperature was 4±3°C filter failure occurred due to pore clogging.

2.7 REMOVAL OF TS AND TDS

Both secondary treatment and nutrient removal decrease the dissolved-organic-solids content of wastewater. Neither process, however, completely removes all dissolved organic constituents, and neither process removes significant amounts of inorganic dissolved solids. Further treatment will be required where substantial reductions in the total dissolved solids of wastewater must be made.

Ion exchange, microporous membrane filtration, adsorption, and chemical oxidation can be used to decrease the dissolved solids content of water. These processes were developed to prepare portable water from a poor-quality raw water. Their use can be adopted to advanced wastewater treatment if a high level of pretreatment is provided. The removal of suspended solids is necessary prior to any of the processes. Removal of the dissolved organic material (by activated carbon adsorption) is necessary prior to microporous membrane filtration to prevent the larger organic molecules from plugging the micropores.
Advanced wastewater treatment for dissolved solids removal is complicated and expensive. Treatment of municipal wastewater by these processes can be justified only when reuse of the wastewater is anticipated.

2.8 REMOVAL OF NUTRIENTS

Although the quantities of nutrients contributed by wastewater discharges may be less than those contributed by agricultural runoff and other sources, point-source nature of wastewater discharges makes them more amenable to control techniques. Thus, wastewater-treatment plants that discharge to water bodies that are delicately balanced with respect to nutrient loads may have nutrient limitations imposed on their effluents. The nutrients most often of interest are nitrogen and phosphorous compounds. Processes for removing these nutrients from wastewater are discussed in the subsections as below.

2.8.1 Nitrogen Removal

In domestic wastewater, nitrogen compounds result from the biological decomposition of proteins and from urea discharged in body waste. This nitrogen may be bound in complex organic molecules and is referred to simply as organic nitrogen rather than by specific compound. Organic nitrogen may be biologically converted to free ammonia (NH$_3^0$) or to the ammonium ion (NH$_4^+$) by one of several different metabolic pathways. These two species, together termed ammonia nitrogen, exist in equilibrium according to the following relationship:

$$\text{NH}_4^+ \leftrightharpoons \text{NH}_3^0 + \text{H}^+$$

Ammonia nitrogen, the most reduced nitrogen compound found in wastewater, will be biologically oxidized to nitrate as follows if molecular oxygen is present.

$$\text{NH}_4^+ + 3/2 \text{O}_2 \leftrightharpoons \text{NO}_2^- + 2\text{H}^+ + \text{H}_2\text{O}$$

$$\text{NO}_2^- + 1/2\text{O}_2 \leftrightharpoons \text{NO}_3^-$$

These reaction result in the utilization of about 4.6 mg of O$_2$ per each mg of NH$_4^+$-N oxidized, with about 7.1 mg of alkalinity needed to neutralize the acid(H$^+$) produced.
In raw wastewater, the predominant forms of nitrogen are organic nitrogen and ammonia. Biological treatment may result in conversion to nitrate, provided the processes are aerobic and provided the treatment periods are long enough. Contact times in most secondary treatment systems, though sufficient to complete the conversion from organic nitrogen to ammonia, may not be sufficient for significant nitrification. Because of oxygen demand exerted by ammonia and because of other environmental factors, removal of ammonia may be required. The most common processes for removing ammonia from wastewater are (1) stripping with air and (2) biological nitrification - de nitrification.

### 2.8.2 Phosphorus Removal

Phosphorus is a ubiquitous constituent of municipal wastewater, averaging around 10 mg / l in most cases. The principal forms are organically bound phosphorus, polyphosphate and orthophosphates. Organically bound phosphorus originates from body and food waste and, upon biological decomposition of these solids, is released as orthophosphates. Polyphosphates are extensively in synthetic detergents and often contribute up to one-half the phosphorus in wastewater. Polyphosphates can be hydrolyzed to orthophosphates. Thus the principal form of phosphorus in wastewater is assumed to be orthophosphates, although for the other two forms may coexist.

Orthophosphates consist of the negative radicals PO$_4^{3-}$, HPO$_4^{2-}$, and H$_2$ PO$_4^-$ and may form chemical combinations with cations or positive radicals. In most cases the compounds are quite soluble, and phosphate removal in conventional primary treatment is negligible. Because phosphorus is a component of microbial cells, most phosphate may be removed in the biomass in secondary treatment processes. However, microorganisms need relatively little phosphorus as compared with carbon and nitrogen, and less than 3 mg/l of phosphorus is usually removed in conventional secondary treatment. When effluent requirement necessitates greater removal efficiencies additional treatment must be provided.

The principal means of phosphorus removal is chemical precipitation. At slightly acidic $\text{pH}$, orthophosphates combine with trivalent aluminum or iron cations to form a precipitate.
Because domestic wastewater usually contains only trace amount of iron and aluminum, the addition of these materials is necessary. Salts of these metals, such as those discussed in sections 4-6, can be added for this purpose.

At higher pH values, calcium forms an insoluble complex with phosphate. The addition of lime can provide both the calcium and pH adjustment necessary.

\[ 5\text{Ca(OH)}_2 + 3(H_n\text{PO}_4)^{(3-n)^{-}} \rightleftharpoons \text{Ca}_5(\text{OH})(\text{PO}_4)_3 + \text{nH}_2\text{O} + (9-\text{n})\text{OH}^{-} \quad \text{(c)} \]

This reaction requires a pH of at least 9.0 for significant phosphorus removal. Higher pH values generally increase removal efficiencies. However, recarbonation may be necessary to lower the pH after the precipitation process has removed the phosphorus.

Chemical requirements for phosphates precipitation exceed the stoichiometric requirements indicated in equation (a) through (c). Aluminum and iron salts react with alkalinity in the wastewater to produce metallic hydroxide flocs [Al(OH)₃] and Fe(OH)₃ and may increase the required dosages by up to a factor of 3. Fortunately, this increase is not totally wasted, as the metallic hydroxides assist in the flocculation and removal of the metallic phosphate precipitate, along with other suspended and colloidal solids in the wastewater, and are thus useful in the treatment process. At high pH values calcium reacts completely with wastewater alkalinity to form calcium carbonate. Lime additions equivalent to the alkalinity plus that required for phosphate precipitation and pH adjustment are required.

Phosphorus removal can be incorporated into primary or secondary treatment or may be added as tertiary process. Section of the point of application depends on efficiency requirements, wastewater characteristics, and the type of secondary treatment employed. The advantages and disadvantages of each system are summarized in Table 2.4. Where effluent phosphorus concentrations of up to 1.0 mg/l are acceptable, the use of aluminum or iron salts in the secondary system is often the process of choice, while high pH precipitation by lime in a tertiary unit is required to obtain very low levels of
effluent phosphorus. Where nitrogen removal by ammonia stripping is also practiced, tertiary lime precipitation at a pH of 11.5 serves in both processes.

**Table 2.4: Comparison of Point of Application for Phosphorus Removal Systems (Howard and Donald: 1985)**

<table>
<thead>
<tr>
<th>Primary</th>
<th>Secondary</th>
<th>Tertiary</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advantages</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Applicable to all plants</td>
<td>Lowest capital</td>
<td>Lowest phosphorus in effluent</td>
</tr>
<tr>
<td>Increased BOD and suspended solid removal</td>
<td>Lower chemical dosages than primary</td>
<td>Most efficient metal use</td>
</tr>
<tr>
<td>Lowest degree of metal leakage</td>
<td>Improved stability of activated sludge</td>
<td>Lime recovery possible</td>
</tr>
<tr>
<td></td>
<td>Polymer not required</td>
<td>Separation of organic and inorganic sludge</td>
</tr>
<tr>
<td><strong>Disadvantages</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Least efficient in utilization of metal</td>
<td>Careful pH control to get phosphorus &lt; 1 mg/l</td>
<td>Highest capital cost</td>
</tr>
<tr>
<td>Polymer required for Flocculation</td>
<td>Overdose of metal may cause low pH toxicity</td>
<td>Highest metal leakage</td>
</tr>
<tr>
<td>Sludge more difficult to dewater than primary sludge</td>
<td>Cannot use lime because of excessive pH</td>
<td></td>
</tr>
</tbody>
</table>

### 2.9 REMOVAL OF COD

COD, an indicator of organic matters which is chemically oxidizable present in the wastewater can be removed by biological treatment and these treatment systems are widely discussed in the literature elsewhere.

### 2.10 REVIEW ON METALS

#### 2.10.1 General

Over 40 elements in the environment are classified as metals. Many, such as the alkaline earth group and some trace elements, are essential for life; other have great potential for toxicity. Macronutrients such as calcium, magnesium, iron, potassium, and
sodium are particularly important in sustaining life but may become toxic in excessive concentrations. Trace elements such as chromium, cobalt, copper, manganese, Nickel, selenium, and Zinc are structurally part of important molecules and may serve as cofactors of enzymes in metabolic process. Excessive of these elements are also toxic harmful. Some elements such as lead, cadmium, and mercury have harmful effects on biological tissues at any concentration.

Contamination of the environment by heavy metals has been on the increase due to the industrial development of the last few decades; consequently, there has been an adverse effect on our environment because of the toxicity of the heavy metals involved. Both air and water have been found contaminated by heavy metals as a result of smelting processes in various industries. Water pollution due to heavy metals is an issue of great environmental concern. To avoid hazards due to heavy metals it is essential to remove these toxic heavy metals from wastewater before its disposal. An attempt has been made in this section to throw light on sources effects and removal of metals from wastewater streams.

2.10.2 Sources of Metals

The earth’s crust is the one and only source of all metallic elements found in the environment. Metals are neither created nor destroyed by human but are redistributed naturally in the environment by both geological and biological cycle.

Thus trace metals naturally cycle through and between the lithosphere, atmosphere, and hydrosphere (Michael et al.: 2001). Enriched levels of trace metals may occur naturally because of the weathering of a geologic substrate or volcanic emissions, or from anthropogenic sources such as industrial effluent, or nonpoint sources such as urban storm runoff and atmospheric washout of particulate or gaseous emissions. Mining, fossil fuel combustion, smelting, plating, and other historical anthropogenic activates have altered the biogeochemical cycling of trace metals and frequently enriched the levels of trace metals in the environment. The release from a hazardous waste site may represent a significant local source, but rarely the only source of exposure to local biota.
Thus it is mainly the human activity, which has added enormous quantities of these elements in various components of the environment. Further these sources are discussed in detail as below.

Natural sources like volcanoes, forest fires and sea salt sprays are also found to be sources of metal and are significant, but it is the human activities that are increasing the environmental load of metals. Municipal and industrial wastewater treatment plants are point sources of metal pollutants to water. Paved roads and construction sites are among sources from which metal particulates can be blown away in wind or runoff with rainwater. Fertilizers, pesticides, sewage sludge and animal wastes applied to soil have higher metal concentrations than natural soil levels.

Combustion of fossil fuel releases about 20 toxicologically important metals, into the environment including arsenic, beryllium, cadmium, lead and Nickel. Industrial products and used industrial material may contain high concentrations of toxic metals. For example, mercury is used by the chlor-alkali industry to produce chlorine and caustic soda in the pulp and paper industry and in the production of battery cells, fluorescent bulbs, electrical switches, paints, agricultural products, dental preparations, and pharmaceuticals.

The environment release of lead from the combustion of tetraethyl lead containing auto or industrial fuels remains the greatest source of exposure.

Cadmium, a by-product of Zinc and lead mining, is an important environmental pollutant. It has many industrial uses in paints, pigments, batteries, and plastics. Another use is an anticorrosive agent for steel, iron, copper, brass, and other alloys.

Mining of minerals and their processing to obtain the required metal have created enormous ecological disaster areas at many places around globe. Most of the mineral deposits occur as complex mixture of a number of elements. In the process of mining and extraction of particular metal the entire mass is excavated, laid bare and exposed to environmental agencies of weathering, degradation and transportation. This results in extensive contamination of surrounding areas. Smelting and subsequent
treatment of ores results in emission of arsenic, lead, cadmium, mercury, sulphur dioxide etc. in large quantities.

Over the past decade, the consumption of metals and chemicals in the process industries has increased dramatically. Industrial uses of metals such as metal plating, tanneries, industrial processes utilizing metal as catalysts, have generated large amount of aqueous effluents that contain high levels of heavy metals. These heavy metals include cadmium, chromium, cobalt, copper, iron, manganese, mercury, molybdenum, Nickel, silver, and Zinc.

Zinc is present in wastewater streams from steelworks, rayon yarn and fiber manufacture, ground wood-pulp production, and recirculating cooling water systems employing cathodic treatment (Eckenfelder: 2000). Zinc is also present in wastewaters from the plating and metal-processing industry.

Nickel comparatively a rare metal in nature but its wide spread usage in many industrial applications lead to relatively high concentrations in aquatic environment. The major source of Nickel into water bodies is from electroplating industry, where Nickel is used to improve the values of treated metals by providing improvement such as corrosion resistance, durability, electrical properties etc. Wastewaters containing Nickels originate primarily from metal industries, particularly during plating operations. Nickel is a well known heavy metal pollutant and is present in the effluents of plating industries to the tune of 20 – 200 ppm. High levels of Nickel have also been reported in wastes from silver refineries.

Industry is probably the biggest contributor of chromium in the natural water bodies. Industrial wastes primarily contain chromium in the hexavalent form, as chromate and dichromate. Hexavalent chromium is used in the manufacture of inks, industrial dyes and paint pigments. It is also used in chrome tanning, aluminum anodizing and other metal cleaning, preplating and electroplating operations. Chromate is also contained in some preservatives and fire retardant chemicals used in wood preservative treatment. Manufacturers of automobile parts are one of the largest producers of Chromium plated metal parts. Frequently, the chromic acid bath and rinse water used in electroplating operations are the major sources of waste chromium.
Industries that involve manufacturing of the glass, ceramics, photographic films, in organic pigments including anodizing compounds, textile dye, etc., employ trivalent chromium directly in manufacturing processes. Some of the proprietary trivalent chrome plating solutions have been developed as substitutes for chromic acid plating baths, although their use is limited.

Heavy metals present in fertilizers Cd, Cr, Cu, manganese, molybdenum, Nickel and Zinc. The major environmental sources of arsenic are pesticides, herbicides, and other agricultural products. Lead arsenate, in addition to being a component of industrial effluents, has been used as an agricultural pesticide. Fungicides containing mercury contribute to environmental contamination. Eventually, many of these metals may accumulate in agricultural soils and pose a hazard to plant growth and animal nutrition.

For humans, the ingestion of food and food additives may represent the largest source of exposure of metals. The ingestion of metals normally follows two primary routes: the first involves direct, accidental contact with metal-bearing food or material. Ingestion of foreign substances such as lead-containing paint chips by children is one of the best examples of this method. Since paint chips may contain 50 to 100 mg of lead in a 1 cm paint chip, even a few chips a day may exceed the acceptable daily intake.

The second route of ingestion of metals is through the bioaccumulation of metals in the chain. The well known Minamata disease is the result of massive human exposure to methylmercury-contaminated fish. Microorganisms in sediments methylate mercury into methylmercury. Methylmercury can then be assimilated by fish through ingestion of contaminated food sources and accumulation in their tissues. Uptake by fish in Minamata Bay apparently occurred as the industrial release of mercury compounds into the bay preceded the accumulation of mercury by edible fish. Other toxic metals such as cadmium are found in meat, fish, and fruit. Shellfish such as mussels, scalps, and oysters are a major source of dietary cadmium.

Sewage sludge containing nitrogen, phosphorus, and sulphur as well as the toxic metals cadmium, chromium, copper, lead, mercury, Nickel, and Zinc has been applied to agricultural soils to improve crop production. Although leaching of heavy metals
through soils is limited, plant uptake may translocate the meals into the food chain, eventually being consumed by humans at the highest tropic level.

2.10.3 Effects of Metals on Health and Environment

In aquatic systems, these trace metals may be present as both soluble and insoluble forms within the water column, sediments, and biotic tissues. Trace metal toxicity occurs when a receptor is exposed to a available form of a trace metal for a sufficient duration at a concentration that elicits an adverse response. The potential for trace metal toxicity to aquatic organisms depends on numerous factors, including the chemical and physical characteristics of the water and sediment, composition and health of the biological communities present and the magnitude and availability of the trace metal.

Many trace metals are essential micronutrients for the maintenance of aquatic life and toxic only when available to organisms at levels that exceed nutritional requirements. Trace metals such as copper, iron, zinc, manganese, cobalt and selenium are essential to metabolism; yet, exposure of aquatic organisms to these elements at elevated levels can adversely affect development and health, or cause death. Other trace metals such as lead, cadmium and mercury do not play an essential role in daily maintenance, but adversely affect an organism if available at toxic levels.

Upon exposure, uptake occurs by three main processes: from the water column through respiratory surfaces (e.g., gill); adsorption from water onto body surfaces; and from ingested food, particles, or water through the digestive system.

The human body cannot process and dispose of the metals, therefore the metals will deposit in various internal organs. Large deposits may cause adverse reactions and serious damage in the body. Excess of heavy metals can lead to disease, such as Wilson’s disease, Argyria, cancer, heart and liver diseases, nervous system disorders and hypertension. Heavy metals from compounds in the body that can be carcinogenic and mutagenic even at very low levels. Therefore, not only the first generations are effected by heavy metals, but also the effects can be passed onto second and third generations in the form of genetic abnormalities and birth defects.
The mechanisms of metal toxicity are divided into three general categories: blocking of essential functional groups of biomolecules (e.g., protein and enzymes), displacing the essential metal ion in biomolecules and modifying the active conformation of biomolecules. These mechanisms of action may cause death at high-level exposure, but also may manifest nonlethal effects on structure (histology/morphology), function (growth, development), biochemistry (blood and enzymes) and reproduction.

Many free-swimming or mobile aquatic organisms (e.g., fish) actively excrete trace metals, particularly essential nutrients, through the gills, gut, feces and urine, while less mobile or sessile organisms (e.g., plants and bivalves) are less capable of regulating internal metal concentrations. Once the processes that regulate metals have been saturated, bioaccumulation within tissue or other tolerance mechanisms may preclude an adverse effect. However, these protective mechanisms are often too transient or insufficient to preclude toxicity.

The heavy metals are generally deposited in liver, muscles, kidneys, spleen, skin, bone and soft tissues of human beings. USEPA (United States Environmental Protection Agency) considers eight trace metals as high priority and critical, namely, As, Cd, Cu, Cr, Pb, Hg, Ni and Zn. chromium appears to be necessary for glucose and lipid metabolism and for utilization of amino acids in several systems. It is also responsible for the prevention of mild diabetes and atherosclerosis in human beings. However, hexavalent chromium at 10 mg/kg of body weight will result in liver necrosis, nephritis, and ultimately death in human beings; lower doses will cause irritation of the gastrointestinal mucosa. Hexavalent chromium in high doses may be the cause of digestive tract cancers in man. It can produce cutaneous and nasal mucous membrane ulcers and chromititis (from skin contact).

Chromium has been considered as one of the top 16th toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern.

Hexavalent form is more toxic than trivalent and requires more concern. Strong exposure of Chromium(VI) causes cancer in the digestive tract and lungs and may cause
epigastria, nausea, vomiting, severe diarrhea and hemorrhage. It is therefore, essential to remove Chromium(VI) from wastewater before disposal.

Chromium(VI) is carcinogenic causing cancer to the respiratory organs in chromate workers chronically exposed to chromium containing dusts. Chromium(VI) has been implicated in poisoning in Japan. Besides this, it acts as irritant to eyes, nose and throat. Chronic exposure may lead to liver and kidney damage.

Among several heavy metals reported Nickel possesses special characteristics. Nickel salts in water produce hazardous effects and Nickel is carcinogenic. Nickel appears to be relatively non-toxic to mammals and exhibits only low toxicity but causes reduction in fecundity and survival by 50% at 1.6 ppm. The plants and animals readily take up Nickel in the ionic form (Ni^2+) from the soil or solution. Plant leaves are the major sinks for Nickel. It is accumulated even in seeds and husk. Even low concentration of Nickel is toxic to a wide variety of plants. Thus the movement of Nickel in the ecosystem is of great concern to mankind.

Exposure to Nickel through dermal, oral or inhalatory routes has been reported to cause allergy, dermatitis, eczema, rhinitis, sinusitis, bronchitis, pneumonitis, asthma, perforation of the nasal septum, inhibition of phagocytosis and the T-cell-mediated immune response, and mutagenic, carcinogenic and teratogenic effect in animals and man. The most common form of human toxicity of Nickel is dermatitis. Epidemiological studies showed high incidence of lung, larynx, and sinus cancers among workers exposed to Nickel in refinery, smelting and electrolysis works.

Lung is the primary target organ for Nickel toxicity. The signs and symptoms include dyspnoea, cough, intense chest pain, cyanosis and bronchoalveolar hyperplasia. Industrial exposure may cause lung cancer. Employees of electroplating and electrolytic refinery works, who inhale vapours of water soluble Nickel salts, develop chronic respiratory diseases, such as asthma bronchitis, rhinitis, sinusitis, nasal polyps, pneumoconiosis and perforation of the nasal septum.

Zinc generated from phosphate fertilizers, distillery, pharmaceuticals and electroplating cause depression cough, vomiting, headache and metal fume fever.
The absorption of ingested Zinc takes place in small intestines, particularly through the distal duodenum and proximal jejunum. It is equally well adsorbed as oxide, carbonate and free metal, but poorly sulphate or as mixed oxides of Zinc, iron and manganese. Metallotheionein plays an important role in the homeostatic regulation of Zinc absorption and metabolism.

Ingestion of large doses causes irritation and corrosive damage to the gastrointestinal tract, with symptoms of nausea, vomiting, cramps, colic, diarrhoea, fever and fatal shock. Its toxicity may occur from an intake of acidic fruit juices stored in galvanize, i.e., Zinc plated, containers where Zinc concentration may reach up to 2 g/l.

The carcinogenic properties of Zinc have not been fully investigated. Like other chromates, Zinc chromate is a carcinogen. Application of hydrocarbon carcinogens causes a decrease in skin Zinc content. The metal is needed for cellular proliferation of existing tumours. Tumour growth is, therefore, retarded in Zinc deficiency. The metal does not pose a risk for carcinogenesis in humans. However, a significantly low concentrations of Zinc in blood, plasma or serum have been reported in bronchial carcinoma, Hodgkin’s disease, lymphoma, multiple myeloma and chronic lymphocytic leukemia. In cases of carcinoma of prostate glands, the organ contained low Zinc concentration but the values will be high in hyperplastic prostate glands. Significantly high Zinc levels were found in the liver of carcinoma patients. No comparable increase in the Zinc content of kidney spleen, heart, or pancreas was observed in autopsy samples of these patients.

2.10.4 Heavy Metals Removal Techniques

The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, electrodialysis, ion-exchange, reverse osmosis, solvent extraction and ultrafiltration.

Chemical precipitation of metals is achieved by the addition of coagulants, such as alum, lime, iron, salts and other organic polymers. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage. In Electrodialysis process, the ionic components (heavy metals) are separated through the
use of semi permeable, ion selective membranes. Application of an electrical potential between the two electrodes causes migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes, cells of concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides, which clog the membrane. In Ion exchange process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the ion exchange resin. The disadvantages include high cost and partial removal of certain ions. Reverse osmosis is a process in which heavy metals are separated by a semi permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in wastewater. The disadvantage of the method is that is expensive. Ultrafiltration are pressure driven membrane operations that use porous membranes for the removal of heavy metals. The main disadvantage of this process is the generation of sludge, selection of proper membrane.

Hence, the disadvantages, like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal has made it imperative to look for a cost-effective treatment method, that is capable for removing heavy metals from aqueous effluents. As alternatives, slowly, biological tools are being substituted in pollution abatement programmes. This technology has been loosely grouped together under the term ‘bioremediation.’ Biological methods, such as biosorption, bioaccumulation, phytoremediation for the removal of heavy metals ions may provide an attractive alternative to physico-chemical methods. Phytoremediation is the use of certain plants to clean up soil, sediment, and water contaminated with metals. The disadvantage include that it takes a long time for removal of metals and the regeneration of the plant for further biosorption is difficult.

2.11 SPECIFIC REVIEW ON METALS

Coconut coir pith, an agricultural solid waste was used as biosorbent for the removal of Chromium(VI) after modification with a cationic surfactant, hexadecyltrimethylammonium bromide by Namasiyayam and Sureshkumar: (2008). Optimum pH for Chromium(VI) adsorption was found to be 2.0. Reduction of Chromium(VI) to chromium(III) occurred to a slight extent during the removal. The
adsorption capacity of the biosorbent was found to be 76.3 mg/g, which is higher or comparable to the adsorptions capacity of various reported in literature.

The feasibility of using pre-consumer processing agricultural waste to remove Chromium(VI) from synthetic wastewater under different experimental conditions has been reported by Manjeet Bansal et al. (2008). For this rice husk, has been used after pre-treatments (boiling and formaldehyde treatment). Effect of various process parameters, namely, pH, adsorbent dose, initial chromium concentration and contact time has been studied in batch systems. The removal of chromium was dependent on the physico-chemical characteristics of the adsorbent, adsorbent concentration and other studied process parameters. Maximum metal removal was observed at pH 2.0. The efficiencies of boiled and formaldehyde treated rice husk for Chromium(VI) removal were 71.0 % and 76.5 % respectively for dilute solutions at 20 g/l adsorbent dose. The results revealed that the Hexavalent chromium is considerably adsorbed on rice husk and it could be an economical method for the removal of hexavalent chromium from aqueous systems.

Removal of Chromium(VI) from aqueous solution by walnut hull (a local low cost adsorbent) was studied by Xue Song Wang et al. (2008). The extent of adsorption was investigated as a function of solution pH, contact time, adsorbent and adsorbate concentration, reaction temperature and supporting electrolyte (sodium chloride). The Chromium(VI) removal was pH-dependent, reaching a maximum (97.3 %) at pH 1.0. the uptake of Chromium(VI) per weight of adsorbent increased with increasing initial Chromium(VI) concentration up to 240-480 mg/l and decreased sharply with increasing in adsorbent concentration ranging from 1.0 to 5.0 g/l. Compared to the various other adsorbents reported in the literature, the Walnut hull shows very good promise for practical applicability.

Adsorption of Chromium(VI) ions on wheat bran has been studied using batch adsorption techniques by Nameni et al. (2008). The results of this study showed that adsorption of chromium by Wheat bran reached equilibrium after 60 min and after that a little change of chromium removal efficiency was observed. Higher chromium adsorption was observed at lower pHs, and maximum chromium removal (87.8 %) obtained at pH of 2.0. The adsorption of chromium by wheat bran decreased at higher
initial chromium concentration and lower adsorbent doses. The results indicate that wheat bran can be employed as a low cost alternative to commercial adsorbents in the removal of Chromium(VI) from water and wastewater.

The removal of Chromium(VI) from aqueous solution by rice straw, a surplus agricultural byproduct was investigated by Hui Gao et al. (2008). The optimal pH 2.0 and Chromium(VI) removal rate increased with decreased Chromium(VI) concentration and with increased temperature. Decreased in straw particle size led to an increase in Chromium(VI) removal. The authors concluded rice straw may be a new kind of low cost material which could convert Chromium(VI) to the less toxic and more stable chromium(III) and could be used economically in the field to treat Chromium(VI) contaminated wastewaters.

Adsorption of Chromium(VI) from aqueous solutions by spent activated clay has been investigated by Chih-Huang Weng et al. (2008). Spent activated clay (SAC), a waste produced from an edible oil refinery company after pressure steam treatment was used as an adsorbent. The rate of removal was found to speed up with decreasing pH and increasing temperature. The maximum adsorption capacities for Chromium(VI) ranged from 0.743 to 1.422 mg/g for temperature between 4 and 40°C under a condition of pH 2.0. The studies conducted show the process of Chromium(VI) removal to be spontaneous at high temperature and endothermic in nature.

Rumi Chand et al. (2008) have carried out studies to evaluate grape waste as a biosorbent for removing Chromium(VI) from aqueous solution. An adsorption gel was prepared from grape waste by cross linking with concentrated sulfuric acid. It was characterized and utilized for the removal of Chromium(VI) from synthetic aqueous solution. Adsorption tests were conducted in batch mode to study the effects of pH contact time and adsorption isotherm of Chromium(VI). Crossed lined grape waste gel has been found to be selective to Chromium(VI) ion and highly effective for its removal from synthetic aqueous solution. The adsorption of Chromium(VI) on the gel was highly pH dependent and maximum adsorption occurred at pH 4.0. The adsorption capacity was found to increase with increasing solute concentration as described by the Langmuir adsorption model. The maximum adsorption capacity of Chromium(VI) was 1.91 mol/Kg at pH 4.0. The Chromium(VI) occurs by esterification reaction which is
confirmed by FTIR measurement. Since most of the industrial wastewaters contaminated with Chromium(VI) are highly acidic, cross-linked grape waste gel can be a good candidate for wastewater treatment. Due to large generation of grape waste every year and the simple production process of cross-linked grape waste gel, it seems to be a promising adsorbent.

The effect of different parameters such as contact time, sorbate concentration, pH of the medium and temperature on removal of Chromium(VI) from aqueous solutions using agricultural waste maize bran were investigated by Hasan et al. (2008). Maximum uptake of Chromium(VI) was 312.52 (mg/g) at pH 2.0, initial Chromium(VI) concentration of 200 mg/l and temperature of 40°C. Effect of pH showed that maize bran was not only removing Chromium(VI) from aqueous solution but also reducing toxic Chromium(VI) into less toxic chromium(III).

The adsorption of Chromium(VI) from aqueous solutions on formaldehyde treated saw dust (SD) and sulphuric acid treated saw dust carbon (SDC) of Indian rosewood, a timber industry waste, was studied at varying Chromium(VI) concentration, adsorbent dose, and pH and agitation time Garg et al. (2004). Similar experiments were conducted with commercially available coconut based activated carbon to compare the results. The Chromium(VI) adsorption efficiency on SDC was higher than SD. An initial pH of 3.0 was most favorable for Chromium(VI) removal by both the adsorbents. Maximum Chromium(VI) was sequestered from the solution within 60 min after the beginning for every experiment.

Narsi Ram Bishnoi et al. (2004) carried out investigations to evaluate the possible use of activated rice husk (ARH) and activated alumina (AA) as the adsorbents of Chromium(VI) from synthetic solution and the effect of operating parameters. The activated rice husk carbon was prepared thermally in two sizes 0.3 and 1.0 mm. Based on the present investigation the authors concluded that the adsorption capacity of ARH is comparable with the commercially based AA. The smaller the particle size, greater is the adsorption capacity, as evident from 93.28 % and 81.78 % Chromium(VI) removal with 0.3 and 1.0 mm ARH, respectively. The removal is pH dependent. The efficiency of ARH was fairly high at pH 2.0 whereas with AA it was at pH 4.0. Adsorption increased with increasing dose and time at initial stages and then it become somewhat
constant. The adsorption efficiency for different adsorbent was AA > ARH (0.3 mm) > ARH (1.0 mm).

Shiny et al. (2004) carried out studies to explore the possibility of utilizing two common aquatic ferns, Salvinia molesta Mitchell and Azolla Rubra R.Br. for scavenging chromium from solutions. Chromium removal from spiked solutions ranged from 40 – 99 % during the seven day exposure. Results reveal their bio removal capabilities and potential for use in wastewater decontaminant system.

The activated carbon prepared by carbonization of rice husk with sulfuric acid followed by CO2 activation showed 88 % removal of total chromium and greater than 99 % removal of Chromium(VI), (Srinivasan et al.: 1988). The removal was maximum at a minimum proton to chromium ratio of 5 and chromium to carbon ratio of 0.0065. The above ratios were found to be valid over a wide range of Chromium(VI) concentrations. Column studies showed capacity of 8.9 mg/g and 6.3 mg/g for Rice Husk and commercial carbon respectively, for Chromium(VI) removal. The average percentage of Chromium(VI) recovery was found to be 22.5 % and 30.6 % respectively when alkali followed by acid were used for regeneration.

Renugadevi, et al. (2008) have carried out studies to evaluate the removal of Chromium(VI) from aqueous solution using activated carbon from thiruvottukai (Crescantia cujeta L). Various parameters such as initial concentration of the adsorbate, contact time, pH and adsorbent dosage were studied by conducting batch mode experiments. Maximum removal of Chromium(VI) was noted at pH 3.0. The equilibrium adsorption data correlated well with Langmuir and Freundlich adsorption isotherms. The adsorption of Chromium(VI) followed Lagergren first Order Kinetics.

Adsorption isotherms of chromium ions in aqueous solution have been experimentally measured on a granular activated carbon (GAC) and on a char of South African coal (CSAC) by Natale et al.: (2007). Experimental results show that the adsorption capacity for the GAC strongly depends on solution pH and salinity, with maximum values around 7.0 mg/g at neutral pH and low salinity levels. On the contrary, the CSAC shows a smaller adsorption capacity near 0.3 mg/g, which slightly decreases by increasing pH and salinity levels. chromium adsorption mainly depends on the

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availability of chromium ions in solution and on the occurrence of redox reactions between the surface groups and the Chromium(VI) which lead to formation of chromium(III). The reduction of Chromium(VI) and the following sorption of chromium(III) cations appear as the leading mechanism for chromium uptake on the CSAC. A similar behavior can be observed for the GAC at pH below 3.0.

Removal of toxic Chromium(VI) in aqueous medium was investigated using activated carbon adsorbent prepared from Simarouba glauca seed shells by Neelavathi et al. (2004). The pH effect, Chromium(VI) concentration, adsorbent dosage and contact time period were studied in batch experiment. Four activated carbons one non-impregnated and the remaining three impregnated with Zinc chloride in 1:1, 1:2, 1:3 ratio were used for experimentation. Important characteristics of activated carbons are also investigated. The removal of Chromium(VI) of around 97% was observed with 1:2 impregnated activated carbon at pH 3.0 where as other adsorbents showed much lower activities.

Suitability of activated alumina for removal of Hexavalent chromium from electroplating wastewater has been investigated (Sudipta Sarkar and Anirban Gupta.: 2003). The study revealed that activated alumina may be considered as a good adsorbent for use in the chrome plating industries for removal of chromium from its wastewater and pH has no pronounced effect on sorption capacity.

Shashikant and Rajamanya (2003) have studied the effect of adsorption of Chromium(VI) on pH, particle size concentration, contact time and dosage by activated carbon derived from Sorghum Vulgare (dried stem of jowar). They reported that:

- Raw material of Sorghum vulgare has low efficiency in Chromium(VI) removal
- Sorghum vulgare can be effectively used for the preparation of activated carbon
- Activated Carbon of Sorghum vulgare has good Chromium(VI) removal potential
• The adsorption of Chromium(VI) is pH dependent. The removal efficiency of adsorbent increase with decrease in pH. Maximum adsorption takes place at pH 2.0

• The recovery of Chromium(VI) can be achieved by washing adsorbed carbon with 1N NaOH compared to 1N HCL and distilled water

• Reused carbon is also effective in removing Chromium(VI). Small amount of efficiency lost compared to fresh carbon using the recovery reuse technique.

Removal of Chromium(VI) from aqueous solution using carbon waste from domestic water purifier have been carried out at 30°C by Renugadevi, et al. (2007). By varying initial concentration of adsorbate, pH, adsorbent dosage and agitation time. Further the authors reported the increase in removal of Chromium(VI) from 54 to 61 % in 60 min of agitation and 69 to 81 % in 180 min of agitation time when the pH varied from 6.3 to 3.5. For the adsorbent dosage variation of 60 to 120 mg, 66 to 74 % increase in Chromium(VI) have been observed. Increase in the uptake of Chromium(VI) from water by activated waste carbon from domestic purifiers from 41 to 69 %, when the agitation time was varied from 10 to 180 min have been observed.

A corbonaceous sorbent prepared from an indigenous plant namely pitchellobium dulce benth by acid treatment and also by pyrolysis was tested for its efficiency in removing Chromium(VI) (Prabavathi Nagarajan et al.: 2006). The process parameters studied include agitation time, concentration, carbon dose, pH and temperature. PPC adsorption capacity of 45.63 mg/g and 16.08 mg/g for APC were observed. This authors opined that PPC carbon is a better adsorbent than APC for Chromium(VI) removal.

The adsorption capacity of the composite biosorbent prepared by coating chitosan onto acid treated oil palm shell charcoal was evaluated by measuring the extent of adsorption of chromium metal ions from water under equilibrium conditions at 25°C by Saifuddin and Kumaran Palanisamy (2005). Using Langamuir isotherm model, the equilibrium data yielded the following ultimate capacity values for the coated
biosorbent on a per gram basis of chitatan: 154 mg chromium/g. Bioconversion of Chromium(VI) to chromium(III) by chitosan was also observed.

Studies on removal of Chromium(VI) from aqueous solution using activated soyabean hull carbon at 32°C by Jambulingam, et al. (2005) revealed that soyabean hull carbon is an effective low cost adsorbent for the removal of Chromium(VI) from aqueous solution. The adsorption of Chromium(VI) ions is dependent on the initial concentration of metal ion, pH, amount of adsorbent and agitation time. Maximum removal of Chromium(VI) is noted at pH 2.0.

Joshi and Srivastava (2005) carried out studies to evaluate removal of Chromium(VI) from aqueous solutions of different concentration by using carbonized organic material like pipal bark and found to posses 40 to 76 % Chromium(VI) removal efficiency. However, removal efficiency observed with rice husk and saw dust varied from 27 to 72 % and 39 to 91 %, respectively. Better removal efficiency was observed at pH 2.0.

Arti Nigam and Rama (2003) carried out investigative studies on the removal of hexavalent chromium from aqueous solution using the sugar cane leaves as an adsorbent. The study involves batch experiments to find-out the effect of pH, concentration of Cr(VI), adsorbent dosage, contact time and temperature, since the removal of chromium was dependent of these factors. The removal of Hexavalent chromium was found effective with 95 % of removal at pH 2.0 to 3.0 and at 30°C temperature.

Gharde et al. (2005), conducted adsorption studies on the removal of chromium from aqueous solution using Fredonia of elefuntum fruit shell as an adsorbent. Studies indicated that sorption of chromium increased with the increase in pH and contact time. The removal efficiency was found good at 60 min. contact time; hence ferronia elefuntum fruit shell is economical and effective in removing heavy metals from industrial wastewater.

Water hyacinth has been used for the removal of chromium for chrome tannery effluent. (Santhaveerana Goud, et al.: 1996). It has been observed that the plant is
capable of removing 75% of the chromium when the chromium concentration in the wastewater in 25 mg/l. It was also observed that, the uptake of chromium by the water hyacinth plants was high when the pH value of the effluent was around seven. Lower the initial chromium concentration the percentage removal of chromium was more and the percentage removal decreases with increase in the initial concentration of chromium. The stirring of the effluent enhances the uptake of chromium by water hyacinth from the tannery effluent.

The ability to remove Chromium(VI) from the contaminated water by transforming Chromium(VI) to chromium(III) by Ipomea aquatic a wetland plant, which floats in water bodies has been studied by Subhas Chandra Bahat, et al. (2005). They found that contact time required to bring down Chromium(VI) concentration below the permissible level (0.05 mg/l) is 30 to 40 days for this plant and that varies with varying initial concentration. The lower level of contamination requires greater contact time than the higher one to bring down Chromium(VI) below the permissible level.

The removal of Hexavalent chromium from synthetic effluents in batch stirred electro coagulation with iron-aluminum electrode pair has been studied by Mahesh et al. (2007). Several working Parameters, such as pH, current density, metal ion concentration and operating time were studied in an attempt to achieve the higher removal capacity. Results obtained with synthetic wastewater revealed that most effective removal capacities of Chromium(VI) could be achieved when the pH was kept between 7.0 and 8.0. In addition, the increase of current density in a range of 6.7 to 26.7 mA/cm² enhanced the treatment rate to reduce metal ion concentration under admissible legal levels. For higher operating time, remarkable removal of Chromium(VI) was observed.

Chromium reduction from the chrome tannery wastewater was studied electrolytically, using a stainless steel plate as cathode and graphite rod as Anode, (Verma Babita and Shuklan.:1999). The electrode potential was maintained from 1 to 6 voltages and the current was varied from 19 mA to 410 mA over a time period of 15 min to 120 min. The chromium reduction was found to be directly proportional to the chromium concentration in the solution. The concentration as well as the removal rate
decreased with time. Almost 100% chromium reduction was observed. The chromium reduction was higher at 500 mg/l concentration when time was kept constant at 1 min.

The maximum Chromium(VI) reduction of 85.2-92.0% at optimum pH 1.0 by Abstract has been reported by Goyal and Surendra Kumar (2005). They also reported the no effect of temperature on Chromium(VI) reduction.

Studies on Adsorptive removal of copper and Nickel ions from water using chitosan coated PVC beads were carried out by Srinivasa et al. (2009). The effect of pH, agitation time, concentration of adsorbent and amount of adsorbent in the extent of adsorption was investigated. The experimental data were fitted to Langmuir and Freundlich adsorption isotherms. The data were analyzed on the basis of Lagergren pseudo first order, pseudo-second order and Weber-Morris intraparticle diffusion models. The maximum monolayer adsorption capacity of chitosan coated PVC sorbent as obtained from Langmuir adsorption isotherm was found to be 87.9 mg/g for copper(II) and 120.5 mg/g for Nickel(II) ions respectively. In addition, breakthrough curves were obtained from column flow experiments. The experimental results demonstrated that chitosan coated PVC heads could be used for the removal of copper(II) and Nickel(II) ions from aqueous medium through adsorption.

The removal of Zinc(II) ions from dilute aqueous solution using maize (zea mays) leaf as the adsorbent is reported by Adesola Babarinde et al. (2008). The batch biosorption studies have shown that the biosorption is pH dependent and the optimum pH for the removal is in the range of 4–7. The amount of Zinc ions biosorbed increased with increased initial metal ion concentration. Maximum adsorption was obtained within the first 40 minutes and on an average 90-92% Zinc removal was recorded. Thus the authors recommended the use of maize leaf biomass, an agricultural waste, as potential biosorbent for the removal of Zinc(II) from aqueous solutions.

The batch removal of heavy metals lead (Pb), Zinc (Zn) and copper (Cu) from industrial wastewater effluent under different experimental conditions using hydrogen peroxide was investigated (Badmus et al.: 2007). Removal of heavy metals was optimum at pH 7.6, a temperature of 30°C, 1.5% hydrogen peroxide concentration and
60 min holding time, reducing the amounts of Pb, Zn and Cu by 83.5, 85.5 and 82.23 % respectively.

Studies on removal of copper and Zinc by adsorption on activated peel waste biomass have been carried out in synthetic wastewater by Kanimozhi and Marline Sheela (2008). Various parameters such as pH, contact time, initial concentration adsorbate and adsorbent dose were optimized. Optimized values for copper and Zinc were more or less same. As compared to the commercial activated carbon the removal efficiency was approximately same but as compared to the cost it is cheap.

A simple and cost effective treatment procedure was proposed for the removal of heavy metals through the adsorption on sand. (Muhammad Masud Aslam et al.: 2004). This study records lab scale experiments to test efficiency of sand on removing a heavy metal, Zinc(II) from wastewater of electroplating industry. This method of heavy metals removal proved highly effective as removal efficiency increased with increasing pH ranging from 71-87 % and maximum adsorption occurred at depth 1 m as compared to 0.6 m and 0.8 m depth. Since sand is cheap and easily available, the authors concluded that the sand filtration, which is efficient and effective, has the potential to be used for removal of heavy metals from water and industrial wastewater.

The possibility of cadmium (Cd^{2+}) and Zinc (Zn^{2+}) toxic cations removal from simulated liquid effluents by a relatively innovated treatment, named galvanochemical, using the galvanic pair iron-carbon, was investigated by Prochaska et al. (2001). The study showed that there is a great potential for the application of galvanochemical method to the purification treatment of metal-laden wastewaters from small-to-medium industrial units, as the residual metal concentrations were found to be below the legislation limits, under the optimized operating conditions.

Scott et al. (2000) tested four filtration media in controlled laboratory experiments to determine their effectiveness for concurrent metals removal and toxicity abatement in synthetic stormwater. Media tested included commercially available leaf compost (CSF®) media, a zeolite/perlite mix, and a polyamine sponge, as well as the recently developed citric acid modified soybean hull media. The CSF® media removed up to 75 % of the Zinc and reduced toxicity significantly for influent concentrations of
up to about 300 ppb Zinc. Variations of the CSF® media improved Zinc removal modestly compared to the standard version. The soybean hull material removed 80 to 99% of the Zinc over all influent concentrations though it reduced pH to toxic levels. After pH adjustment, the effluent from the soybean material was non-toxic overall concentrations tested. Augmenting the soybean material with leaf compost media or activated carbon effectively buffered effluent pH to circum-neutral ranges. Other media tested removed modest amounts of Zinc and were capable of sufficiently reducing toxicity only in the lowest concentrations tested, while some media appeared to generate toxicity.

Studies on the removal of Zinc by adsorption on two types of flyashes, namely Bokaro Thermal Power Plant Fly ash and Fluidized Bed combustion fly ash from Tata steel, Jamadoba were carried out by Srivastava, et al. (2007). Batch adsorption experiments were done. The effects of various parameters such as contact time, initial concentration, pH, fly ash dosage on the removal of Zinc ions were studied. In case of fluidized bed Combustion fly ash the maximum removal capacity was 0.0515 mg of Zn^{2+}/gm of ash, in thirty minute where as in case of Bokaro Thermal Power Plant flyash the maximum removal capacity was 0.0925 mg of Zn^{2+}/gm of ash. The loss on ignition of fluidized bed Combustion fly ash was 17.15% and that of Bokaro thermal Power Plant fly ash was 6.67%. So the quantity of Zinc by the two types of flyash may be related to the difference in their unburnt carbon. Higher the unburnt carbon better is the adsorption capacity. At low pH values the flyash particle is positively charged while at high pH value the flyash particle is negatively charged. So adsorption is favored when the particles are negatively charged, that is in alkaline medium.

Semra Ilhan et al. (2004) investigate selective biosorption of chromium, lead and copper ions by microorganism from industrial wastewater. The effects of pH, temperature and initial concentration of metal ions on the biosorption capacity were investigated. The optimum pH values for chromium, lead and copper biosorption was found to be 2.0, 4.5 and 3.5 respectively. The maximum adsorption was observed for Cr^{6+}, Pb^{2+} and Cu^{2+} at the initial concentrations of 193.66 mg Cr^{6+}/l; 100 mg Pb^{2+}/l and 105 mg Cu^{2+}/l and 44.94 Cu^{2+}/l, respectively.
The effectiveness of soluble starch Xanthate (SSX) for removal of Cd(II), Chromium(VI) and Cu(II), insoluble starch Xanthate (ISX) for Chromium(VI) and Cu(II) have been evaluated under different aqueous phase conditions (Vinod Tare et al.: 1988). Comparison between ISX and SSX, based on the equivalents of metal removed per mole of ISX/SSX added indicated that ISX has better binding capacity for metals. However, with due consideration to yield and chemical requirements for the synthesis of ISX and SSX, SSX appears to have higher capacity for metal removal. The order of preference of metal binding capacity of SSX is found to be as Cr(VI) > Cu(II) > Cd(II) whereas of ISX as Cr(VI) > Cu(II).

**Bilquees Ara Siddiqui, et al. (1999)** Carried out series of experiments in batch process to determine the adsorption studies on phosphates treated saw-dust for removal of Cr(VI), Nickel and Zinc removal from aqueous solution of electroplating waste. The effect of initial concentration pH and adsorption doses were studied and they observed that the removal of these metals were dependent on the contact time, pH, Adsorbent dosage.

Experiments were conducted to assess the influence of various parameters, such as adsorbent dose, contact time, effects of pH and dilution for SAC and CAC on adsorption (Raju and Saseetharan.: 2008). The results of the experiment provided that SAC was found to be efficient in removing the Nickel bearing effluents. The maximum percentage of Nickel(II) removal was observed (92 %) with a optimum contact time of 20 min. For SAC the percentage removal increases with increase in pH and the removal was optimum at the original pH 4.3. It is also noted from the present study that the granular form of SAC was more efficient when compared to the costlier conventional CAC.

An attempt was made to remove Nickel using live bacterial cultures from single metal aqueous solutions by Khasim Beebi, et al. (2007). The result obtained from the bacterial studies showed that the live bacterial biomass of gram positive Bacilli, Diplo cocci, and Pseudomonas species have the potential to remove Nickel from single metal solution.
Nickel biosorption ability was evaluated in two bacterial strains: Acinetobacter baumannii UCR-2971 and Pseudomonas aeruginosa UCR-2957, resulting in greatest adsorption at pH 4.5 and a residence time of 100 minutes (Carlos et al.: 2006). The maximum adsorption rates were 8.8 and 5.7 mg/g for A. baumannii and P. aeruginosa, respectively; It is suggested that both strains could be used for wastewater treatment, as long as the concentration of Ni^{2+} is within the range of 4-13 mg/l.

The adsorption isotherm of Ni(II) on the testa of groundnut shell was carried out by the batch adsorption process (Mohammad Ajmal et al.:2006). Various parameters such as initial concentration, pH and amount of the adsorbent doses were studied. The experimental adsorption data obtained followed both Langmuir as well as Freundlich isotherms. Maximum adsorption (85 %) was observed at pH 6. The monolayer adsorption capacity was found to be 18.79 mg/g, which is greater than most of the low-cost adsorbents reported.

Investigations were conducted on the topic titled Studies on Removal and Recovery of Cr(VI) from Electroplating Wastes by Mohammad Ajmal et al. (1996). Authors inferred that phosphate treated saw dust shows remarkable increase in sorption capacity of Cr(VI) as compared to untreated saw dust. The adsorption process is pH dependent. 100 % adsorption of Cr(VI) was observed in the pH range < 2.0 for the initial Cr(VI) concentration of 8-50 mg/l. The effect of various adsorbent doses at pH-2.0 confirms Langmuir adsorption isotherms. 100 % removal of Cr(VI) from synthetic waste as well as from electroplating waste containing 50 mg/l Cr(VI) was achieved by batch as well as by column process. The adsorbed Cr(VI) on phosphate treated saw dust was recovered (87 %) using 0.01 molar sodium hydroxide.

Feasibility studies of using treated fly ash in the removal of Nickel from aqueous solutions were performed by Suwan et al. (2006). Batch adsorption experimentation were used to investigate the adsorption efficiency of treated fly ash for the removal of Nickel. Concentrations of Nickel varied in the range of 1-10 mg/l. The adsorption efficiency was found to increase with increasing tested fly ash concentration. At treated fly ash concentrations above 1.25 g/l the removal was almost instantaneous. Adsorption equilibration was usually attained within 30 min at a pH of 3-5. 86 to 92 % removal of Nickel(II) from industrial wastewaters was recorded.
Studies on the removal of metal ions, like Nickel(II) by adsorption on surface of orange peel (OP) was carried out at room temperature (30±1°C) by Kannan and Inbaraja (2006). The effect of process parameters like initial concentration, contact time, dose of adsorbent (op) and initial pH was studied for the removal of metal ions. The studies revived the 20 to 35 % removal of Nickel(II) at optimum pH adsorbent dosage and contact time of 5.0, 110 gm/l and 50 minutes respectively.

Activated carbon prepared from silk cotton hull was used to remove Nickel(II) from aqueous solution by adsorption (Shanmugavalli et al.: 2006). Batch mode adsorption experiments were carried out by varying contact time, metal-ion concentration and pH to assess kinetic and equilibrium parameters. The adsorption capacity of 56.40 mg/g of activated carbon at initial pH of 5.0 for the particle size 125 – 250 μm was observed.

Removal of Nickel ions from industrial effluents has been studied using activated alumina prepared by the galvanic oxidation of aluminum at ambient temperature as the adsorbent (Revathi et al.: 2005). The effect of various factors, such as initial concentration of Nickel, contact time, dose of adsorbent and pH of the solution has been investigated. Batch and column type of adsorption studies have been made. The results indicate that the adsorption process is favored at pH 9.0. The following conclusions are drawn from the present investigation. The percentage of Nickel removal from the effluent increases with increasing amount of alumina. The optimum dosage for effective Nickel uptake of Nickel ions in the adsorbent sites increase with increasing contact time. The optimum contact time for effective Nickel removal is 60 minutes. Column type of adsorption process is more efficient (99.6 %) compared to batch process (86 %) because of more close packing of adsorbent sites. The adsorbent used in this process could be regenerated at the end and can be used for subsequent treatment process, thereby eliminating the need of new adsorbent. It is also noted from the present investigation that the Gibbsite form of activated alumina was more efficient in removing Nickel ions compared to commercially available alumina, which could remove only 40 % of Nickel ions from the effluent.

Anima et al. (2004) have carried out investigations to study the removal of Nickel using a non-conventional adsorbent, rice husk. The effects of contact time,
adsorbent dosage, pH, concentration of the metal ion and isotherm models are studied in a batch process. A steady trend was observed for all variables. The adsorption percentage increased with increase in contact time, adsorbent dosage and pH, but there was a decrease in adsorption with increase in concentration of the metal ion. Adsorption intensity values showed that rice husk, a non-conventional adsorbent is efficient in removing Nickel(II) from an aqueous solution. The adsorption data fitted well into Freundlich adsorption isotherm.

Adsorption characteristics of Nickel on activated carbon at different pH values have been evaluated by Amal Raj (2004). The adsorption capacity of activated carbon was found to be dependent on pH of influent solution and better at pH below 4.5 the author reports 85 to 95 % removal at pH below 4.5.

Murali and Sai Suseela (2001) studied the removal of Nickel from aqueous solution by using Tephrosia purpurea leaf powder as an adsorbent. The study was carried out in batch experiment in three phases to find-out the effect of concentration of Nickel at different concentrations different contact time, rpm and dosage of adsorbent. Each phase was involved with different contact time, rpm and dosage and results of each phase were recorded. In the third phase at a contact time of 60 min. and at 40 rpm with a dosage of 4.5 gm the removal of Nickel from aqueous solution was found effective with 97.86 % of removal and with same set at 1.5 gm of adsorbent the removal of Nickel was found to be 58.65 %. They revealed that the percentage of removal increased with increased doses; hence the Tephrosia purpurea can be useful adsorbent for removal of Nickel from industrial wastewater.

The biosorption of Zn^{2+}, Ni^{2+} and CrO_{4} was studied over a range of metal ion concentrations, adsorption time, pH and co-anions, by fungal mycelium pellets of Aspergillus niger 405 as an adsorbent (Zeljka et al.: 2000). The results showed better biosorption for the ions at pH ranging from 4.0 to 6.0. On the contrary, pH values from 3.0 to 7.0 had no influence on sorption of chromium. Comparison of metal uptake in single and multi-component solutions Zn-Ni-Cr was discussed. Fungus Aspergillus niger 405 showed a good affinity for binding of Zn^{2+} and Ni^{2+} ions in single, while in multi-component solution it occurred only for Zinc.
Studies were carried out for the removal of Zinc metal from synthetic stock solution, by the adsorbent material bentonite, (Prasanna Kumar et al.: 2006). Parameters studied include time of contact, size of bentonite particles, dosage of the adsorbent, initial concentration of the solution, initial pH of the solution and volume of the solution.

The saw dust used for adsorption was sieved (50 – 60 mesh) and washed several times with distilled water. It was then treated with 0.1M aqueous solution of Di-sodium hydrogen phosphate for 24 hrs. The material was then filtered and washed several times with distilled water to release phosphate and dried at 40°C in an oven. Then 50 ml of solution containing required amount of metal ions was treated with 1mt of this adsorbent in 250 ml conical flask. The mixture was filtered after contact time of 24 hrs and filtrate was analyzed for heavy metals in Atomic Absorption spectrophotometer.

They found that percentage adsorption of Zn(II), Ni(II) and Cr(VI) is maximum in neutral media. The percentage of adsorption remains 80 % even up to their initial concentration of 30 mg. maximum adsorption is observed at pH 7.0 – 8.0, the adsorption of these metals follow the trends at various pHs.

\[ pH \ 7.0 = Cu(II) > Zn(II) = Ni(II) >> Cr(VI) \]
\[ pH \ 2.0 = Cr(II) >> Cu(II) > Ni(II) > Zn(II) \]

The studies were carried out to examine a possible strategy for the removal of Chromium(VI). Employing dead biomass of Aspergillus Niger in batch experiments. (Sneha Narvekar and Varsha K. Vaidya: 2008). Evaluation of the effect of pH (2.0-9.0) on biosorption indicated that a decrease in the pH of the solution increased the rate of removal of Chromium(VI), showing highest biosorption of 20.17 % Chromium(VI) removal at pH 2.0. Optimization indicated that the rate of removal of Chromium(VI) increased with a decrease in Chromium(VI) concentrations and with increases of biomass concentrations.

The adsorption studies on the removal of Nickel(II) and Zinc(II) from aqueous solution using treated GAC (Granular Activated Carbon) and carbon aerogel were carried out under varying experimental conditions by Ajay Kumar Meena et al.
Treated GAC showed 98 % and 94 % and carbon aerogel 92 % and 96 % adsorptive removal of Nickel(II) and Zinc(II) respectively under optimized conditions of pH 8.0 and dosage 1.2 gm/100 ml for 3 mg/l Nickel and Zinc(II) from aqueous solutions in 48 hr contact time. The adsorption was found to be pH dependent and maximum adsorption occurred at pH 8.0 and 6.0 for treated GAC and carbon aerogel, respectively. Authors concluded that, these experimental studies on low cost adsorbents would be quite useful in developing an appropriate technology for the removal of Nickel(II) and Zinc(II) from contaminated plant effluents.

Akira OTSUKI et al. (2004). Reported that Nickel (Ni) and Zinc (Zn) found in wastewater from industrial factories can be effectively removed by physicochemical adsorption using mainly natural zeolite. They achieved best results while 50 mg/l of natural zeolite and 0.5 mg/l of aluminum ion were added into solution at pH 10. More than 98 % of Nickel and Zinc and more than 94 % of phosphorus were removed from the wastewater.

Sing et al. (2000), polymer grafted used tea leaves (PGUTL) has been used as adsorbent in this study for removal of 7 heavy metals Mi, Mn, Cu(II), Zn, Cd(II), Hg, Pb from an aqueous solution, Adsorption isotherms and thermodynamic parameters were also studied. The effects of contact time, Initial concentrations, pH, and temperature for removal of heavy metals have been studied in these experiments.

2.12 PROBLEM IDENTIFICATION

The scanning of literature revealed that the investigators have carried out extensive research to assess the potential of various adsorbents in removing metals under varied experimental conditions. The metals tried include hexavalent chromium, Ni, Zn, copper, lead etc. Metals removal potential of adsorbents viz. rice husk, maize bran, grape waste, rice straw, walnut hull, coconut coir pith, activated alumina, activated carbon, activated clay, wheat bran, saw dust, activated sugar cane leaves, orange peel, silk cotton hull etc. have been investigated. However the studies were found to be carried out by using synthetic samples containing single metal in most of the cases. Further the investigations referred to batch mode of experimentation. From the literature survey it was clear that the literature is silent on columnar studies to assess
adsorption techniques. Moreover the need of the day is to treat the wastewater containing more than one metal along with the organic matter toxicants and nutrients. Specially it is opined that behaviour of the adsorbents in removing metals from the domestic wastewater which is nutrient rich and contains pathogens and organic matter is not documented in the literature elsewhere.

The soil aquifer treatment systems to treat the wastewater have been investigated by researchers. The literature throws light on the removal potential of nutrients, organic matter from domestic wastewater and removal of metals from industrial effluent by SAT system. The author is of the opinion that the studies carried out are still premature and further investigations are needed to label the reproducibility of the results of SAT system in treating wastewaters. In particular studies on SAT system in conjunction with adsorbents have not been carried out.

Thus based on the literature review it was felt that there is a need to evaluate the potential of SAT system in conjunction with adsorbents in removing metals, nutrients, organic matter and solids from domestic wastewater and industrial effluents.

Therefore it was decided to carryout investigation in this direction and hence the title of the present research work “Wastewater Treatability Studies by Soil Aquifers Treatment” was framed, variables were identified, experimental design was outlined and investigations were carried out.