CHAPTER 1

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1.1 Introductions

Wastewater containing heavy metal ions result from many sources, industries, such as metal plating operation or fertilizer manufactures; lose heavy metal ions to the environment. Since such metal ions will not be degraded, accumulation and distribution of these metal ions to our environment occur, which is of concern to the public [1].

In response to these considerations, researches have been focused with considerable interest in developing methods for treating and deposing of toxic waste. Treatment methods such as chemical precipitation, electrode position, ion exchange, membrane separation, and absorption have been applied.

1.2 Wastewater treatment processes

Wastewater treatment processes are classified into three steps:

1.2.1 Primary treatment

this step involves the preparation of wastewater for biological treatment[2] large solids are removed by screening and grit is allowed to settle out equalization in a mixing basin levels out the hour –to- hour variation in flows and concentration these should be a spill to pond retain slugs of concentrated wastes that could upset the downstream process. Neutralization when required, follow equalization because streams of different pH partly neutralize each other when mixed oils greases and suspended solids are removed by flotation sedimentation or filtration [3]

1.2.2 Secondary treatment

By this step the biological degradation of soluble organic compounds will occur [2], this is usually done aerobically in a pond or a closed vessel after biotreatment of the microorganisms and other carried over solids are allowed to settle.

A fraction of sludge is recycled in certain processes but ultimately the excess sludge along with sedimented solids has to be disposed of many existing wastewater treatment systems for removing materials that would be toxic to microorganisms. Until recently this was adequate but now it is not, so new facilities have to be designed and old facilities retrofitted to include additional capabilities to remove priority pollutants and residuals toxic to aquatic.

1.2.3 Tertiary treatment

Tertiary treatment processes followed the biological treatment in order to remove specific types of residuals. Filtration to remove suspended or colloidal solids adsorption to remove organics and color chemical oxidation to remove organics.

Unfortunately tertiary systems used have to treat a large volume of wastewater and so they are expensive .they can also be inefficient because the processes are not pollutant-specific [2-4]

1.3 Selections of wastewater treatment processes

The selection of a wastewater – treatment process or a combination of processes depends on:

1- The characteristics of the wastewater, this considers the form of the pollutant, i.e., suspended, colloidal, or dissolved, the biodegradability, and the toxicity of the organic and inorganic components.

2- The required effluent quality, consideration should also be given to possible restrictions such as an effluent bioassay aquatic toxicity limitation.

3- The costs and availability of land for any given wastewater-treatment problem [4].

1.4 Treatment methods for heavy metals

There are various treatment techniques available for the removal and recovery of heavy metal ions from wastewater .some of these are well-established methods that have been in practice for decades; others are more recent innovations. The most commonly used are precipitation, ion exchange, membrane processes, and adsorption.

1.4.1 Precipitation

In chemical reactions, precipitation is the phenomenon that occurs when a dissolved substance in a liquid passes out of solution into solid form as result of a chemical reaction.

The completion of reaction in coagulation or precipitation processes is almost instantaneous after the chemicals are dissolved fully. the precipitates first formed by the chemical reactions are crystals of molecular size .the initial growth or increase in size of these colloidal crystals and coagulated solids is caused by charge reduction and Brownian movement. Additional growth is a result of gentle but turbulent stirring of the suspension (flocculation) [5].

Precipitation is employed for the removal of heavy metal ions from wastewaters. Heavy metal ions are generally precipitated as hydroxide through the addition of lime or caustic to a pH of minimum solubility. However, several of these compounds are amphoteric and exhibit a point of minimum solubility.

When treating industrial wastewaters containing metal ions, it is frequently necessary to pretreat the wastewaters to remove substances that will interfere with the precipitation of the metal ions. Cyanide and ammonia form complexes with many metal ions that limit the removal which can be achieved by precipitation .Cyanide can be removed by alkaline chlorination or other processes such as catalytic oxidation on carbon .Cyanide wastewaters containing nickel or silver are difficult to treat by alkaline chlorination because of the slow reaction rate of these metal complexes. Ferrocyanide

$[Fe\ (CN)_6]^{4-}$ is oxidized to ferricyanide $[Fe\ (CN)_6]^{3-}$ which resists further ammonia oxidation can be removed by stripping, break-point chlorination, or other suitable methods prior to the removal of metals.

Heavy metal ions can be removed from an industrial wastewater by lime precipitation .heavy metals may also be precipitated as the sulfide and in some cases as the carbonate, as in the case of lead.

For many metals such as cadmium and arsenic, coprecipitation with iron or aluminum is highly effective for removal to low residual levels. In order to meet low effluent requirements, it may be necessary in some cases to provide filtration to remove floc carried over from the precipitation process. Using precipitation and clarification alone, effluent metal ions concentrations may be as high as 1 to 2 mg/l .filtration should reduce these concentrations to 0.5 mg/l or less.

1.4.2 Ion exchange

Ion exchanges can be used for the removal of undesirable anions and cations from wastewater. Cations are exchanged for hydrogen or sodium and anions for hydroxyl ions.

Ion exchange resins consist of an organic or inorganic network structure with attached functional groups. Most ion exchange resins used in wastewater treatment are synthetic resins made by the polymerization of organic compounds into a porous three-dimensional structure. The degree of cross linking between organic chains determines the internal pore structure, with high cross linking which would enhance diffusion of ions through large pores. However, physical strength decreases and swelling in water increases as crosslink density is lower. The functional ionic groups are usually introduced by reacting the polymeric matrix with a chemical compound containing the desired group. Exchange capacity is determined by the number of functional group per unit mass of resin.

Ion exchange resins are called cationic if they exchange positive ions and anionic if they exchange negative ions. Cation exchange resins have acidic functional groups such as sulfonic, whereas anion exchange resins contain basic functional groups such as amine. ion exchange resins are often classified by the nature of the functional group as strong acid, weak acid, strong base ,and weak base. The strength of the acidic or basic character depends upon the degree of ionization of the functional groups.

The most common strong acid ion exchange resin is prepared by copolymerizing of styrene and divinylbenzene followed by sulfonation of copolymer. The degree of cross linking is controlled by the fraction of divinylebenzene in the initial mixture of monomers. [4]

Types of Ion-exchange Resins

There are three basic types of resins: cationic, anionic and mixed.

The cationic group includes

$R\text{-}SO_3H$	sulfonic
R-OH	phenolic
R-COOH	carboxylic
$R\text{-}PO_3H_2$	phosphonic

The anionic resins include

$R\text{-}NH_2$	primary amine
R-R NH	secondary amine
$R\text{-}R_2$ N	tertiary amine
$R\text{-}R_3\ N^+\ OH^-$	quaternary amine

where in each case R indicates a hydrocarbon polymer and R indicates a specific group, for example, CH_2 .the mixed- bed resins are combinations of these tow types. Note also that the salts of these resins can serve as the exchange medium and actually more commonly do. A particular example is the use of sodium salt in water softening because of the feature of simple recharging. A note should be made that this results in the product ions of water with high sodium concentration, which is not recommended for cardiac patients.

1.4.3 Membrane processes

Membranes are materials that selectively stop or slow the passage of particular types of molecules (allow passing water and not sodium chloride). They may consist of dry solids, solvent swollen gels, or immobilized liquids and for particle purposes are considered to be constructed of polymers. In general, membranes of interest have a highly porous structure, although the pores may be as small as 10 Å in size. Pore shape is generally irregular, although certain gel membranes have both a highly regular and highly uniform diameter. Basic mechanisms of selectivity by uncharged membranes are based on sieving, diffusion, and solubility effect .charged membranes also select by ion exchange and therefore can be used as ion-exchange systems.

The classical membrane process is osmosis. Here the potential of two solutions separated by a membrane is different because of a difference in salt concentrations. Water diffuses through the membrane until the potential is equal on both sides. there is an interaction between the pressure potential and the chemical potential cased by the concentration gradient, which results in balance being made by a combination of the two. The osmotic process can be reversed[i.e., reveres osmosis (RO)] by increasing the pressure on the saline side of the membrane. A similar result can be achieved by introducing an electrical potential across the membrane (electrodialysis).

Selectivity of a given membrane is strongly affected by the method of manufacture. For example, cellulose acetate membranes are normally about 100 μm thick with a 0.2 μm thick surface skin that is much denser than the core, i.e., less porous or with smaller porous. This skin is formed during casting by exposing the surface to air. At this stage of manufacturing, the skin allows permeation of sodium chloride. Further treatment of the membrane by an annealing process increases the density of the skin and greatly decreases the permeability to sodium chloride. [6].

The more common membranes are:

1- tubular: manufactured from ceramics, carbon, or any number of porous plastics, these tubes have inside diameters ranging from 1/8 inch (3.2 mm) up to approximately 1 inch (2.54 cm).the membrane is typically coated on the inside of the tube, and the feed solution flows through the interior from one end to the other, with the " permeate,, or "filtrate,, passing through the wall to be collected on the outside of the tube.
2- Hollow fiber: similar to the tubular elements in design. Hollow fibers are generally much smaller in diameter and require rigid support such as those obtained from the "potting, of a bundle inside a cylinder. As with tubular elements, feed flow is usually down the interior diameter of the fiber.
3- Spiral wound: this device is constructed from an envelope of sheet membrane wound around a permeate tube that is perforated to allow collection of the permeate or filtrate.
4- Plate and frame: this device incorporates sheet membrane that is stretched over a frame to separate the layers and facilitate collection of the permeate [7].

1.4.4 Adsorption

Adsorption is a physico-chemical treatment process for wastewater, which is gaining prominence as a mean for producing good quality effluents, which are low in concentration of dissolved organics. This process is exploiting the ability of certain solids preferentially to concentrate specific substances with attract with the solid surfaces, so it is used as a separation technique [8]. The adsorption process generally depends on:

1.4.4.1 **Factors Influencing Adsorption:**

The molecules or ions of the solute are removed from solution and taken up by the adsorbent during the process of adsorption. The majority of molecules or ions are adsorbed onto the large surface area within the pores of a carbon particle and relatively few are adsorbed on the outside surface of the particle. The transfer of solute from solution to adsorbent continues until the concentration of solute remaining in solution is in equilibrium with the concentration of solute adsorbed by the adsorbent. When equilibrium is reached, the transfer of solute stops and the distribution of solute between the liquid and solid phases is measurable and well-defined .To explain the mechanism of adsorption, three distinct steps must be considered:

1. The adsorbed molecule or ions must be transferred from the bulk phase of the solution to the surface of the adsorbent particle. This process is referred to as film diffusion.
2. The adsorbate molecule or ions must be transferred to an adsorption site on the inside of the pore. This process is referred to as pore diffusion.
3. The particle must become attached to the surface of the solute, i.e. to be adsorbed.

Many factors influence the rate at which adsorption reactions occur and the extent to which a particular material can be adsorbed.

1- Agitation

The rate of adsorption is controlled by either film diffusion or pore diffusion, depending on the amount of agitation in the system. If relatively little agitation occurs between the solid particle and the fluid, the surface film of liquid around the particle will be thick and film diffusion will likely be the rate-limiting step. If adequate mixing is provided, the rate of film diffusion will increase to the point that pore diffusion becomes the rate-limiting step. The pore diffusion is generally rate – limiting for batch-type contacting systems which provide a high degree of agitation.

Film diffusion will most likely be the rate-limiting step for continuous-flow systems at flow rates of 10 gal/min per square foot or less.

2- Characteristics of the Adsorbent

Particle size and surface area are important properties of an activated solid with respect to its use as an adsorbent. The adsorption rate increases as the particle size decreases .thus, the adsorption rate increases as the particle size decreases. Thus, the adsorption rates are faster for powdered solids than for granular carbon. On other side, the total adsorptive capacity of a solids particle depends on its total surface area. The size of solids particle does not have a great effect on total surface area, since most of the surface area lies within the pores of the solids particle.

Thus, equal weights of the same solids would have essentially the same capacity in the powdered form.

There has been a considerable amount of study on the oxygen-containing functional groups present on the surface of solids. It has been observed that oxidation and reduction of active carbon markedly influences the nature of the phenol and nitrobenzene isotherms. Coughlin and Ezra [8] showed that oxidation of active carbon considerably lowers the capacity of both active carbon and carbon black for adsorption of phenol and nitrobenzene in the low solute concentration regions of the isotherms. On other side reduction of the carbon resulted in the opposite effect suggesting that the adsorption of phenol takes place with pi-electron system of the graphitic rings of the carbon basal planes, and that the presence of additional acidic surface oxygen groups produced by oxidation of carbon, at the basal plane edges, serves to withdraw electron from the pi-system of basal planes.

The adsorption isotherm for phenol on carbon usually shows a two-step process, resulting in two plateaus. The second step of the isotherm is attributed to an uncovering part of the surface and readsorption of the phenol molecules with different orientation .This reorientation involves a change from a flat configuration to an end-on configuration where the hydroxyl group is directed away from the carbon surface.

3- Solubility of the Adsorbate

For adsorption to occur, a molecule must be separated from the solvent and becomes attached to the solids surface. Soluble compounds have a strong affinity for their solvent and thus are more difficult to adsorb than insoluble compounds.

However, there are exceptions, since some compounds that are slightly soluble are difficult to adsorb, whereas some very soluble compounds may be adsorbed. The adsorption of some aliphatic organic acids on carbon from aqueous solution increases in the order: formic<acetic<propionic<butyric, whereas the order is reversed for adsorption from toluene.

The properties of solute molecules are discussed better in terms of polarity, which has a profound effect on absorbability from water. A general rule for prediction of the solute polarity on adsorption is that a polar solute will refer the phase which is more polar. In other words, a polar solute will be strongly adsorbed from a nonpolar solvent by a polar adsorbent, but will much prefer a polar solvent to a nonpolar adsorbent, since solubility of organic solutes in water involves formation of hydrogen bonding between the partially positive hydrogen atoms of water and the partially negative atoms of organic molecule, increasing the polarity is expected to increase solubility and in turn to decrease absorbability.

4- Size of Adsorbate Molecules

Molecular size of adsorbate molecules or ions is logically an important parameter in the adsorption process, where the molecules or ions must enter the microspores of carbon particles so as to be adsorbed. Within a homologous series of aliphatic acids, aldehydes, or alcohols, the adsorption increases as the size of the molecule becomes greater. This can partly explained by the fact that the forces of attraction between carbon and a molecule are greater the closer the size of the molecule is to the size of the pores in the carbon molecule . So, the adsorption is very strong when the pores are just large enough to permit the molecules or ions to enter.

Most wastewater contains mixture of compounds representing many different sizes of molecules ans ions. In this situation there would appear to be a danger of size screening. i.e., large molecules or ions blocking the pores to prevent the entrance of small molecules. However, the irregular shape of both the molecules or ions and the pores, as well as the constant motion of the molecules, prevents such blockage from occurring. Furthermore, the greater mobility of the small molecules or ions allows them to diffuse faster and to enter the pores ahead of the large molecules or ions.

5- pH Value

The importance of the pH value of the solution is attributed to the fact that hydrogen ions themselves are strongly adsorbed and partly that pH influences the ionization, and thus the adsorption of many compound.

In general, the adsorption of typical organic pollutants from water is increased with decreasing pH value. In many cases this may result from the neutralization of negative charges at the surface of the solid with increasing hydrogen-ion concentration, thereby reducing hindrance to diffusion and making available more of the active surface of the solid . This effect can be expected to vary in degree for different solids, because the charges at the surfaces of the solid depend on the composition of the raw materials and on the technique of activation [8].

pH is generally acknowledged to be the principal factor governing concentrations of soluble and plant available metal ions. Metal ions solubility tends to increase at lower pH and decrease at higher pH values [8].In acid conditions, adsorption is a more important process than the precipitation of solid phases in decreasing the concentration of metal ions in solution and the reverse is true in alkaline media.

6- Temperature

The effect of temperature on reaction rates is well known and important in understanding reaction mechanisms. Svante Arrhenius, a Swedish physical chemist who received the 1903 Nobel Prize for chemistry, noted that for most reactions, the increase in rate with increasing temperature is nonlinear **[9]**.

Since the process of adsorption is spontaneous, it is accompanied by a decrease in the system's free energy. There is always a decrease in entropy due to the loss of degree of freedom of the solute on passing from the dissolved state to the adsorbed state. An increase in the temperature, therefore, will result in a reduction of the equilibrium adsorptive capacity, whereas lower temperatures will favor an increased capacity [9].