Chapter I

INTRODUCTION AND OBJECT OF INVESTIGATION

IA. INTRODUCTION

Environmental pollution, as a consequence of the industrialization process, is one of the major problems that has to be solved and controlled.

Wastewaters can contain compounds that are non-biodegradable or toxic to biological organisms. This may include heavy metals such as (cadmium, **cobalt**, mercury, **lead**, zinc, copper, arsenic, **strontium**, chromium,……. etc) and organic compounds as **dyes**, chlorinated aromatic compounds; poly-chlorinated bi-phenols (PCBs) and poly aromatic hydrocarbons (PAHs).

Heavy metals are not biodegradable and have become an ecotoxicological hazard of prime interest and increasing significance owing to their harmful effect on human physiology and other biological systems when they exceed the tolerance levels. In addition mining, mineral processing, electric and electronic industries, dye and paint manufacture, textile production, plating works, photography, battery manufacturing, and extractive metallurgical operations also generate toxic liquid wastes **[Goyal and Ahluwalia, (2007) & Olayinka et al., (2007) & Olayinka et al., (2009)]**.

A number of technologies for the removal of heavy metal ions and dyes from aqueous solutions have been developed over the years **[Romero-Gonzales et al., (2001)]**. The most important treatment processes for metals and dyes contaminated waste streams include chemical precipitation, membrane, filtration, ion exchange, carbon adsorption, and coprecipitation/adsorption **[Bailey et al., (1999)]**. However, all these techniques have their inherent advantages and limitations in application. Some examples are summarised in Table (I.1) **[Luqman Chuah Abdullah et al., (2010)]**.

Table (I.1): Current treatment technologies for heavy metals and dyes removal involving physical and/or chemical process

Physical and/or chemical process	Advantages	Disadvantages
Oxidation	Rapid process for dye removal	High energy costs and formation by-products
Ion-exchange	Good removal of a wide range of metals and dyes	Absorbent requires regeneration or disposal
Membrane filtration technologies	Good removes of heavy metals and dyes	Concentrated sludge production, expensive
Coagulation/flocculation	Economically feasible	High sludge production and formation of large particles
Electrochemical treatment	Rapid process and effective for certain metal ions	High energy costs and formation of by-products
Ozonation	Applied in gaseous state: alteration of volume	Short half life
Photochemica	No sludge production	Formation of by-products
Irradiation	Effective at lab scale	Required a lot of dissolved O2
Electrokinetic coagulation	Economically feasible	High sludge production
Fentons reagents	Effective decolourisation of both soluble and insoluble dyes	Sludge generation
Biological treatment	Feasible in removing some metals and dyes	Technology yet to be established and commercialized

The previous processes usually need expensive facility and high maintenance cost. Therefore, there is a need for more economical alternative technologies or sorbents for the treatment of metals and dyes contaminated waste streams.

This work is focused on the removal of certain metal ions and some organic materials from waste streams using two techniques: adsorption by bone char and liquid emulsion membrane (LEM).

IA.1 ADSORPTION TECHNIQUE:

Adsorption is an effective purification and separation technique used in industry especially in water and wastewater treatments. Sorption treatment can be used independently and in combination with biological treatment as a method of preliminary purification or primarily polishing. In this context, it is desirable to distinguish between three principal types of adsorption:

IA.1.1. Exchange Adsorption:

Adsorption of the first type falls within the of ion–exchange and is often referred to as "*exchange adsorption"*. Exchange adsorption is, as the term implies, a process in which ions of one substance concentrate at a surface as a result of electrostatic attraction to charged sites at the surface. For two potential ionic adsorbates in like concentration and in the absence of other specific sorption effects, the charge on the ion

is the determining factor for exchange adsorption. In a system containing a monovalent ion under the stated conditions, the influence of kinetic energy to remain in solution phase is the same for each, but the trivalent is attracted much more strongly toward a site of opposite charge on the surface of the adsorbent. For ions of equal charge, molecular size (hydrated radius) determines order of preference for adsorption, the smaller ion being favored.

IA.1.2. Physical Adsorption (Ideal Adsorption):

Adsorption occurring as a result of van der Waal's forces is generally termed *" physical adsorption "* a term which has come to represent cases in which the adsorbed molecule is not affixed to a specific site at the surface but is rather, free to undergo translational movement within the interface. Physical adsorption is usually predominant at low temperature, and is characterized by a relatively low energy of adsorption, that is the adsorbate is not held as strongly to the adsorbent as for chemical adsorption. Adsorption of this type is sometimes referred to also as *"ideal adsorption"*

IA.1.3. Chemical Adsorption:

If the adsorbate undergoes chemical interaction with the adsorbent, the phenomenon is referred to as *"chemical adsorption"*, *"activated adsorption "* or *" chemisorption"*. Chemically adsorbed molecules are considered not to be free to move on the surface, or within the interface.

Chemical adsorption processes exhibit high energies of adsorption because the adsorbate forms strong localized bonds at active centers on the adsorbent. Chemical interaction between the adsorbent and the adsorbate is favored at higher temperature because chemical reactions proceed more rapidly at elevated temperatures than at lower temperatures.

Most adsorption phenomena are combinations of the two forms (physical and chemical adsorption) that is, the several forces which influence the different types of adsorption often interact to cause concentration of a particular solute at interface. Thus, it is generally not easy to distinguish between physical and chemical adsorption.

IA.1.4. Main Factors Influence The Adsorption Process:

Many factors influence the rate at which adsorption reactions occur and the extent to which a particular material can be adsorbed. Some of the more important factors will be discussed.

IA.1.4.1. Characteristics of the adsorbent.

Particle size and surface area are important proprieties of an adsorbent with respect to its use as an adsorbent. The size of carbon particle influences the rate at which adsorption occurs: adsorption rates increase as particle size decrease **[Najm et al., (1990)].**

IA.1.4.2. Solubility of adsorbate.

For adsorption to occur, a molecule must be separated from the solvent and become attached to the adsorbent surface. Soluble compounds have strong affinity for their solvent and thus are more difficult to adsorb than insoluble compounds. However, there are exceptions, since many compounds that are slightly soluble are difficult to adsorb, whereas some very soluble compounds may be absorbed readily **[Benefield et al., (1982)]**.

IA.1.4.3. Size of adsorbate molecules.

Molecular size would logically be important in adsorption, since the molecules of adsorbate must enter the micropores of a adsorbent particle so as to be adsorbed. Research studies have shown that within a homologous series of aliphatic acids, aldehydes or alcohols, adsorption usually increases as the size of molecule becomes greater **[Benefield et al., (1982)]**. This can partly be explained by the fact that forces of attraction between adsorbent particle and adsorbate molecules are greater the closer the size of the molecule is to the size of the pores in the adsorbent. Adsorption is strongest when the pores are just large enough to permit the molecules to enter. Most wastewaters contain a mixture of compounds representing many different sizes of molecules. In this situation there would appear to be a danger of molecular screening, i.e. large molecules blocking the pores to prevent the entrance of small molecules. However, irregular shape of both the molecules and the pores as well as the constant motion of the

molecules, prevents such blockage from occurring. Further more, the greater mobility of the small molecules allows them to diffuse faster and to enter the pores ahead of the large molecules**[Benefield et al., (1982)]**.

IA.1.4.4. Temperature.

The temperature at which an adsorption process is conducted will affect both the rate of adsorption and the extent to which adsorption occurs. Adsorption rates increase with the increased temperature and decrease with decreased temperature. However, since adsorption is an exothermic process, the extent of adsorption will increase at lower temperatures and decrease at higher temperatures **[Benefield et al., (1982) & Weber et al., (1972)]**.

IA.1.4.5. Initial concentration.

In a multisolute system, the adsorptive capacity is the function of the initial concentration of the adsorbate, which doesn't occur in the single-solute system**[Najm et al., (1991) & Huang et al., (1996)].**

IA.1.4.6. Contact time"Equilibrium time".

Perhaps the most important consideration in determining an equilibrium isotherm is selection of an equilibration (contact) time long enough to ensure that equilibrium is actually reached or closely approached. Failure to do so can result in data of questionable value, and use of such data can lead to

gross underestimation of adsorptive capacity **[Randtke and Snoeyink, (1983)]**.

Generally equilibrium time is defined as the time through which equilibrium occur between adsorbate and adsorbent or in other words is the period of time after which there is no further decrease in the solution concentration. This time may be hours, days or even weeks **[Randtke and Snoeyink, (1983)]**.

IA.1.4.7. Adsorption of mixed solutes.

In the application of adsorption for purification of waters and wastewaters the material to be adsorbed commonly will be a mixture of many compounds rather than a single one. In systems with more than one adsorbate, competition between the adsorbates for surface sites may occur. The degree of competition is dependent on the type and concentration of the competing ions, number of surface sites and the affinity of the surface for adsorbate. The presence of second adsorbate does not always decrease metal removal. **Huang, (1984)** reported that the presence of organic adsorbates did not adversely affect the removal of several heavy metal .

IA.1.4.8. Effect of pH.

pH is the primary variable governing metal adsorption onto hydrous solids (activated carbon, metal oxides, clays, etc.**) [Stumm and Morgan, (1981)].**

For cationic heavy metals, adsorption increases with increasing pH (the fraction of metal removed increases from zero to one over a relatively narrow pH rang). The opposite is observed when the metal exists as an anion (removal generally increases with decreasing pH). The pH affects the status of the outer hydration sheaths of the metal ion, metal solution speciation, complexation and solubility and the behavior of the carbon surface groups .

IA.1.4.9. Metal type and concentration.

In general, the lower the pH at which cationic metals form aqueous hydroxide complexes [$Me^{x}(OH)_{n}^{(x-n)}$] and solids [$Me(OH)_{2(s)}$], the better the metal will be removed. The formation of the first metal hydroxide species can be represented by the following chemical reaction :

$$Me^{2+} + H_2O \leftrightarrow Me(OH)^{+} + H^{+};\ K_1$$

The concentration of the metal ion affects the removal mechanism as well as the surface loading. If the concentration of the cationic metal is large enough such that $Me(OH)_{2(s)}$ forms, then surface precipitation can occur. If the metal concentration is less than the metal`s solubility, then the primary removal mechanisms are sorptive in nature (physical / chemical adsorption, ion exchange).

Many investigators have studied the feasibility of using cheap, commercial available materials as potential adsorbents

e.g. activated carbons, **bone char**, alumina, silica, bauxite, bentonite, fuller's earth, molecular sieves, peat, lignite, chitin, chitosan, and ion exchange resins **[Mckay, (1995) & Srivastava et al., (1997)]**.

IA.1.5. Activated Carbon:

The term active carbon (AC) actually implies a rather broad family of substances, with highly developed internal surface area, porosity and individual species being characterized by sorptive and catalytic properties rather than by definite structure or specific chemical composition **[Timothy, (1999)]**. Porous carbon materials or activated carbons have been used for thousands of years and have become extremely versatile adsorbents. Active carbon is a broad-spectrum agent that effectively removes toxic and bio-refractive substances such as insecticides, herbicides, chlorinated hydrocarbons, heavy metal ions, and phenols, typically present in many water supplies **[Hassler, (1974) & Austin and Shreve, (1985) & Bandosz, et al., (2003) & Kadirvelu et al., (2001) Ansari and Masoudi, (2004) & Ansari, (2004) & Ansari and Omidvari, (2005) & Ansari and Nikravan Shalmani, (2005) & El-Shafey et al., (2002) & Mostafa, (1997)]**.

The major applications of activated carbon are in solution purification and for the removal of taste, color, odors and other objectionable impurities from liquids, water supplies and vegetable and animal oils. In the recent years, it has been increasingly used for the preventation of environmental

pollution and antipollution laws have increased the sales of active carbons for control of air and water pollution.

Activated carbon can be manufactured from any material that has reasonable elemental carbon content. Any lignocellulosic material can be converted to an activated carbon. The literature mentions many precursors for activated carbon such as bagasse **[Ahmedna et al., (2000)]** scrap tires and saw dust **[Nadhem K. Hamadi et al., (2001)]**, almond, pecan, English walnut, black walnut and macadamia nut **[Christopher A. Toles at al., (1998)]** pistachio **[Wartelle and Marshall, (2001)]** hazelnut shells **[Kobya, (2004)]** rice husk **[Nevin Yalem and Vadettin Sevine, (2000)]** rice bran **[Mubeena Akhtar, (2005)]**.

Particular properties may be imparted to an active carbon either by starting with different raw material or by utilizing different preparative procedures.

IA.1.5.1 Preparation of active carbon.

According to **Bansal et al., (1988) & Satya et al., (1997)**, the preparation of activated carbons involve two main steps; carbonization of the carbonaceous raw material at temperature below 700 ^{0}C in the absence of oxygen, and activation of the carbonized product. During carbonization most of the non- carbon elements such as oxygen and hydrogen are first removed in gaseous form by the pyrolytic decomposition of the starting material. The free atoms of elementary carbon

are grouped into sheets of condensed aromatic ring systems with a degree of planar structure. The arrangement of these aromatic sheets is irregular and leaves interstices between them, which may, filled with tarry matter or products of decomposition or at least blocked partially by disorganized carbon. The important parameters that determine the quality and the yield of the carbonized product are:(i) rate of heating, (ii)final temperature and (iii) soaking time **[Manocha, (2003)]**.

Simple cooking or carbonization does not give rise to products that have adsorption capacity because of their less developed pore structure and low surface area. This pore structure is enhanced during the activation process, which convert the carbonized raw material into a form that contain the greatest possible number of randomly distributed pores of various shapes and size giving rise to an extended and extremely high surface area of the product **[Bansal et al., (1988)]**.

The objective of the activation process is to enhance pore volume and to enlarge diameter of the pore, which were created during carbonization process, and to create new porosity. Activation process removes the disorganized carbon, exposing the aromatic sheets to the activation agent in the first phase and leads to the development of microporous structure. In the later phases of the reaction the significant effect is widening the existing pores or the formation of large-sized pores by complete burn- off of the walls between the adjacent pores

I A.1.5.2 Methodes of activation.

Typically, the activation of carbon can be divided into two processes. First, the physical method consists of the pyrolysis of the precursor material and gasification of the resulting char in steam, nitrogen gas, air or carbon dioxide. The formation of the porous structure is achieved by elimination of a large amount of internal carbon mass. High porosity carbons can be obtained only at a high degree of char burn off. For the chemical method, pyrolysis char would be impregnated with some chemical reagents, such as $ZnCl_2$, H_3 PO_4, NaOH and KOH. Because of the dehydrogenation process, the chemical reagents promote the formation of cross-links, leading to the development of a rigid matrix, less prone to volatile loss and volume contraction upon usage. According to **Zhonghua and Vansant, (1995) & Ahmadpour and Do, (1996) & Lillo-Ródenas et al., (2003) & Lillo-Ródenas et al., (2004)** major advantages of the chemical activation compared to the physical activation are lower treatment temperatures and shorter treatment times. In addition, activated carbon obtained by chemical activation exhibits a larger surface area and better developed mesoporosity than physical activation.

IA.1.5.3 Structure of activated carbon.

Activated carbons are highly porous materials with surface areas of up to 3000 m^2.g-1. The surface area of a typical activated carbon is about 1000 m^2.g-1. These high surface areas are the result of development of mainly micro- and mesopores while a little contribution is also come from macropores.

According tothe IUPAC classification, pores having the radii less than 2 nm are called micropores whereas pores having the size of radii in between 2 to 50 nm are identified as mesopores. Macropores are defined as pores having the radii size above 50 nm. Cokes, chars and activated carbons are often termed as amorphous carbon. X-ray diffraction and electron microscopy have shown that these materials have crystalline characteristics, even though they may not show certain features, such as crystal angles and faces, usually associated with the crystalline state. The existence of submicroscopic dimensions in so called amorphous carbons makes the microcrystal structure known as crystallites. The basic structural character of amorphous carbons is closely approximated by the structure of pure graphite. The graphite crystal is composed of layers of fused hexagons held approximately 0.335 nm apart by van der Waals forces **[Smisek and Cerny, (1970)]**.

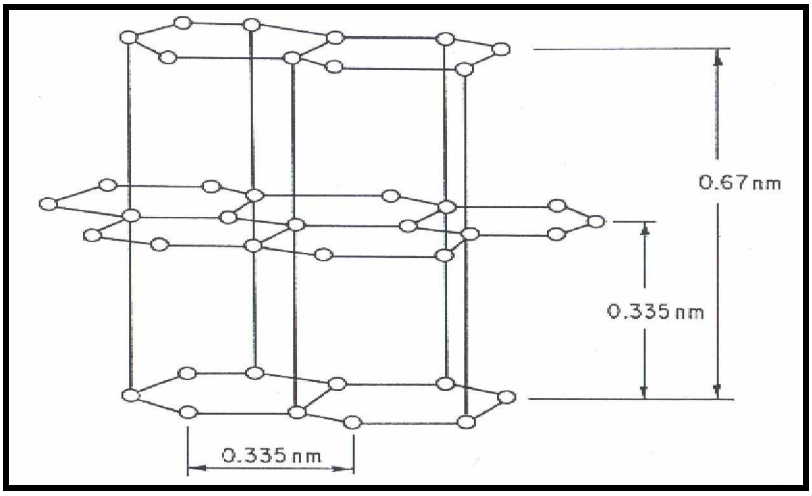

Figure (IA.1): Carbon Atom Arrangements in Graphite Crystal