

*REVIEW OF
LITERATURE*

2.0 REVIEW OF LITERATURE

The review of literature pertaining to the study “Adsorption of copper from synthetic metal solution using selected agrowastes” is discussed under the following headings:

2.1 Industrial pollution

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2.4.2.1 Adsorption by activated carbon

2.4.2.2 Biosorption

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2.4.2.2.2 Adsorption by indigenous materials

2.5 Adsorption isotherms

2.1 Industrial pollution

Environment literally means the surrounding. It can comprehensively be defined as the sum total of all the conditions and influences that affect the development and life of organisms. Pollution has been recognized as any undesirable change in the physical, chemical and biological characteristics of our air, land and water, which may harmfully affect the human, animal and plant life. Thus, the contamination of environment with impurities which make it unfit for its intended use is

known as environmental pollution and any substance whose presence in the environment causes pollution may be termed as a pollutant (Omkar, 2003).

Environmental pollution has become reality impossible to circumvent in developing countries when taking into account its fast growth noted during these last years. This growth is due to the industrialization policy and the space extension very little controlled consequence of a very strong demographic growth. This situation contributes in a dominating way to a permanent environmental pollution (Adouby *et al.*, 2007).

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed great problem worldwide. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products (Gupta *et al.*, 2001).

Industrial effluents frequently contain a mixture of metal ions. Concentration of these ions varies according to the type of industry (Al-Subu *et al.*, 2001).

Man's exposure to heavy metals comes from industrial activities like mining, smelting, refining and manufacturing processes (Akporhonor and Egwaikhide, 2007).

Environmental pollution by toxic metals occurs globally through agricultural and industrial processes and also through waste disposal. Metals discharged into the environment often not only cause large environmental

impact but also economic and health problems (Chaiyasith and Septhum, 2004).

The release of industrial wastewaters to the environment causes several adverse effects. These wastewaters commonly include cadmium, lead, copper, nickel and cobalt. These heavy metals are non-biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals, plants and human beings (Needlemana and Bellinger, 2001).

2.2 Metal pollution

Urban and industrial wastewater effluents as well as street run off contain heavy metals, which could pose a threat to the environment and have different management opportunities. Heavy metal contamination in run offs could affect receiving waters and aquatic life. Groundwater is susceptible to contamination when the pollutant is highly mobile, soluble and has high concentrations and high detection frequencies (Mentler *et al.*, 2005).

The contamination of water by toxic heavy metals through the discharge of industrial wastewater is a worldwide environmental problem (Ajmal *et al.*, 2003). Their presence in streams and lakes has been responsible for several health problems with animals, plants and human beings. Numerous metals such as antimony, chromium, cadmium, copper, lead and mercury have toxic effects on human and environment (Taty *et al.*, 2003).

The presence of heavy metals in the environment is a major concern due to their toxicity. Many industrial processes produce aqueous effluents containing heavy metal contaminants. According to the World Health Organization, the metals of most immediate concern are aluminum, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead (Ulmanu *et al.*, 2002).

Heavy metals can pose health hazards to man and aquatic lives if their concentrations exceed allowable limits. Concentration of heavy metals below these limits even has potential for long-term contamination, because heavy metals are known to be accumulative within biological systems (Malakootian *et al.*, 2008).

Heavy metals cannot be metabolized and bio-accumulated in the body. These toxic metals can move up in biological chain, thereby reaching human being where they cause chronic and acute ailments (Tunalli *et al.*, 2006).

Considerable research has been carried out over the last decade on the protection against degradation of plant and animal life. Several big cities contribute to increase in this problem, as they are sources of industrial effluents. In order to reduce the environmental pollution, a number of studies have been considered to minimize the problems caused by the commonly employed treatment of metal bearing effluents (Valdman and Leite, 2002).

Industrialization and urbanization have led to an increase in metal contamination of aquatic environments. The increased amount of heavy metals has resulted in toxicity of soil, air and water. Unlike organic pollutants, which in most cases can eventually be destroyed, metallic species released into the environment tend to persist indefinitely. They circulate and eventually accumulate throughout the food chain, thus posing a series of threats to animals and man. Elevated levels of heavy metals may come from a variety of sources such as metal plating, metallurgy, ceramics, photography and from many other industries (Al-Fawwaz and Maznah, 2008).

The increased use of metals and chemicals in the industrial processes has resulted in the generation of large quantities of aqueous effluents creating serious environmental disposal problems. Mining, mineral processing and extractive metallurgical operations generate huge volumes of toxic liquid waste (Antunes *et al.*, 2003).

Toxic metals are often discharged by a number of industrial processes and this can lead in turn to the contamination of freshwater and marine environment. Heavy metals are major pollutants in marine, ground, industrial and even treated wastewaters. Industrial waste constitutes to the major source of various kinds of metal pollution in natural waters (Mahvi *et al.*, 2005).

Pollution by heavy metals comes from several industrial processes namely coke manufactures, chip manufactures, fertilizers, pigments, mining and metallurgical processing (Khatab, 2007).

2.3 Copper pollution and its effects

Copper is present in the wastewater of several industries, such as metal cleaning and plating baths, refineries, paper and pulp, fertilizer and wood preservatives and it is highly toxic (Gundogan *et al.*, 2004).

Copper (Cu), a widely used material in industry, is an essential trace element for human health and plays an important role in carbohydrate and lipid metabolism and in the maintenance of heart and blood vessel activity. The adult human body contains 100-150mg of copper, but excess amounts in the body can be toxic. The use of biomaterials for removing heavy metals from contaminated wastewater has emerged as a potential alternative method to conventional techniques (Harry, 1999).

The copper processing industry refines copper from metal ores. The final stage of copper mine complexes in South Iran does the electro refining of copper. The process of refining produces a waste electrolyte, which has to be disposed. Sulfuric acid, copper (Cu II) and nickel (Ni II) ions are the main constituents of the disposed electrolyte. Copper and nickel ions are very harmful if they are discharged into natural water resources and may pose a serious health hazard (Sepehran *et al.*, 2008).

Copper is a biogenic element that is involved in enzymatic reactions in organisms. Excessive copper is harmful to living organisms. Copper compounds are toxic for fish and concentrations as low as 1-5 mg/l produce an unpleasant taste of water. Excess of copper damages intestinal flora and irritates mucous membranes in pharynx, stomach and bowels. It may

accumulate in liver or kidney and result in Wilson disease (Kynd *et al.*, 2008).

2.4 Metal removal from wastewater

The removal of heavy metals from aqueous solutions can be achieved by several methods. Ion exchange, chemical precipitation, membrane filtration, alum or iron coagulation and adsorption are some of the most commonly adopted processes. Adsorption with activated carbon is widely used for the removal of heavy metals at trace levels. Despite the versatility of carbon as an adsorbent in water treatment, it remains costly. In recent years the use of low cost materials as alternatives to carbon has been investigated as they can be obtained readily and are in great abundance (Low *et al.*, 2004).

2.4.1 Conventional methods

Some of the conventional techniques for removal of metals from industrial wastewater include chemical precipitation, adsorption, solvent extraction, membrane separation, ion exchange, electrolytic techniques, coagulation/floatation, sedimentation, filtration, membrane process and chemical reaction (Badmus *et al.*, 2006a).

These techniques have significant disadvantages including incomplete metal removal, the need for expensive equipment and monitoring systems, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal (Goksungur *et al.*, 2002).

Chemical precipitation leads to the production of toxic sludge. Due to the economics of dealing with large volumes of liquids and of solvent losses, solvent extraction is limited to streams containing more than 1g/l of the targeted heavy metal. Application of the ion exchange process also is not practicable due to the cost of synthetic resins. Furthermore, they are not always selective enough to allow an effective recovery of metals present in the waste (Tomko *et al.*, 2006).

2.4.2 Adsorption

Many physicochemical methods have been proposed for metal removal from industrial effluents (Iqbal *et al.*, 2002). Adsorption is an effective purification and separation technique used in industry especially in water and wastewater treatments (Al-Asheh *et al.*, 2000).

Adsorption is a term commonly used for several different processes involving physical as well as chemical interactions between the solid surfaces of a substance and dissolved metal pieces. Thus adsorption in general can be influenced by changes in hydrochemical parameters such as pH and flow rates (Aslam *et al.*, 2004).

2.4.2.1 Adsorption by activated carbon

The increasing stringent environmental regulation and enforcement of discharge limits require effective decontamination and purification method. From the analytical point of view, it is known that solid phase extraction (adsorption) is an attractive technique based on the use of the sorbent that retain analytes. The adsorption process has proved its advantage over the other processes because of its cost effectiveness and the high quality of the

treated effluent it produces. Activated carbon is widely used as an adsorbent due to its high adsorption capacity (Najim *et al.*, 2008).

Adsorption onto solid adsorbents can effectively remove pollutants from both aqueous and gaseous streams and therefore has considerable environmental significance. Activated carbon, the most popular adsorbent, has been traditionally used for the removal of odour, taste and colours, which are designated as trace pollutants. Its high adsorptive capacity and versatility have expanded its application to the treatment of numerous industrial waste streams. Other commercial adsorbents having increased reversibility, have been recently reviewed and although their versatility and adsorptive capacity are generally less than those of activated carbon, they are advantageous for certain applications. Such low cost adsorbents have found use in laboratory scale for treatment of various pollutants from water and wastewater (Sharma and Bhattacharya, 2005).

2.4.2.2 Biosorption

Generally, polluted wastewaters with heavy metals were treated by chemical processes such as precipitation, electrochemical treatment and ion exchange. These processes only can treat portion of heavy metals of wastewater. So, it will be very expensive when concentration of heavy metals is low. Therefore use of biological processes may be economical and effective as alternatives for the removal of heavy metals (Leung and Wong, 2000).

The biosorption process involves a solid phase (sorber or biosorber; usually a biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, a metal ion). Due to the affinity of the sorber for the sorbate species, the later is attracted and bound with different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion that remains in the solution. While there is a preponderance of solute (sorbate) molecules in the solution, there are none in the sorber particle to start with. This imbalance between the two environments creates a driving force for the solute species. The heavy metals adsorb on the surface of biomass and thus, the biosorber becomes enriched with metal ions in sorbate (Alluri *et al.*, 2007).

Biomass can come from activated sludge or fermentation waste from industries like those of food, dairy and starch. Also, organisms (eg. bacteria, yeast, fungi and algae) coming from their natural habitats are good sources of biomass. Fast growing organisms that are specifically cultivated for biosorption purposes (eg. crab shells, seaweeds) can be used as biosorbents (Regine and Volesky, 2000). Apart from the microbial sources, even agricultural products such as wool, rice, straw, coconut husks, peat moss, exhausted coffee (Dakiky *et al.*, 2002) waste tea (Ahluwalia and Goyal, 2005), walnut skin, coconut fiber, cork biomass (Chubar *et al.*, 2003) seeds of *Ocimum basilicum* (Melo and D'Souza, 2004), defatted rice bran, rice hulls, soybean hulls and cotton seed hulls (Teixeria *et al.*, 2004), wheat bran, hardwood (*Dalbergia sissoo*) saw dust, pea pod, cotton and mustard seed cakes (Saeed *et al.*, 2002) also have proved as good biomass sources.

However, seaweeds, moulds, yeasts and bacteria have been tested for metal biosorption with encouraging results (Regine and Volesky, 2000).

2.4.2.2.1 Adsorption by microbes

Biosorption is a promising alternative, which utilizes inactive or dead biomass to bind and concentrate heavy metals from the aqueous solutions. Different types of biomaterials have shown different levels of metal uptake. Among the most promising biomaterials studied is algal biomass (Singh, 2007).

Seaweeds are large group of marine benthic algae. They offer several advantages for biosorption because of their larger surface area. This feature offers a convenient basis for the production of biosorbent particles suitable for sorption process. They contain many polyfunctional metal-binding sites for both cationic and anionic metal complexes. Potential metal cation binding sites of algal cell components include carboxyl, amine, imidazole, phosphate, sulphate, sulfhydryl, hydroxyl and chemical functional groups contained in cell proteins and sugars (Crist *et al.*, 1981). Brown algae stand out as very good biosorbent of heavy metals (Romero *et al.*, 2006).

Saccharomyces cerevisiae was found to remove toxic metals, recover precious metals and clean radio-nucleotides from aqueous solutions to various extents. *S. cerevisiae* is a product of many single cell and alcohol fermentations; it can be procured in large quantity at low cost. *Saccharomyces* has the ability to differentiate between different metals such as selenium, antimony and mercury based on their toxicity. This property

makes *S. cerevisiae* useful in analytical measurements (Wang and Chen, 2006).

2.4.2.2.2 Adsorption by indigenous materials

The need for economical and effective methods of removing heavy metals from wastewater has resulted in the search for unconventional materials that may be useful in reducing the levels of accumulation of heavy metals in the environment (Egwaikhide *et al.*, 2002).

Biosorption of heavy metals from aqueous solutions is a relatively new technology for the treatment of industrial wastewater. Adsorbent materials derived from low cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from wastewater streams. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials (Qaiser *et al.*, 2007).

In recent years, researches in the removal of heavy metal ions have focused more on new technologies rather than traditional methods, which are expensive and often inefficient. The need for economical, effective, and safe methods of removal of heavy metal ions from water has resulted in the search for many unconventional materials that might be useful for that purpose. It is advisable that the adsorbents for the removal of heavy metals are locally available in large quantities, are cheap and easy to regenerate. It was established that the different lignocellulosic waste materials have good adsorption characteristics for heavy metals (Lee and Rowell, 2004).

An emerging field of interest is employing agricultural by products as adsorbents for the removal of heavy metals from aqueous solutions. Many agricultural wastes that are available at low cost have been reported to be capable of removing substantial amounts of metal ions from aqueous solutions (Igwe *et al.*, 2005).

Many types of low cost agricultural wastes such as apple waste (Lee and Yang, 1997), peanut hull pellet (Johnson *et al.*, 2002), olive pomace (Pagnanelli *et al.*, 2003), banana pith (Low *et al.*, 1995), sawdust (Larous *et al.*, 2005), wheat shell (Basci *et al.*, 2004), wheat bran (Farajzadeh and Monji, 2004), carrot residue (Nasernejad *et al.*, 2005), sugar beet pulp (Aksu and Isoglu, 2005), oil palm fiber (Low *et al.*, 1993), mustard oil cake (Ajmal *et al.*, 2005) and grape stalk waste (Villaescusa *et al.*, 2004) have been used as sorbents for heavy metal removal from wastewater in recent years. For improving the physicochemical properties or sorption capacity of agricultural wastes various chemical modifications were employed (Shukla *et al.*, 2006).

There are several surveys conducted to initiate and test low cost and efficient materials such as removal of iron from ground water by ash, multi component adsorption of silver, cadmium and copper by natural carbonaceous materials and adsorption of metal ions on lignin (Hanzlik *et al.*, 2004; Guo *et al.*, 2008).

In recent years, considerable attention has been focused on the removal of organic and inorganic compounds from aqueous solutions using adsorbents derived from low cost materials. Several adsorbents, such as clay

minerals (Onkal-Engin *et al.*, 2000; Bektas and Kara, 2004), sewage sludge ash (Pan *et al.*, 2003), anatase-type titanium dioxide (Kim *et al.*, 2003), olive mill residues (Veglio *et al.*, 2003), various industrial solid wastes (Agarwal *et al.*, 2004), inorganic colloids (Subramaniam and Yiaccoumi, 2001), functionalized silica, red mud and fly ash (Bois *et al.*, 2003), paper mill sludge (Calace *et al.*, 2000) and activated carbon (Goyal *et al.*, 2001; Monser and Adhoum, 2002) have been used for the treatment of Cu (II) rich effluents at the solid solution interface.

Sugarcane bagasse has proved to be an effective adsorbent for certain heavy metals (Rao *et al.*, 2002; Syna and Valix, 2003). Sugarcane bagasse, a by product of cane sugar processing industry is generated in huge quantities in Asian countries. About 54 million ton of bagasse is produced annually throughout the world. Bagasse was used previously as a fuel for boilers by the sugar factory or as raw material for the manufacturing of pulp and paper products, various types of building boards and certain chemicals (Garg *et al.*, 2007).

2.5 Adsorption isotherms

The Langmuir isotherms

Sorption uptake at different metal concentrations is normally represented by isotherm equilibrium models. The most well known ones are the Langmuir and the Freundlich models. The linearized form of Langmuir isotherm model can be written as

$$1/q = (b/q_m)1/c + 1/q_m$$

where q (mg Cu/mg sorbent) is metal uptake on the day at the equilibrium metal concentrations C (mg/l); q_m (mg Cu/mg sorbent)

represents the maximum sorbent capacity and b is related to the energy of adsorption.

The parameters can be obtained from the experimental data by plotting $1/q$ versus $1/c$; the intercept and the slope of the resultant straight line can be used for the determination of q_m and b respectively (Al-Asheh *et al.*, 2002).

The Freundlich isotherms

The Freundlich isotherm, which is an empirical model based on sorption onto a heterogeneous surface, can be written in linearized form as:

$$\ln q = \ln K_f + (1/n) \ln C$$

where K_f is responsible for the relative maximum sorption of the sorbent and $1/n$ is related to the sorption intensity. These parameters are obtained by blotting $\ln q$ versus $\ln C$; the intercept and the slope of the resultant straight line can be used for the determination of K_f and $1/n$ respectively (Al-Asheh *et al.*, 2002).