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# A Review of Potentially Low Cost Sorbents for Heavy Metal Removal and Recovery

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## ABSTRACT

The incidence of toxic substances in the environment has increased as a result of industrialization. These toxic substances are mostly found in wastewater effluents. Heavy metals are one group of these toxic substances, whose toxicity to both man and the environment has been on the increase. The environmentally adverse effects of heavy metal toxicity are so much that their removal and recovery have become very important. Many conventional methods of heavy metal removal from aqueous streams have been used, including: Precipitation, ion exchange, coagulation, reverse osmosis, adsorption, among others. These conventional methods are very expensive and sometimes generate effluent sludge, which causes more disposal problems. Bioremediation of these heavy metals using low cost biosorbents have been in focus recently. These consist of a group of applications, which involve the detoxification of hazardous substances by means of microbes and plants, instead of transferring them from one medium to another. This process is characterized as less disruptive and can often be carried out on site, eliminating the need to transport the toxic materials to treatment sites. Biosorbents are prepared from naturally abundant and/or waste biomass. Due to the high uptake capacity and cost effective source of the raw materials, biosorption is a progression towards a perspective method. Therefore, this paper reviews the toxicity of heavy metals and the use of potentially low cost sorbents for their removal. The removal efficiency of these heavy metals using biosorbents compares favourably with conventional adsorbents based on certain sorption parameters, hence making biosorbents a viable alternative for metal removal and recovery.

**Keywords:** biosorbents, detoxification, environment, wastewater

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## INTRODUCTION

The presence of heavy metals in the environment is of major concern because of their toxicity and the threat to human life and the environment. As a result of the proliferation of industries, development in technology and urbanization, the input of these heavy metals into the environment has been on the increase. Although metals are released into the environment by natural sources such as volcanic eruptions, the inputs by anthropogenic sources of heavy metals are much more. These anthropogenic sources may include wastes from electroplating and metal finishing industries, metallurgical industries, tannery operations, chemical manufacturing, leather tanning industries, fertilizer industries, pigment manufacturing industries, leachates from land fills and contaminated ground water from hazardous waste sites (Haung and Fu 1984; Jackson and Alloway 1991; Reed *et al*. 1994; McLaughlin *et al*. 1996; Faisal and Hasnain 2004). Heavy metals are also emitted from resource recovery plants in relatively high levels on fly ash particles (Neal *et al*. 1990).

These toxic metal compounds coming to the earth's surface not only reach the earth's waters (seas, lakes, ponds and reservoirs), but can also contaminate underground water in trace amounts by leaking from the soil after rain and snow (Uzun and Guzel 2000). Therefore, the earth's waters may contain various toxic metals. Drinking water is obtained from springs, which may be contaminated by various toxic metals. One of the most important problems is the accumulation of toxic metals in food structures (Uzun and Guzel 2000). As a result of accumulation, the concentrations of metals can be more than those in water and air. The contaminated food can cause poisoning in humans and animals. Although some heavy metals are essential for the growth of plants, after certain concentrations heavy metals become poisonous for both plants and heavy metal organisms (Uzun and Guzel 2000). These include those organisms that naturally contain heavy metals, which are beneficial to them at certain lower concentrations.

Also, Uzun and Guzel (2000) reported that another important risk concerning contamination is the accumulation of these substances in the soil in the long term. Heavy me-

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tals are held in soil as a result of adsorption, chemical reaction and ion exchange of soil. Heavy metals have an effect on enzymes. It has been determined that various metal ions hinder various enzymes responsible for mineralization of organic compounds in the earth (Uzun and Guzel 2000). Therefore, studies on the removal of heavy metal pollution are increasing.

The treatment of aqueous wastes containing soluble heavy metal ions requires the concentration of metal ions followed by recovery for secure disposal (Qadeer and Akhtar 2005). Many techniques such as chemical precipitation, ion exchange, reverse osmosis, solvent extraction and adsorption are used for wastewater treatment, that is, removal of metal ions (Qadeer and Akhtar 2005). The adsorption techniques, both bio and chemical adsorption, has a definite edge over the other techniques (Volesky 1994). The adsorbent used is a material containing organic carbon such as activated carbon, charcoal, lignite, wood bark and many inorganic chemicals and clay. Therefore, the focus of this article is to review the conventional methods of heavy metal removal, the disadvantages of these conventional methods and the need for the search for potentially low cost adsorbents for metal removal. Also, the effectiveness of low cost agricultural by-products is compared with that of conventional adsorbents.

## HEAVY METAL TOXICITY

Heavy metals are defined simply as those metals with high densities. The transition elements may be strictly defined as those elements that have partly filled d or f shells in any of their commonly occurring oxidation states (Cotton and Wilkinson 1985). By virtue of the fact that none of the transition elements has more than two electrons in the outermost principal quantum level of its atoms, all transition elements have a surplus of outer vacancies over electrons and therefore exhibit typical properties of the metallic state. Their metallic bonding is much stronger than that of any major group metal and on the average considerably stronger than that of the inner transition metals. They are called transition elements because they separate the more s-filled orbital from the more electronegative elements and have, with few exceptions, an $(n\text{-}1)^{2s}$ $(n\text{-}1)^{6p}$ $(n\text{-}1)$ $d^{1\text{-}9}$ $ns^2$ outer configuration.

Heavy metal salts in solution may constitute a very serious form of pollution because they are stable compounds, not readily removed by oxidation, precipitation or any other natural process. A characteristic feature of heavy metal pollution is its persistence for years after the pollution operations have ceased. Elements in every group of the periodic table have been found to be stimulatory to animals (that is, it makes certain part of their body function) (Ho *et al.* 2002). Most metals in the fourth period are carcinogenic. It can be assumed that the carcinogenicity is related to the electronic structure of transition and inner transitional metals (Lucky and Venugopal 1977).

The elemental form of cadmium is insoluble in water. Cadmium is found in seawater at a level of less than 0.08 mg/l. Its level in marine plants is approximately 0.4 mg/l, while in marine animals a range of 0.15 to 3.0 mg/l has been found. Cadmium is moderately toxic to all organisms and it is a cumulative poison in mammals (Klaassen, 2001). Atmospheric, terrestrial and aquatic sources are considered as the exposure routes of humans to cadmium (Lopez *et al.* 1994; Wolnik *et al.* 1995). The disease of "itai-itai" characterized by excruciating pain in the bone has been reported as the most severe form of cadmium toxicity in humans (Kasuya *et al.* 1992; Yasuda *et al.* 1995). In humans, kidney dysfunction, hepatic damage and hypertension have been reported as other health implications of cadmium (Klaassen 2001). Also, it has been shown that zinc and copper competitively inhibit cadmium uptake by cells (Endo *et al.* 1996) and that the overall nutritional status (rather than mere cadmium content of food) is a more critical factor in determining cadmium exposure (Vahter *et al.* 1996).

Lead is found as a local pollutant of rivers near mines and from the combustion of leaded gasoline. The effects of lead on neurobehavioral development (Dietrich *et al.* 1990), and brain cell function (Goldstein 1990) have been investigated. The accumulation of lead in riverbeds especially in India and Bangladesh (Saikia *et al.* 1987) has been detected and gives cause for concern (Ho and McKay 1999). Copper has been reported as one of the most widely used heavy metals in electrical and electroplating industries (Igwe and Abia 2006). Since copper is an essential metal in a number of enzymes for all forms of life, problems arise when it is deficient or in excess (Ho *et al.* 2002). Excess copper accumulates in the liver, brain, skin, pancreas and myocardium (Davis *et al.* 2000), and the most toxic form of copper is thought to be $Cu^+$ (Ho *et al.* 2002). Its toxicity is highly pH dependent and it has been reported to be more toxic to fish at lower pH values (Sharma *et al.* 1992).

Chromium is a common pollutant introduced into natural waters from a variety of industrial wastewaters including those from the textile dyeing, leather tanning, electroplating and metal finishing industries (Faisal and Hasnain 2004; Ahalya *et al.* 2005). It exists in several oxidation states. The most stable and common forms are the trivalent Cr (III) and the hexavalent Cr (VI) species, which display quite contrasting chemical properties such as toxicities, mobility and bioavailability (Saifuddin and Kumaran 2004). Cr (VI) considered to be the most toxic of chromium is readily mobile, a strong oxidizing agent and capable of being absorbed through the skin (Park and Jung 2001). It is usually associated with oxygen as chromate ($CrO_4^{2-}$) or dichromate ($Cr_2O_7^{2-}$) ions depending on chromium concentration and pH (Udaybhaskar *et al.* 1990). The hexavalent form of chromium is considered to be a group "A" human carcinogen (Cieslak-Golonka 1996) because of its mutagenic (Cheng and Dixon 1998), carcinogenic (Shumila *et al.* 1999) and terartogenic (Asmatullah *et al.* 1998) properties. Whereas, Cr (VI) is the toxic form of chromium released during many industrial activities, Cr (III) is an essential element required for normal carbohydrate and lipid metabolism (Mertz 1993; Anderson 1998).

Mercury in the liquid form is not dangerous and it is used in a number of industries, but in the vapour form it becomes very poisonous. Arsenic occurs mainly as As(III) and As(V). The occurrences, chemistry and toxicity of arsenic have been well documented (Sadiq *et al.* 1983; Chakrabarty and Saha 1987; Namasivayam and Senthilkumar 1998; Igwe and Abia 2006).

Therefore, it is obvious that these metals have caused, and are still causing a lot of damage to the environment. This has lead to the emergence of more stringent environmental protection acts, hence, arose the need for treatment and removal methods for these metals from metal-bearing wastewater before discharge.

## SEPARATION METHODS

Several physico-chemical methods have been used to selectively collect and/or concentrate heavy metals in solution. This methods have consequently been applied in separation or purification processes. Some of these methods include distillation, reverse osmosis, electro-deposition, ion exchange, solvent extraction and pH adjustment.

Distillation is based on the difference in the boiling point of the components. For water, most of its impurities have boiling points above 100°C, which is the boiling point of water. During distillation, pure water vapourises at 100°C, is condensed and collected leaving impurities behind. This method is the standard laboratory technique. The problem associated with using this technique in wastewater treatment is that it usually requires too much energy for it to compete favourably with other methods.

Reverse osmosis, also called ultra filtration, is a process of removing ionic and molecular species whose diameters are higher than that of a water molecule (Igwe 2002). An osmosis membrane is made use of in this technique and they usually have pore sizes, which are very small, of the order of diameters <20Å, called micro pores (Srivastava *et al*. 2006). Cellulose acetate and cellulose xanthate are examples of osmotic membranes. Normally, water molecules pass through the membrane, hence filtration. But since there is a greater tendency for dilution, pressure has to be applied to counter this tendency for dilution. The minimum pressure necessary to act against this tendency is the osmotic pressure π given by

$$\pi = nRT/V = MRT \qquad (1)$$

where M is the number of moles of solutes per litre of the solution above the membrane, R is the gas constant and T is the system temperature. The problems encountered here, is that very high pressures of the order of 200 atmospheres are required to reverse the normal osmotic pressure and it is difficult to support the rather fragile membrane so that it does not break in the process.

If the heavy metal to be recovered is valuable, electrodeposition techniques could be used to obtain it in a pure form. The dilute solution is concentrated by evaporation and placed in an electrolytic cell. Depending on the different potentials, different metals will deposit at the cathode. An insoluble material such as graphite is used as the anode of such cells.

Ion exchange materials are also called resins, and these are insoluble substances containing ions, which are capable of replacement by ions from a solution containing electrolytes (Vogel 1978; Mendham *et al*. 2004). There are both cationic and anionic exchange resins. When heavy metal ions in solution come in contact with a cationic exchange resin, some of the hydrogen ions will go into solution having been replaced by the heavy metal ions. However, it is necessary that before the exchange reaction, that the resin be loaded with hydrogen ions by running a strong acid over it. The exchange reaction is as follows:

$$n\ \text{Resin-H}^+ + M^{n+}(aq) \rightleftharpoons (\text{resin})\text{-}nM^{n+} + nH^+(aq) \qquad (2)$$

Ion exchangers are extremely efficient water purifiers, but they are also very expensive, especially when there is much wastewater to be treated.

In solvent extraction the metal ions are converted into chelates by treatment with suitable organic reagents called ligands. The resulting complexes are soluble in organic solvents and can thus be extracted from the aqueous solution. With this technique, metals can be systematically sequestered into the organic phase and removed from water. Acetylacetone, ethylene diaminetetractic acid (EDTA), 8-hydroxyquinoline (or oxine) are common chelating agents. However, the application of solvent extraction is restricted to small systems since the method is expensive.

Adjustment of the pH of a solution containing heavy metals can be used to selectively collect or concentrate such metals. Many of the hydroxides of these metals are insoluble; therefore appropriate pH adjustment can cause them to precipitate. Materials often used for this purpose are lime or limestone. Some of the common metal ions will precipitate at pH values as given in **Table 1** (Igwe 2002). However, there are two main problems associated with hydroxide precipitation: (i) it is difficult to separate the metals if recycling is desirable; (ii) many metal hydroxides are flocculent and extremely hydrophilic, hence making complete removal of water more difficult.

Several other conventional methods exist for the removal of heavy metals from aqueous solutions. Most of these like the ones discussed above have one disadvantage or another ranging from sludge formation to the expensive nature of the process. Also, Volesky (1990) reported that these methods are inefficient for metal removal from diluted solutions containing from 1 to 100 mg/L of dissolved metal. As a result of these shortcomings of conventional methods, the toxicity and bioaccumulation of heavy metals, the search for less expensive methods of metal removal became very important. Hence, the adsorptive removal of metal ions became preferable and popular.

**Table 1** pH at which metals precipitate.

| Metal | pH | Metal | pH |
|---|---|---|---|
| $Fe^{3+}$ | 2.0 | $Ni^{2+}$ | 6.7 |
| $Al^{3+}$ | 4.1 | $Cd^{2+}$ | 6.7 |
| $Cr^{3+}$ | 5.3 | $Zn^{2+}$ | 6.7 |
| $Cu^{2+}$ | 5.3 | $Co^{2+}$ | 6.9 |
| $Fe^{2+}$ | 5.3 | $Hg^{2+}$ | 7.3 |
| $Pb^{2+}$ | 6.0 | $Mn^{2+}$ | 8.5 |

Source: Igwe 2002

## ADSORPTION PROCESS

Adsorption has been widely employed in separation science. The adsorption of reaction species plays a vital role in catalytic processes (Vasant and Mukund 1999). Adsorption simply is the ability to adhere or attach to a substance. It has been used to remove dilute pollutants as well as to recover valuable products from aqueous streams. The use of activated carbon, zeolite and active alumina in the adsorption process is referred to as conventional adsorption. In conventional adsorption, the particle size of the adsorbent is restricted because of hydrodynamic phenomena such as a pressure drop (Lin and Liu 2000).

Adsorption can be classified into two based mainly on the energy of adsorption. One is due to forces of a physical nature called van der Waal's force. These are relatively weak and play an unimportant part in connection with surface reactions (except for certain atomic processes), because they are not sufficiently strong to influence appreciably the reactivity of the molecule adsorbed. The second type is considerably stronger; heat evolved is higher and known as chemisorption as compared to physiosorption (Motoyuki 1990). Physical adsorption is non-specific, rapid and reversible. The adsorbents are being held at the interface by van der Waals interaction (for instance dispersion of polar interactions). This is a long range but weak interaction and the amount of energy released when a molecule is physiosorbed is of the order of the enthalpy of condensation. The heat evolved in the physiosorption can be determined by measuring the rise in temperature and enthalpy changes of less than 40 $Kjmol^{-1}$ are often observed. These energies are insufficient to lead to bond breaking and so in physiosorption the molecules retain its identity although it might be stretched or bent on account of the proximity of the surface (Gregg and Sing 1984). A physiosorbed molecule vibrates and because the binding energy is low it may shake itself on the surface. This suggests that a molecule remains on the surface for only a short time. Physiosorption is appreciable only at temperature below the boiling point of the adsorbate and a multiplayer normally occurs (Namasivayam *et al*. 1996). On the other hand, chemisorption is simply the formation of a two-dimensional compound. The molecules stick to the surface as a result of the formation of a chemical and usually a covalent bond. It can occur at high temperatures and the energy of attachment is very much greater than in physiosorption and typical values are in the region of 200 $Kjmol^{-1}$. The large heat of adsorption can be explained by the chemical nature of the interaction between the adsorbent and the adsorbed molecules. Chemical adsorption is highly specific in nature and depends on the chemical properties of both the surface molecules and the adsorbed molecules. A molecule undergoing chemisorptions may be turn apart at the demand of the unsatisfied valences of the surface atoms and so it may also lose its identity. In fact, the extension of molecular fragments on the surface as a result of chemisorption of whole molecule is one of the reasons why surfaces can exhibit catalytic activity (Gregg and Sing 1984; Namasivayam *et al*. 1996).

Also, the adsorption process can be classified into two based on the type of process taking place and also based on the phases of the components involved. The first classifica-

**Table 2** Conventional adsorbents used in heavy metal removal from aqueous solution.

| Adsorbent | Adsorbate | Source of pollutants | References |
|---|---|---|---|
| Commercial granular activated carbon | Hg (II) | Metal solution | Namasivayam and Periasamy 1993 |
| | Cd (II) | Wastewater | Periasamy and Namasivayam 1994 |
| | Pb (II) | Metal solution | Periasamy and Namasivayam 1995a |
| | Ni (II) | Metal solution and nickel plating wastewater | Periasamy and Namasivayam 1995b |
| | Cu (II) | Metal solution and nickel plating wastewater | Periasamy and Namasivayam 1996 |
| $Bi_2O_3$ | Cr (VI) | Metal solution | Bhutani and Kumari 1994 |
| Hydrous zirconium oxide | Hg (II) | Metal solution | Mishra *et al.* 1996 |
| Lanthanum-impregnated silica gel | F and P; As (V) | Aqueous solution | Wasay *et al.* 1996a |
| Basic yttrium carbonate | As (III); As (V) | Aqueous solution | Wasay *et al.* 1996b |
| Activated alumina | As | Metal solution | Gupta and Chen 1978 |
| Activated bauxite | As | Metal solution | Gupta and Chen 1978 |
| Activated carbon | As | Metal solution | Gupta and Chen 1978 |
| | Mn (II), Fe (II), Ni (II), Cu (II) | Aqueous solution | Uzun and Guzel 2000 |
| Activated alumina | Inorganic arsenic | Aqueous solution | Ghosh and Yuan 1987 |
| Activated carbon | Cu (II) and humic acid | Aqueous solution | Chen and Wu 2004 |
| Granular activated carbon | Cr (VI) | Aqueous solution | Sharma and Forster 1996 |
| Activated carbon and zirconium-loaded activated carbon | Arsenic | Wastewater | Birgit *et al.* 2004 |
| Active carbon | Pb (II) | Aqueous solution | Qadeer and Akhtar 2005 |
| Hydrogen peroxide | Heavy metals | Wastewater | Badmus *et al.* 2007 |

tion is monolayer coverage and multilayer coverage. Monolayer depicts saturation after a single layer has been adsorbed while multilayer shows several layers of adsorbate on top of the one originally adsorbed. The other classification is either homogeneous or heterogeneous adsorption process. Furthermore, the adsorption process could be classified into conventional and non-conventional depending on the type of adsorbents used.

The conventional adsorbents that have been in use are activated carbon, silica gel, active alumina, zeolite and metal oxides. **Table 2** shows a list of some of the conventional adsorbents that have been reported in the literature and the heavy metals removed. Generally, these adsorbents possess the characteristics of a very large surface area and polarity. Thus, a large specific surface area is preferable for providing a large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small-sized pores between adsorption surfaces. These small-sized pores are known as micro pores and these determine the accessibility of adsorbate molecules to the adsorption surface. Therefore, the pore size distribution of a micropore is another important property for characterizing the adsorptivity of these adsorbents (Motoyuki 1990). Therefore, generally, adsorbents are characterized in terms of some physical properties such as packing density, surface area, micropore and mesopore volumes and pore half-width (Ali *et al.* 1998).

The non-conventional adsorbents, also called low cost agricultural or biological by-products, are those adsorbents that were not regularly in use but are being developed for adsorption processes because of a need. Most of these non-conventional adsorbents are development from locally available and cheap materials. Also, at times they are developed from wastes, which ordinarily would have been a problem to the environment in terms of pollution. **Table 3** shows a list of these potential low cost sorbents and their sorbates used in bioremediation. Algal, fungi and bacteria biomass have also been utilized.

## BIOSORPTION OR BIOSEPARATION PROCESS

The use of potentially low cost biological or agricultural by-product biomass in the removal of heavy metals has been termed biosorption, bioseparation or bioremediation. These consist of a group of applications, which involve the detoxification of hazardous substances by means of microbes and plants, instead of transferring them from one medium to another. This process in characterized as less disruptive and can be often carried out on site, eliminating the need to transport the toxic materials to treatment sites (Gavrilescu 2004). As a result of the high uptake capacity and very cost-effective source of the raw material, biosorption is a progression towards a perspective method. Various biomaterials have been examined for their biosorptive properties and different types of biomass (**Table 3**), have shown levels of metals uptake high enough to warrant further research (Volesky and Holan 1995).

The mechanism by which microorganisms remove metals from solutions have been reported as: (i) extra cellular accumulation/precipitation; (ii) cell-surface sorption or complexation and (iii) intracellular accumulation (Muraleedharan *et al.* 1991). Among these mechanisms, using viable microorganisms, cell-surface sorption, may facilitate extra cellular accumulation/precipitation or complexation can occur with live or dead microorganisms, while intracellular accumulation requires microbial activity (Asku *et al.* 1991). Cheng and Yang (2005) reported that marine algae have rich contents of polysaccharides in the cell wall, which are mainly responsible for higher metal biosorption. Several important functional groups such as carboxyl, sulphate and amino have been identified in marine algae (Lodeiro *et al.* 2004; Raize *et al.* 2004). Few key chemical interactions, including ion exchange, surface complex formation, micro-precipitation, chelation and coordination, are used to explain the biosorption mechanisms.

Tree fern has been reported as an agricultural by-product and has been defined as a complex material containing lignin and cellulose as major constituents (Newman 1997), just like other agricultural by-products, maize cob, cocoa pod husk, etc., as listed in **Table 3**. Chemical sorption can occur by the polar functional groups of lignin, which include alcohols, aldehydes, ketones, acids, phenolic, hydroxides and ethers as chemical bonding agents (Adler and Lundquist 1963). It was therefore, concluded that tree fern can be a suitable sorbate for the sorption of metal cation because of its polar and acid characters (Ho 2003). By extension, this argument could be said to hold for other agricultural by-products. Also, Gang and Weixing (1998) reported that the mode of sorption on agricultural by-products could be attributed to two main terms, intrinsic adsorption and columbic interaction. While columbic interaction results from the electrostatic energy of interactions between the adsorbents and adsorbates, the intrinsic adsorption is determined by the surface area of the adsorbents as observed by the effect of different sizes of adsorbent on adsorption capacity (Igwe and Abia 2003). Thus, because the modes of sorption on conventional adsorbents are the same as those of agricultural by-products, then the latter is a potential and good adsorbent for metal sequestration. Also, a comparison of the sorption capacity of conventional and

**Table 3** Low cost potential agricultural or biological by-products used in bioremediation.

| **Adsorbent** | **Heavy metal** | **Sources of pollutants** | **Reference** |
|---|---|---|---|
| *Pseudomonas aeruginosa* | Hg (II) | Metal ion solution | Chang and Hong 1994 |
| *Penicillin biomass* | Pb (II) | Aqueous solution | Niu *et al.* 1993 |
| *Thiobbacillus thiooxidans* | Zn (II), Cu (II) | Metal ion solution | Liu *et al.* 2004 |
| *Rhizopus arrhizus* | (a) Cu (II) | Metal ion solution | Rome *et al.* 1987 |
| | (b) Cr (VI) | | Niyogi *et al.* 1998 |
| *Cladosponium resinae* | Cu (II) | Metal ion solution | Rome *et al.* 1987 |
| *Penicillinium italicum* | Cu (II) | Metal ion solution | Rome *et al.* 1987 |
| Waste tea leaves | Pb (II), Cd (II), Zn (II) | Metal ion solution | Tan *et al.* 1988 |
| Spent grain | Cd (II), Pb (II) | Aqueous solution | Low *et al.* 2000 |
| *Candida vulgaris* | Cd (II) | Aqueous solution | Aksu 2001 |
| Tree fern | (a) Cu (II) | Aqueous solution | Ho 2003 |
| | (b) Zn (II), Cu(II), Pb (II) | | Ho *et al.* 2002 |
| | (c) Cd (II) | | Ho and Wang 2004 |
| Pine bark | Cd (II) | Wastewater | Al-Asheh and Duvnjak 1997 |
| Banana pith | Metal ions | Electroplating waste | Low *et al.* 1995 |
| Peanut shells | Metal ions | Wastewater | Wafwoyo *et al.* 1999 |
| Hazelnut shell | Cr (VI) | Wastewater | Ciminon *et al.* 2000 |
| Rice (Jaya) husk | Zn (II) | Aqueous solution | Mishra *et al.* 1997 |
| Saw dust | (a) Pb (II),Cu (II) | Aqueous solution | Yu *et al.* 2001 |
| | (b) Hg (II), Ni (II), Pb (II) | | Igwe *et al.* 2006 |
| | (c) Cu (II) | | Valshya and Prasad 1991 |
| | (d) As (V) | | Igwe and Abia 2007b |
| *Tamrix gallica* leaves | Cu (II) | Aqueous solution | Zaggout 2001 |
| *Sphagnum Peat moss* | Pb (II) | Aqueous solution | Allen *et al.* 1992; Ho *et al.* 1996; Ho and Mckay 1999 |
| *Eichornia crassipes* | Pb (II) | Aqueous solution | Heaton *et al.* 1986 |
| Marine algae | (a) Pb (II), Ni (II) | Wastewater | Holan and Volesky 1994 |
| | (b) Pb (II) | | Jalali *et al.* 1995 |
| Chemically reinforced biomass of marine algae | Cd, Cu, Ni, Pb, Zn | Aqueous solution | Leusch *et al.* 1995 |
| Pseudomonas aeruginosa PUZI | Pb, Cu, Cd | Aqueous solution | Chang *et al.* 1997 |
| Fly ash | Cu (II) | Aqueous solution | Panday *et al.* 1985 |
| Peanut Hulls | Ni (II), Cu (II) | Aqueous solution | Randall *et al.* 1994; Periasamy and Namasivayam 1995, 1996 |
| Coconut husk | As | Aqueous solution | Manju *et al.* 1998; Igwe and Abia 2006, 2007a |
| Oil palm fiber | Cu (II), Ni (II), Pb (II) | Metal ion solution | Low *et al.* 1993; Abia and Asuquo 2006 |
| Maize cob and husk | Cd, Pb, Zn | Aqueous solution | Igwe and Abia 2003, 2005, 2007b |
| Sunflower stalks | Cu (II), Zn (II), Cd (II), Cr (III) | Aqueous solution | Gang and Weixing 1998 |
| Groundnut husk | Cd, Pb | Aqueous solution | Okieimen *et al.* 1991 |
| Bengal husk (*Cicer arientinum*) | Cr (VI) | Aqueous solution | Ahalya *et al.* 2005 |
| *Pinus sylvestris* | Cr (VI) | Aqueous solution | Ucun *et al.* 2002 |
| Cassava waste biomass | Cd (II), Zn (II), Cu (II) | Aqueous solution | Abia *et al.* 2003; Horsfall and Abia 2003; Horsfall *et al.* 2004 |
| Shea butter seed husk | Fe, Zn, Pb | Aqueous solution | Eromosele and Otitolaye 1994 |
| *Medicago sativa* (alfalfa) | Cd, Cr, Pb, Zn | Aqueous solution | Gardea-Torresday *et al.* 1998 |
| Chitosan | Au (III) | Aqueous solution | Ngah and Liang 1999 |
| Sugar beat pulp | Cr (II), Cr (VI) | Metal ion solution | Reddad *et al.* 2003 |
| Sago waste | Pb (II), Cu (II) | Aqueous solution | Quek *et al.* 1998 |
| *Zoogloea ramigera* | Metal ions | Metal ion solution | Sag and Kutsal 1995 |
| Pumpkin seed husk | Zn (II), Ni (II) | Aqueous solution | Ikhuoria and Omonmhenle 2006 |
| Melon seed husk | Pb (II) | Aqueous solution | Okieimen *et al.* 1986 |
| Maize leaf | Pb (II) | Aqueous solution | Babarinde *et al.* 2006 |

non-conventional adsorbents will show their potential as low cost adsorbents for metal removal and recovery.

## SORPTION PARAMETERS

In water and wastewater treatment systems, the sorption of metal ions from aqueous solution plays an important role. One advantage of sorption treatment over the other treatment methods is that it eliminates the need for huge sludge-handling processes (Ho and McKay 1999). The sorption of metal ions on low-cost agricultural sorbents is usually evaluated based on certain sorption parameters such as sorption capacity and sorption isotherm, sorption kinetics and intraparticulate diffusivity. The results obtained based on these parameters are useful in determining the maximum sorption capacity, the rate at which the sorption process takes place, the mechanism of the sorption process, among other things.

Again, the use of low cost agricultural sorbents for heavy metal removal have been studied varying mainly initial concentration of metal ion solution or wastewater (Ho *et al.* 2002; Igwe and Abia 2007a), agitation time (Abia and Asuquo 2006; Ho 2004), weight of adsorbent used (Saifuddin and Kumaran 2005), pH of metal ion solution or wastewater (Horsfall and Spiff 2004b; Igwe *et al.* 2005), temperature of metal ion solution or wastewater (Horsfall *et al.* 2004b), and agitation speed of reaction. Another advantage of using low cost agricultural sorbents is their ability to remove metal ion concentrations as low as <100 mg/L (Volesky and Holan 1995). Majority of the research on the use of low cost biological or agricultural by-products were carried out in the laboratory using synthetic wastewater solutions (metal ion solutions) though a few of them have been done on real wastewater from industries (Low *et al.* 1995; Al-Asheh and Duvnjak 1997; Wafwoyo *et al.* 1999; Ciminon *et al.* 2000).

Also, the surface characteristics of the adsorbent have been modified with a view to increasing the sorption capabilities of the adsorbents. The modification methods that have been used include; mercaptoacetic acid (MAA) modification of cassava waste (Horsfall *et al.* 2004), EDTA modification of maize cob (Abia *et al*. 2005), thiolated and carboxymethylated modification of sawdust (Igwe *et al*. 2006), gluteraldehyde, formaldehyde, NaOH, HCl and $CaCl_2$ (Cheng and Yang 2005) and so on. In most of these studies, it was found out that the modification methods enhanced the amount of the metal ions adsorbed. Therefore, as long as the modification methods do not result to the introduction of recalcitrant products into the environment, it is a good improvement. The opinion here is that the recycling of the modified used adsorbents should be investigated for an improved application of these adsorbents. This is a very good area of research. Generally, the results obtained from these laboratory investigations have helped in the design of an adsorber for heavy metal removal (Ho and McKay 1999) and also the proposal for the fabrication of a bioseparation process plant (Igwe and Abia 2006b) for the removal of heavy metal from wastewater.

## SORPTION ISOTHERM

The equilibrium sorption isotherm is fundamentally important in the design of sorption systems. Sorption isotherms describe the equilibrium relationship between sorbent and sorbate, which is usually the ratio between the quantity sorbed and that remaining in solution at a fixed temperature at equilibrium (Ho 2004). The time it takes equilibrium to be attained in sorption systems differ from one system to another. It is also dependent on certain factors such as the nature of the adsorbent and the sorbent-sorbate interactions. Sometimes equilibrium can take a very short time, less than one hour (Igwe and Abia 2005) or longer, more than sixty hours (Bayard *et al*. 2000). In some other cases, the equilibrium sorption capacity is unknown and when chemisorptions tends to become immeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount (Ungarish and Aharoni 1981).

**Table 4** shows some of the isotherms that have been used to model sorption systems, their equations, linear forms and physical significance of their isotherm constants. The different isotherms are used to model sorption systems based on different reasons. The Langmuir and Freundlich are the earliest known sorption isotherms. Adsorption isotherms have been classified into six characteristic types (Motoyuki 1990). Isotherms are described in many mathematical forms, some of which are based on a simplified physical picture of adsorption and desorption, while others are purely empirical and intended to correlate the experimental data in simple equations with two or at most, three empirical parameters; the more the number of empirical parameters, the better the fit between experimental data (Motoyuki 1990).

The Langmuir equation is used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. A comparison of the maximum sorption capacity of conventional adsorbents and agricultural by-products is shown in **Table 5**. From this table, one can easily see the suitability of the agricultural by-products for replacement as adsorbents over conven-

**Table 4** List of various sorption isotherms, their linear equations and physical significance of their constants.

| Isotherm | Equation | Linear equation | Constants | Reference |
|---|---|---|---|---|
| Langmuir | $qe = q_mKaC_e(1+ KaC_e)$ | $C_e/q_e = 1/q_mKa + C_e/q_m$ | $q_m$ (mg/g) and Ka ($Lg^{-1}$) are the maximum sorption and Langmuir constant respectively | Langmuir 1916 |
| Langmuir dimensionless constant | $K_R = 1/(1 + KaC_o)$ | - | $K_R$ determines the shape of isotherm as follows: $K_R > 1$ unfavourable, $K_R = 1$ Linear, $0 < K_R < 1$ favourable and $K_R = 0$ irreversible | Hall *et al*. 1966 |
| Freundlich | $qe = K_FCe^{1/n}$ | $\log qe = 1/n \log Ce + \log K_F$ | $K_F$ and n are the Freundlich constants and exponent which determines the curvature and steepness of the isotherm | Freundlich 1906; Akgerman and Zardkoohi 1996 |
| Redlich-Peterson | $qe = AC_e/(1 + BC^g_e)$ | $\ln (A\ Ce/qe – 1) = g\ln(Ce)+\ln(B)$ | A, B and g ($O < g < 1$) are constants | Redlich and Peterson 1959; Ho 2003 |
| Dubinin-Radushkevich | $qe = q_D \exp (-B_D[RT \ln(1+1/Ce)]^2)$ | $\ln qe = \ln q_D – 2B_DRT\ln (1+ 1/Ce)$ | $q_D$ is the isotherm constant; $B_D$ is related to the free energy of sorption | Horsfall *et al.* 2004 |
| Energy of adsorption | $E = 1/(2B_D)^{1/2}$ | - | E (KJ/mol) is the apparent energy of adsorption | Horsfall *et al*. 2004 |
| Florry-Huggins | $\theta/c = Ka(1-\theta)^n$ | $\log(\theta/C) = \log Ka + n \log (1-\theta)$ | θ is the degree of surface coverage, n is the number of the metal ions occupying sorption site; Ka is equilibrium constant of adsorption | Horsfall *et al*. 2004 |
| Temkin | $qe = K_TCe^b$ | $\ln qe=\ln K_T + b\ln Ce$ | $K_T$ is the adsorption potential constant and b relates to the heat of adsorption | Motoyuki 1990 |
| BET | - | $X/V(1-X) =1/(V_{mon}C)+X(C-1)/(V_{mon}C)$ | $v_{mon}$ is the STP volume for monolayer, x is vapour pressure and *c* is the equilibrium constant *K*. | Motoyuki 1990 |
| Frumkin | $\beta.X=(\theta/1- \theta) \exp(-2a\theta)$ | $\log(\theta/1- \theta).C = \log(\beta/55.55) + 2a\ \theta/2.303$ | $\Theta = M/M_{ad}$ and $\beta = \exp [\Delta G_{ad}/RT]$ | Motoyuki 1990 |
| Harkins and Jura | - | $\log P/P_s = B-A/V^2$ | $A = 10^{16}KaS^2M^2/2RTN$ | Motoyuki 1990 |
| Gibbs | - | $\mu^B = \mu^B\ \theta+RT\ln a_B$ | μ = chemical potential | Shaw 1970 |

**Table 5** Comparison of maximum sorption capacity ($Q_{max}$) for conventional adsorbents and agricultural by-products.

| Conventional Adsorbents | | | Agricultural by-products | | |
|---|---|---|---|---|---|
| **Adsorbent** | $Q_{max}$ | **Reference** | **Adsorbent** | $Q_{max}$ | **Reference** |
| Activated alumina | 5.02 | Gupta and Chen 1978 | *Rhizopus arrhizus* | 23.88 | Prakasham *et al*. 1999 |
| Activated bauxite | 3.89 | Gupta and Chen 1978 | Sunflower stalk | 29.30 | Gang and Weixing 1998 |
| Activated carbon | 1.05 | Gupta and Chen 1978 | *Sargassum fluitans* | 51.0 | Davis *et al*. 2000 |
| Y(III)-impregnated alumina | 14.45 | Wasay *et al*. 1996 | Bengal gram husk | 91.64 | Ahalya *et al*. 2005 |
| Alumina | 13.64 | Wasay *et al*. 1996 | Maize cob | 1.98 | Igwe and Abia 2007a |
| La(III)-impregnated alumina | 12.88 | Wasay *et al*. 1996 | Tree fern | 39.8 | Ho *et al*. 2002 |
| Activated alumina | 17.61 | Ghosh and Yuan 1987 | *Sargassum vulgare* | 59.0 | Davis *et al*. 2000 |
| Chemvion F-400 GAC | 20.22 | Rajakovic and Mitovic 1972 | *Synechocystis* sp. | 39.00 | Centikaya *et al*. 1999 |
| Activated carbon Darco | 3.75 | Huang and Fu 1984 | Cone biomass | 201.81 | Ucun *et al*. 2002 |
| $A1_2O_3/Fe(OH)_3$ | 0.09 | Hodi *et al*. 1995 | *Rhizopus nigrificans* | 99.00 | Bai and Abraham 2001 |
| Hydrous Fe oxide with polyacrylamide | 43.0 | Shigetomi *et al*. 1980 | Peat | 115.0 | Ho and McKay 1999 |
| Cu(II)-impregnated chemviron F-400 GAC | 17.23 | Rajakovic and Mitovic 1972 | Cassava waste biomass | 127.3 | Horsfall *et al*. 2004 |

**Table 6** Kinetic equations for sorption kinetics of heavy metals on agricultural by products.

| **Equation** Reference | **Rate law** | **Integrated rate law** | **Unit of rate constant** | **Linear plot** |
|---|---|---|---|---|
| Zeroth order [1] | $-d[A]/ dt = K$ | $[A] = [A]_O - Kt$ | M/S | [A] vs. t |
| First order [2] | $-d[A]/dt = K[A]$ | $[A] = [A]_O e - Kt$ | 1/S | ln[A] vs. t |
| Second order [3] | $-d[A]/dt = K[A]^2$ | $1/[A]=1/ [A]_o e +1/Kt$ | 1/M-S | 1/[A] vs. t |
| n-th order [4] | $-d [A]/dt = K[A]^n$ | $*1/ [A]^{n-1} =1/ [A]_o^{n-1}$ | $1/M\text{-}S^{n-1}$,S | $1/[A]^{n-1}$ vs. t |
| Pseudo first order [5] | $dtq /dt = K_1(q_e-q_t)$ | $\log(q_e-q_t) = \log(q_e)-K_1t/2.303$ | $Min^{-1}$ | $\log (q_e-q_t)$ vs. t |
| Pseudo second order [6] | $dtq /dt = K^2(q_e-q_t)^2$ | $1/(q_e-qt) = 1/q_e + Kt$ | $g.mg^{-1}\ min^{-1}$ | t/qt vs. t |
| - [7] | $C -Ce = D\exp (K_ot)$ | $\ln(C-C_e) = \ln D + K_ot$ | $Min^{-1}$ | $\ln(C-C_e)$ vs. t |
| Ritchie's second order [8] | - | $1/q_t=1/(kq_et)+1/q_e$ | $Min^{-1}$ | 1/qt vs. 1/t |

* Except for first order reactions

Reference/source: 1-4: Ungarish and Aharoni 1981; 5: Lagergren 1989; 6: Ho and McKay 1998; 7: Qadeer and Akhtar 2005; 8: Ritchie 1977.

tional adsorbents. The Freundlich isotherm is used to estimate the adsorption intensity of the sorbent towards the adsorbate. The Dubinin-Radushkevich model is used to estimate the characteristic porosity of the biomass and the apparent energy of adsorption. The Florry-Huggins isotherm also gives the degree of surface coverage while the Redlich-Peterson isotherm incorporates the features of the Langmuir and Freundlich isotherm. The Frumkin isotherm is an extension of Langmuir isotherm. It states that adsorbed molecules do interact and affect further adsorption by either repulsion or attraction of molecules. Often molecules do form multilayer, that is, some are adsorbed on already adsorbed molecules and this makes some of the isotherms that propose monolayer sorption such as the Langmuir isotherm to become invalid. Isotherms such as the BET isotherm become valid. The biggest step in BET isotherm is to consider that the successive equilibrium for all the layers except for the first is equal to the liquefaction of the adsorbate. Langmuir isotherm is usually better for chemisorption and BET isotherm works better for physisorption. Adsorption is an exothermic process because energy is liberated, therefore enthalpy is always negative. Adsorption constants are equilibrium constants; therefore they obey van't Hoff's equation:

$$\left(\frac{\partial \ln K}{\partial \frac{1}{T}}\right)_\theta = -\frac{\Delta H}{R}. \qquad (3)$$

As can be seen in the formula, the variation of *K* must be isosteric, that is, at constant coverage. If we start from BET isotherm and assume that the entropy change is the same for liquefaction and adsorption we obtain

$$\Delta H_{\mathrm{ads}} = \Delta H_{\mathrm{liq}} - RT\ln c \qquad (4)$$

that is to say, adsorption is more exothermic than liquefaction. Generally, these isotherms show how adsorptions take place and also serve as design parameters in heavy metal treatment from wastewater.

## SORPTION KINETICS

Sorption kinetics can only be developed when knowledge of the rate law describing the sorption system is known. In chemical reactions, the rate law is usually determined experimentally and cannot be inferred by mere examination of the overall chemical reaction equation. The rate law has three primary requirements (Ho and McKay 1999).

- ❖ Knowledge of all the molecular details of the reaction including the energetic and stereochemistry.
- ❖ Interatomic distances and angles throughout the course of the reaction.
- ❖ The individual molecular steps involved in the mechanism.

Therefore, it is understandable that the study of sorption kinetics in wastewater treatment is significant as it provides valuable insight into the reaction pathways and into the mechanism of sorption reactions (Ho and McKay 1999). It means that the solute uptake rate and the residence time of sorbate uptake at the solid-solution interface are described by kinetics.

**Table 6** shows different kinetic equations that can be used. Most of the sorption systems give very good fit to the pseudo-second order kinetic equation. Ho and McKay (1998) found out that most sorption systems that were arbitrarily assigned a pseudo-first order model were actually of a pseudo second order model. The results from these models are used to calculate rate constants, the equilibrium amount adsorbed and initial sorption rates.

In developing the pseudo-second order kinetic model, Ho (2003) reported that tree fern (an agricultural by-product) contains polar functional groups such as aldehydes, ketones, acids and phenolics. These groups can be involved in chemical bonding and are responsible for the cation exchange capacity of the tree fern and can be represented in two ways as:

$$2(TF)^- + M^{2+} \longleftrightarrow M(TF)_2 \qquad (5)$$

$$2H(TF) + M^{2+} \longleftrightarrow M(TF)_2 + 2H^+ \qquad (6)$$

where $(TF)^-$ and (TF) are polar sites on the tree fern surface and $M^{2+}$ is the metal ion to be removed. The rate expressions for the above two equations gave

$$d(TF)_t/dt = k_2[(TF)_O - (TF)_t]^2 \qquad (7)$$

or

$$d[H(TF)]_t/dt = k_2 [(H(TF))_O - (H(TF))_t]^2 \qquad (8)$$

where $(TF)_t$ and $[H(HF)]_t$ are the number of active sites occupied on the tree fern at time t, and $(TF)_O$ and $[H(TF)]_O$ are the number of equilibrium sites available on the tree fern. Hence, from these equations the pseudo-second order kinetic equation was obtained.

Therefore, it is important to be able to predict the rate at which pollutants are removed from aqueous solution in order to design appropriate sorption treatment plants.

## INTRAPARTICLE DIFFUSIVITY

In aqueous solutions, diffusion usually precedes adsorption. Therefore, certain processes that depend on diffusion will in turn affect adsorption. These processes are: (i) diffusion of the solute from the solution to the film surrounding the particle, (ii) diffusion from the film to the particle surface (external diffusion), (iii) diffusion from the surface to the internal sites (surface diffusion or pore diffusion) and (iv) uptake which can involve several mechanisms (Findon *et al.* 1993; Weber and Digiano 1996). Based on these diffusion processes, the sorption of pollutants on adsorbents has been classified as either particle diffusion-controlled or film diffusion-controlled. The diffusion process that becomes the rate-limiting step determines the mechanism of the sorption process.

**Table 7** shows the different models that have been used to predict the mechanism of the sorption process. Very good fit of the model to the experimental data shows that sorption was particle diffusion controlled. This means that predomi-

**Table 7** Intraparticle diffusivity models for heavy metals sorption on low cost potential adsorbents.

| **Name** | **Equation** | **Linear form** | **Constants** | **References** |
|---|---|---|---|---|
| Elovich | $dqt / dt = \alpha(-\beta qt)$ | $q_t=1/\beta\ln(\alpha\beta)+1/\beta\ln(t)$ | $\alpha$ is the initial adsorption rate (mg $g^{-1}$ $min^{-1}$); $\beta$ is the desorption constant (g-$mg^{-1}$) in one experiment | Chien and Clayton 1890; Sparks 1986 |
| Weber and Morris | $R = K_{id} (t)^a$ | $\log R = \log K_{id} + a \log t$ | a is the gradient of linear plots; $k_{id}$ is the rate factor and the intraparticle diffusion rate constant ($h^{-1}$) | Weber and Moris 1963; Srivastava 1989 |
| Mckay and Poots | $qt = Xi + K^1t^{1/2}$ | $qt = X_i + K^It^{1/2}$ | $K^I$ is the intraparticle diffusion constant and the slope of the initial part of the curve gives the initial rate of sorption; $X_i$ is to proportional the boundary layer thickness | Mckay and Poots 1980 |
| Penetrant transport | $\ln(1 - \alpha) = -Kpt$ | $\ln (1-\alpha) = -Kpt$ | Kp is the intraparticle diffusion contant | Okieimen *et al*. 1991; Abia and Didi 2007 |
| Fractional attainment to equilibrium (FATE) | | $\alpha = [M]_t^{n+}/[M]_\infty^{n+}$ | $\alpha$ is the fractional attainment to equilibrium (FATE); [M] is the concentration of metals ions at time and at infinity ($\infty$) | Okieimen *et al*. 1991; Abia and Didi 2007 |

nant sorption takes place only when diffusion of pollutants into the micropores takes place and is the rate-limiting step. Abia and Didi (2007), proposed a penetrant transport mechanism, where the adsorbent surface and the overlying interface are considered as mass transfer zone. Therefore, the sorption of heavy metals on low cost sorbents is visualized as occurring in stages. First is the approach of the metal ion from infinite distance in solution to the adsorbent surface. Secondly is the deposition of the metal on the adsorbent surface and then followed by adsorption.

## CONCLUSION

So many problems have been caused by heavy metal pollution both in terms of damage to the environment and cost of removal processes. Most energy and cost saving processes such as bioremediation are viable because they can be said to mimic nature. Therefore, the use of biosorbents of biological or agricultural origin in heavy metal removal is a welcome strategy. Most biosorbents used in metal bioremediation have been reviewed, ranging from agricultural by-products such as maize cob and husk to algae and fungi biomasses. The capacity of sorption, sorption isotherm, sorption kinetics and mechanism of uptake has been reviewed. Although biosorption is a promising strategy, its mechanism is not very well elucidated. This knowledge is essential for understanding the process and it serves as a basis for quantitative stoichiometric considerations, which are fundamental for mathematical modeling, design and scale-up.

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