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# THE TRENDS IN REMOVAL OF HEAVY METAL CONAMINANTES FROM THE WASTE WATER BY USING BIOMATERIALS

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## ABSTRACT

The presence of large quantities of toxic metals such as mercury, lead, cadmium, zinc or others, poses serious health risks to humans, and this threat puts the scientific community under pressure to develop new methods to detect and eliminate toxic contaminants from wastewaters in efficient and economically viable ways. Industrial and agricultural effluents are a major cause of heavy-metal contamination, thus the removal and recovery of heavy metals from effluent streams is essential to the protection of the environment. Conventional technologies are either not able to remove and recover heavy metals to a satisfactory level, or they are too costly to implement. But there are some new techniques, which are cheaper and highly effective to removal of heavy metals from the waste water. The present study discussed about the past, present and future trends in waste water treatment methods by using biomaterials.

## INTRODUCTION

Based on different environmental issues, pollution by heavy metals of surface water, ground water and soil in urban areas are the major environmental problems. Mainly in developing countries like Ethiopia rapid industrialization and urbanization have resulted in the generation of large quantities of aqueous effluents, many of which contain high levels of toxic pollutants (Krishnani and Ayyappan, 2006 and Vijayaraghavan and Yun, 2008) because of the their non - biodegradability. Mineral extraction, Paint manufacturing, leather industries, textiles, usage of fertilizers and pesticides to boost up crop productivity etc. contributes such a kind of waste. Particularly the nearby surface water, ground water and soil are at risk to contamination with heavy metals (Biruk Tsegaye, 2011). As water discharged through these areas, it dissolves organic and inorganic components and decomposition products, giving rise to a polluted liquid. Therefore, treatment of this polluted liquid is recognized as one of the most burning issues (Yegenetfere Argaw, 2010).

Various physico-chemical and biological processes are usually employed to remove pollutants from industrial wastewaters before discharge into the environment (Hai *et al.*, 2007). It is important to note that the overall treatment cost of metal-contaminated water varies, depending on the process employed, efficient removal and the local conditions. In general, the technical applicability, plant simplicity and cost-effectiveness are the key factors in selecting the most suitable treatment for organic and inorganic effluent.

Activated carbon is considered a powerful adsorbent due to its high surface area and low cost of treatment, compared to other expensive methods such as membrane filtration, Chemical precipitation, ion – exchange processes and adsorption etc. Now a days, producing activated carbon from biomaterials with larger mesoporosity (>2nm) is unquestionable and popular technique in the removal of larger molecular sized pollutants from the water (Esmaeili *et al.*, 2008).This research provides the information about various metal contaminants in water and their toxicity, past, present and future trends of various techniques used to removal of these contaminants by using various biomaterials.

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## MATERIALS

### Definition and toxicity of heavy metals

Heavy metals are generally considered to be those whose density exceeds 5 g per cubic centimeter (John. Duffus, 2002). A large number of elements fall into this category, but the ones listed in Table 1are those of relevance in the environmental context. Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of the fetal brain. At higher doses, heavy metals can cause irreversible brain damage. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults. Wastewater regulations were established to minimize human and environmental exposure to hazardous chemicals. This includes limits on the types and concentration of heavy metals that may be present in the discharged wastewater. The MCL standards, for those heavy metals, established by USEPA (Babel and Kurniawan, 2003) are summarized in Table 1.

**Table 1. The MCL standards for the most hazardous heavy Sources of heavy metals contaminate the watermetals**

| Heavy metal | Toxicities | MCL (mg/L) |
|---|---|---|
| Arsenic | Skin manifestations, visceral cancers, vascular disease | 0.050 |
| Cadmium | Kidney damage, renal disorder, human carcinogen | 0.01 |
| Chromium | Headache, diarrhea, nausea, vomiting, carcinogenic | 0.05 |
| Copper | Liver damage, Wilson disease, insomnia | 0.25 |
| Nickel | Dermatitis, nausea, chronic asthma, coughing, human carcinogen | 0.20 |
| Zinc | Depression, lethargy, neurological signs and increased thirst | 0.80 |
| Lead | Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system | 0.006 |
| Mercury | Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system | 0.00003 |

Heavy metals are released to water streams from numerous sources. Typical sources are municipal wastewater-treatment plants, manufacturing industries, mining, and rural agricultural cultivation and fertilization. There are two major types of sources, one is industrial and another one is agriculture (Erica R. McKenzie *et al.*, 2009).

### Heavy metals releasing industries

Industrial wastewater streams containing heavy metals are produced from different industries. Electroplating and metal surface treatment processes generate significant quantities of wastewaters containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium) from a variety of applications. These include electroplating, electroless depositions, conversion-coating, anodizing-cleaning, milling, and etching. Another significant source of heavy metals wastes result from printed circuit board (PCB) manufacturing (Barakat, 2011). Tin, lead, and nickel solder plates are the most widely used resistant over plates. Other sources for the metal wastes include; the wood processing industry where a chromated copper-arsenate wood treatment produces arsenic-containing wastes; inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and ferrocyanide (Kurniawan *et al*., 2005). All of these generators produce a large quantity of wastewaters, residues, and sludges that can be categorized as hazardous wastes requiring extensive waste treatment (Babel and Kurniawan, 2004). Pharmaceuticals, leather processing industries, pesticide manufacturing industries, agro chemicals, paint industries etc., are some of the industries that release more amounts of heavy metals in to the water streams via industrial drainage.

### Heavy metals releasing agricultural forms

Animal feedlots, Irrigation, Cultivation Pastures Dairy farming, Orchards Aquaculture, forestry releases phosphorus, nitrogen, metals, pathogens, sediment, pesticides, and some trace elements (e.g. selenium). Farmers use fertilizers and pesticides to promote growth and reduce insect damage. These products are also used on golf courses and suburban lawns and gardens. The chemicals in these products may end up in water. Such pollution depends on the types and amounts of chemicals used and how they are applied. Local environmental conditions (soil types, seasonal snow and rainfall) also affect this contamination. Many fertilizers contain forms of nitrogen that can break down into harmful nitrates.

This could add to other sources of nitrates. Some underground agricultural drainage systems collect fertilizers and pesticides. In addition, chemicals used to treat buildings and homes for termites or other pests may also pose a threat. Again, the possibility of problems depends on the amount and kind of chemicals. In Ethiopia, Sustainable production is becoming an issue, due to the international competition in the Agricultural sector; by large usage of fertilizers are responsible for the environmental pollution. Farms use a lot of fertilizer that are largely washed off in the soil and enter into the water bodies. On the other hand, pesticides are major pollutants, because they introduce toxic metals in the environment. This is because of lack of information about how to use fertilizer and pesticides in a sustainable way at the farm level (UNDP, 2012).

### Nature of heavy metals

Heavy metals have high solubility, and are having acidic or neutral pH. These heavy metals are generally present in very low concentration. Because of high solubility these are easily taken by living organisms and get accumulated in the body. On increasing pH to basic and by changing concentration of metal to more amount metal gets precipitated and can be easily removed from water (Hala Ahmed Hegazi, 2013).

### Analysis of heavy metals

The analysis of wastewater for trace and heavy metal contamination is an important step in ensuring human and environmental health. Wastewater is regulated differently in different countries, but the goal is to minimize the pollution introduced into natural waterways. In recent years, metal production emissions have decreased in many countries due to heavy legislation, improved production and cleaning technology. A variety of inorganic techniques can be used to measure trace elements in waste water including flame atomic absorption spectrometry (FAAS) and graphite furnace (or electrothermal) atomic absorption spectrometry (GFAAS or ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Depending upon the number of elements to be determined, expected concentration range of analytes and the number of samples to be run, the most suitable technique for business requirements can be chosen (Eaton *et al*., 2005).

**Table 2. Analytical techniques used in bio sorption research**

| Analytical techniques Remarks | Analytical techniques Remarks |
|---|---|
| Atomic absorption spectroscopy (AAS) | Determine metal concentration in aqueous phase |
| Inductively coupled plasma (ICP) | Determine metal concentration in aqueous phase |
| UV-Vis spectrophotometer | Determine metal or dye concentration in aqueous phase by measuring its color intensity |
| Scanning electron microscope (SEM) | Visual confirmation of surface morphology of the biosorbent |
| Transmission electron microscope (TEM) | Visual confirmation of inner morpho-logy of biomass, especially cells |
| Energy dispersive X-ray spectroscopy (EDS) | Element analysis and chemical characterization of metal bound on the biosorbent |
| X-ray diffraction (XRD) analysis | Crystallographic structure and chemical composition of metal bound on the biosorbent |
| Electron spin resonance spectroscopy (ESR) | Determine active sites of the biosorbent |
| Nuclear magnetic resonance (NMR) | Determine active sites of the biosorbent |
| Fourier transformed infraredspectroscopy (FT-IR) | Determine active sites of the biosorbent |
| Potentiometric titration | Determine active sites of the biosorbent and its amounts |
| X-ray photoelectron spectroscopy (XPS) | Determine oxidation state of metal bound on the biosorbent and its ligand effects |
| X-ray absorption spectroscopy (XAS) | Determine oxidation state of metal bound on biosorbent and its coordination environment |
| Thermogravimetric analysis (TGA) | Characterize thermal stability of the biosorbent |
| Differential scanning calorimetry (DSC) | Characterize thermal stability of the biosorbent |

## METHODS

This section provides details on the past, present and future developments and efforts in general heavy metals removal from wastewater.

i. Conventional methods for removal of heavy metals from waste water
ii. New Technologies in Heavy Metals Removal from Wastewater

### Conventional methods for removal of heavy metals from waste water

Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, etc(Wang *et al*., 2004). The toxic metals, probably existing in high concentrations (even up to 500 mg/L), must be effectively treated/removed from the wastewaters. If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, whilst the direct discharge into the sewerage system may affect negatively the subsequent biological wastewater treatment (Wan Ngah and Hanafiah, 2008). In recent years, the removal of toxic heavy metal ions from sewage, industrial and mining waste effluents has been widely studied. Their presence in streams and lakes has been responsible for several types of health problems in animals, plants and human beings. Among the many methods available to reduce heavy metal concentration from wastewater, the most common ones are chemical precipitation, ion-exchange, adsorption, coagulation, cementation, electro-dialysis, electro-winning, electro-coagulation and reverse osmosis (See in Figure 1) (Demirbas, 2008; Bailey *et al*., 1999; Sekhar *et al*., 2003 and Sag and Kutsal, 2001).

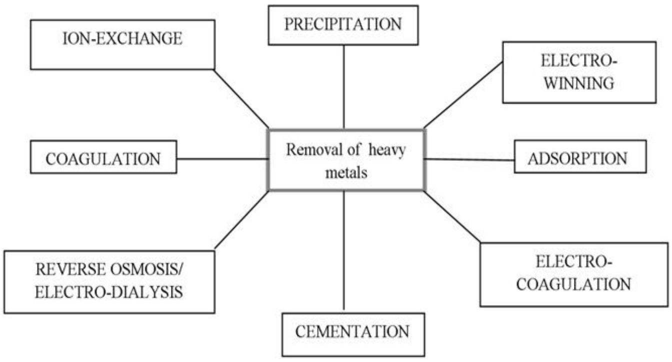

**Figure 1 .Some conventional methods for the removal of heavy metals**

Some conventional methods are explained below (Demirbas, 2008; Bailey *et al*., 1999; Sekhar *et al*., 2003 and Sag and Kutsal, 2001);

1. Precipitation is the most common method for removing toxic heavy metals up to parts per million (ppm) levels from water. Since some metal salts are insoluble in water and which get precipitated when correct anion is added. Although the process is cost effective its efficiency is affected by low pH and the presence of other salts (ions). The process requires addition of other chemicals, which finally leads to the generation of a high water content sludge, the disposal of which is cost intensive. Precipitation with lime, bisulphide or ion exchange lacks the specificity and is ineffective in removal of the metal ions at low concentration.

2. Ion exchange is another method used successfully in the industry for the removal of heavy metals from effluents. Though it is relatively expensive as compared to the other methods, it has the ability to achieve ppb levels of clean up while handling a relatively large volume. An ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is nonselective and is highly sensitive to pH of the solution.
3. Electro-winning is widely used in the mining and metallurgical industrial operations for heap leaching and acid mine drainage. It is also used in the metal transformation and electronics and electrical industries for removal and recovery of metals. Metals like Ag, Au, Cd, Co, Cr, Ni, Pb, Sn and Zn present in the effluents can be recovered by electro-deposition using insoluble anodes.
4. Electro-coagulation is an electrochemical approach, which uses an electrical current to remove metals from solution. Electro-coagulation system is also effective in removing suspended solids, dissolved metals, tannins and dyes. The contaminants presents in wastewater are maintained in solution by electrical charges. When these ions and other charged particles are neutralized with ions of opposite electrical charges provided by electro coagulation system, they become destabilized and precipitate in a stable form.
5. Cementation is a type of another precipitation method implying an electrochemical mechanism in which a metal having a higher oxidation potential passes into solution e.g. oxidation of metallic iron, Fe(0) to ferrous Fe(II) to replace a metal having a lower oxidation potential. Copper is most frequently separated by cementation along with noble metals such as Ag, Au and Pb as well as As, Cd, Ga, Pb, Sb and Sn can be recovered in this manner.
6. Reverse osmosis and electro-dialysis involves the use of semi-permeable membranes for the recovery of metal ions from dilute wastewater. In electro-dialysis, selective membranes (alternation of cation and anion membranes) are fitted between the electrodes in electrolytic cells, and under continuous electrical current the associated.
7. Photocatalytic process in aqueous suspension of semiconductor has received considerable attention in view of solar energy conversion. This photocatalytic process was achieved for rapid and efficient destruction of environmental pollutants. Upon illumination of semiconductor, electrolyte interface with light energy greater than the semiconductor band gap, electronâ€"hole pairs (eâˆ'/h+) are formed in the conduction and the valence band of the semiconductor. These charge carriers, which migrate to the semiconductor surface, are capable of reducing or oxidizing species in solution having suitable redox potential. Various semiconductors have been used: TiO2, ZnO, CeO2, CdS, ZnS, etc. As generally observed, the best photocatalytic performances with maximum quantum yields are always obtained with titanium dioxide.

Most of these methods suffer from some drawbacks such as high capital and operational costs and problem of disposal of residual metal sludge. Ion-exchange is feasible when an exchanger has a high selectively for the metal to be removed and the concentrations of competing ions are low. The metal may then be recovered by incinerating the metal-saturated resin and the cost of such a process naturally limits its application to only the more valuable metals. In many cases, however, the heavy metals are not valuable enough to warrant the use of special selective exchangers/resins from an economic point of view. Cost effective, alternative technologies or sorbents for treatment of metals contaminated waste streams are needed (Volesky, 2007). Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration (Turker, 2007). Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported, and the expense of individual sorbents varies depending on the degree of processing required and local availability. In general, a sorbent can be assumed as 'low cost'' if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry (Mohan and Pittman, 2007). Of course improved sorption capacity may compensate the cost of additional processing. This has encouraged research into using low-cost adsorbent materials to purify water contaminated with metals.

Another major disadvantage with conventional treatment technologies is the production of toxic chemical sludge and its disposal/treatment is not eco-friendly. Therefore, removal of toxic heavy metals to an environmentally safe level in a cost effective and environment friendly manner assumes great importance. Of course improved sorption capacity may compensate the cost of additional processing. Activated carbon has unquestionably been the most popular and widely used as a absorbent in waste water treatment employment throughout the world. However, activated carbon remains a costly material since the higher quality of activated carbon, the will be its cost (Kurniwan *et al*., 2006a). Therefore a searching for a low cost activated carbon and other absorbent materials is of great importance for the removal of heavy metals from the waste water. Some of the reported low-cost sorbents such as bark/tannin-rich materials, lignin, chitin/chitosan, dead biomass, seaweed/algae/alginate, xanthate, zeolite, clay, fly ash, peat moss, bone gelatin beads, leaf mould, moss, iron-oxide-coated sand, modified wool and modified cotton. Important parameters for the sorbent effectiveness are affected by pH, metal concentration, ligand concentration, competing ions, and particle size (Wan Ngah and Hanafiah, 2008; Demirbas, 2008; Bailey *et al*., 1999 and Ahluwalia and Goyal, 2007).

## New technologies in heavy metals removal from wastewater

### Metal Removal from Wastewater Using Peat

Peat has been investigated by several researchers as a sorbent for the capture of dissolved metals from waste streams. The mechanism of metal ion binding to peat remains a controversial area with ion-exchange, complexation, and surface adsorption being the prevalent theories. Factors affecting adsorption include pH, loading rates, and the presence of competing metals. The optimum pH range for metals capture is generally 3.5–6.5. Although the presence of more than one metal in a solution creates competition for sorption sites and less of a particular ion may be bound, the total sorption capacity has been found to increase. Studies have also shown that metals removal is most efficient when the loading rates are low. In addition, recovery of metals and regeneration of the peat is possible using acid elution with little effect on peat's sorption capacity (Brown and Gill, 2000).

### Advantages

- This method is simple, effective and economical means of pollution remediation.
- Peat is plentiful and inexpensive.

### A Novel Method for Heavy Metal Removal Using Fish Scales

Effective removal of metal ions from industrial wastewater by using fish scales was studied in this article (Ustafiz *et al.*, 2002). A series of static tests was performed with 10 g of dried fish scale adsorbent pulverized to micron sizes of 37 or less. Such tests were conducted for lead ions (from lead nitrate solution) at concentrations of 25 ppm, 12.5 ppm, and 6.25 ppm. The dynamic equilibrium results were based on tests on 50 ppm of cobalt chloride solution (flow rate 1 ml/min), followed by 100 ppm of cobalt solution (flow rate 7 ml/min), and then a mixture of cobalt chloride ($CoCl_2$), lead nitrate ($Pb(NO_3)_2$), zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and strontium nitrate (Sr(NO3)2) solutions. The proposed sorption technique offers an acceptable solution for removal of heavy metal ions from wastewater streams. The potential application of this study is an enormous energy cost savings in the electroplating industry, which requires the replacement of wastewater and the burial of metal sludge in landfills. Also, the trimming of energy costs in oil drilling and pipeline corrosion is possible by potential formation of biopolymers developed from "adsorbed scale."

### Seashells for Heavy Metals Clean-Up

On the banks of the Saigon River in Viet Nam, researchers have completed tests on a new way to combat water pollution that could save millions of lives in coastal cities in the developing world. Toxic metals like cadmium, zinc, lead and iron were cleaned using seashells. Dr. Köhler's team has found that pouring metal and acid-laden water over a bed of crushed clam or mussel shells provides an easy fix. The shells are made of aragonite, a form of calcium carbonate that readily swaps its calcium atoms in favor of heavy metals, locking them into a solid form. The shells are alkaline – a pH of 8.3 when dissolved – and needs to be maintained so by adding more shells (http://www.techmonitor.net/techmon/09sep_oct/wat/wam_wastewater.htm).

### Removal of Heavy Metals from Industrial Wastewaters by Adsorption onto Activated Carbon Prepared From an Agricultural Solid Waste

Activated carbon was prepared from coirpith by a chemical activation method and characterized. The adsorption of toxic heavy metals, Hg(II), Pb(II), Cd(II), Ni(II), and Cu(II) was studied using synthetic solutions and was reported elsewhere. In the present work the adsorption of toxic heavy metals from industrial wastewaters onto coirpith carbon was studied (Bodnar *et al.*, 2008). The percent adsorption increased with increase in pH from 2 to 6 and remained constant up to 10. As coirpith is discarded as waste from coir processing industries, the resulting carbon is expected to be an economical product for the removal of toxic heavy metals from industrial wastewaters.

### Physico–Chemical Treatment Techniques for Wastewater Laden with Heavy Metals

This article reviews the technical applicability of various physico–chemical treatments for the removal of heavy metals such as Cd(II), Cr(III), Cr(VI), Cu(II), Ni(II) and Zn(II) from contaminated wastewater. A particular focus is given to chemical precipitation, coagulation–flocculation, flotation, ion exchange and membrane filtration. Their advantages and limitations in application are evaluated. Their operating conditions such as pH, dose required, initial metal concentration and treatment performance are presented. About 124 published studies (1980–2006) are reviewed. It is evident from the survey that ion exchange and membrane filtration are the most frequently studied and widely applied for the treatment of metal-contaminated wastewater. Ion exchange has achieved a complete removal of Cd(II), Cr(III), Cu(II), Ni(II) and Zn(II) with an initial concentration of 100 mg/L, respectively. The results are comparable to that of reverse osmosis (99% of Cd(II) rejection with an initial concentration of 200 mg/L). Lime precipitation has been found as one of the most effective means to treat inorganic effluent with a metal concentration of higher than 1000 mg/L. It is important to note that the overall treatment cost of metal-contaminated water varies, depending on the process employed and the local conditions. In general, the technical applicability, plant simplicity and cost-effectiveness are the key factors in selecting the most suitable treatment for inorganic effluent (Srivastava and Majumder, 2008).

### Microbial and Plant Derived Biomass for Removal of Heavy Metals from Wastewater

Discharge of heavy metals from metal processing industries is known to have adverse effects on the environment. Conventional treatment technologies for removal of heavy metals from aqueous solution are not economical and generate huge quantity of toxic chemical sludge. Biosorption of heavy metals by metabolically inactive non-living biomass of microbial or plant origin is an innovative and alternative technology for removal of these pollutants from aqueous solution. Due to unique chemical composition biomass sequesters metal ions by forming metal complexes from solution and obviates the necessity to maintain special growth-supporting conditions. Biomass of Aspergillus niger, Penicilliumchrysogenum, Rhizopus nigricans, Ascophyllum nodosum, Sargassum natans, Chlorella fusca, Oscillatoria anguistissima, Bacillus firmus and Streptomyces sp. have highest metal adsorption capacities ranging from 5 to 641 mg g−1 mainly for Pb, Zn, Cd, Cr, Cu and Ni. Biomass generated as a by-product of fermentative processes offers great potential for adopting an economical metal-recovery system. The purpose of this paper is to review the available information on various attributes of utilization of microbial and plant derived biomass and explores the possibility of exploiting them for heavy metal remediation (Kadirvelu *et al*., 2001).

## Low-Cost Adsorbents for Heavy Metals Uptake from Contaminated Water: A Review

In this article, the technical feasibility of various low-cost adsorbents for heavy metal removal from contaminated water has been reviewed (Tonni Agustiono Kurniawan *et al*., 2006). Instead of using commercial activated carbon, researchers have worked on inexpensive materials, such as chitosan, zeolites, and other adsorbents, which have high adsorption capacity and are locally available. The results of their removal performance are compared to that of activated carbon and are presented in this study. It is evident from our literature survey of about 100 papers that low-cost adsorbents have demonstrated outstanding removal capabilities for certain metal ions as compared to activated carbon. Adsorbents that stand out for high adsorption capacities are chitosan (815, 273, 250 mg/g of Hg2+, Cr6+, and Cd2+, respectively), zeolites (175 and 137 mg/g of Pb2+ and Cd2+, respectively), waste slurry (1030, 560, 540 mg/g of Pb2+, Hg2+, and Cr6+, respectively), and lignin (1865 mg/g of Pb2+). These adsorbents are suitable for inorganic effluent treatment containing the metal ions mentioned previously. It is important to note that the adsorption capacities of the adsorbents presented in this paper vary, depending on the characteristics of the individual adsorbent, the extent of chemical modifications, and the concentration of adsorbate. Table 3 gives various examples of natural biosorbents (in raw form or after limited chemical treatment) and summarizes the biosorption efficiency of these materials (Sarabjeet Singh Ahluwalia and Dinesh Goyal, 2007).Considering the diversity of the tested materials and the variations in experimental conditions, the quoted efficiencies are relatively homogeneous. As a rule, however, materials of marine origins (seaweeds, chitin/chitosan) offer a high metal-binding potential whereas modified materials (sawdust, apple residues, chitin) display higher biosorption capabilities than raw counterparts. Biosorption is in its developmental stages and further improvement in both performance and costs can be expected in future. We have summarized future directions of biosorption research, mentioned by other researchers in this area and also added our opinions. We must continue fundamental research to better understand the mechanisms of biosorption and on what drives the selectivity of biosorptive and bioaccumulatory processes. It is desirable to develop general-purpose biosorbents that can remove a variety of pollutants.

**Table 3. Various examples of natural biosorbents and summarizes the biosorption efficiency of these materials**

| Materials | Metal tested Metal binding efficiency | Metal tested Metal binding efficiency |
|---|---|---|
| Chitin<br>- raw<br>- deacetylated (chitosan) | Cu (II), Cd, Cr (III), Zn, PbPd, Au(*) Hg(II) Pt(**), PbCu (II), Cr (III), Ni, Zn, Fe (III) | Removal of metals (mg g-1) by commercial chitin from a mixture of metals ions containing 1 mg cm-3 of each metal (pH 6, 25°C): 25.0 (Cu), 15.8 (Zn), 40.1 (Cd), 47.8 (Cr), 38.0 (Pb)Metal removal efficiency of chitosan (mg g-1) in the same test conditions as above: 70.5 (Cu), 20.0 (Zn), 54.3 (Cd), 53.4 (Cr), 40.3 (Pb) Metal uptake (mg g-1 chitosan) from 200-400 mM metal solution: 668 (Pd), 1150 (Au), 882 (Pt), 1123 (Hg), 823 (Pb)Chitosan from prawn waste. Quantity of metal adsorbed (mg g-1): Fe, Cu, Cr 1500 Zn > 1800, Ni 300-350 ([Me]i = 25-100 mM) |
| Wool fibres | Hg (II), Pb, Cd, Zn, Cu (II), Ni | Wool fibres cleaned from grease with petroleum ether. Average uptake rate in mg metal g-1 dry wt. fibres h-1 (50°C, pH 5, contact for 60 min): 26.5 (Hg), 16.0 (Pb), 5.5 (Cu) ([Me]i =200 mg dm-3); 7.5 (Cd), 7.2 (Zn) ([Me]i =100 mg dm-3); 4.0 (Ni) ([Me]i =50 mg dm-3) |
| Egg shell membrane | Au (*), Pt (**), U (***), Pd | Adsorption capacity (25°C, contact for 3 h in 3 mM metal solution): 550 mg Au g-1 dessicated hen egg shell membrane (pH 4); 270 mg Pt g-1 (pH 2-4); 240 mg Pd g-1; 280 mg U g-1 (pH 6) |
| Bone gelatin | Cu (II) | Gel beads of gelatin (25% wt.) + propylene glycol alginate (2% wt.) crosslinked with NaOH. Adsorption capacity at pH 5.5: 30 mg Cu g-1 dry gel |

*……………..Continue*

| | | |
|---|---|---|
| (*) As AuCl4<br>- | (**) As PtCl4<br>2- | (***)As UO2<br>2+ |
| - from weeds (Amaranthus spinosus and Solanum nigrum | Cu(II) | Maximum adsorption capacity (mg Cu g-1 dry biomass): 13.1 (A. spinosus), 9.7 (S. nigrum). In continuous experiments (biomassloaded alginate beads in packed-bed column; [Me]i, 100 mg Cu dm-3, flow rate, 0.5 cm3 min-1): 15.6 mg Cu g-1 (A. spinosus), 11.6 mg Cu g-1 (S. nigrum) |
| Plant roots<br>- from tomato and tobacco | Sr | Maximum adsorption capacity (mg Sr g-1 dry biomass): 25.8 (tomato), 18.3 (tobacco). Overall adsorption loading in continuous operation (biomass-loaded carrageenan beads in packed bed column; [Me]i, 10 mg Sr dm-3, flow rate, 0.5 cm3 min-1; 25°C; pH 5.35-5.95): 3.35 mg Sr g-1 biomass |
| Plant and tree leaves<br>- waste tea leaves | Hg (II)Pb, Cd, Zn | Adsorption capacity (mg Hg g-1 dry leaves): 175 (redwood), 250 (senna). Acid-washed (10-2 M HN03) and oven-dried (110°C). Maximum adsorption capacity (mg g-1): 79 (Pb), 32 (Cd), 12 (Zn) |
| Tree bark<br>- from black oak<br>- from Pinus pinaster | Pb, Hg (II), Pd, Ag, Zn, Cd Pb, Cu (II), Zn | Metal uptake (mg g-1 dry bark): 153 (Pb), 124 (Hg), 96 (Pd), 79 (Ag), 41 (Zn), 26 (Cd). Bark pretreated with acidified formaldehyde solution. Adsorption capacity (mg g-1 dry wt.) at 22°C and an initial pH of 6.3: Pb, 4.2 100 mg dm-3); Cu, 2.3 ([Me]i 50 mg dm-3); Zn, 1.9 ([Me]i 50 mg dm-3) |
| Sawdust<br>- untreated, oven-dried (110°C) and sieved<br>- from Red Fir (Abies magnifica), untreated<br>- from spruce (Picea engelmanii), crosslinked and chemically modified (phosphorylated) | Cr(VI)Cr (VI),Cu (II)Pb,Cd, Ni | Maximum adsorptive capacity: 39.7 mg g-1 dried sawdust ([Me]i 1000 mg dm-3; pH 2.0; 25°C). Maximum adsorption capacity (mg g-1 air dried sawdust): 10.1 (Cr), 7.1 (Cu). Adsorption rate: 1.5 mg Cu g-1 h-1([Me]i , 200 mg dm-3; 60 g sawdust dm-3; pH 5; 45°C) - somewhat lower rate for Cr. Highest metal uptake (mg g-1 biosorbent): 224 (Pb), 56 (Cd), 26 (Ni). Raw sawdust: 15 mg Pb g-1 |
| Coconut husk fibres | Cr(VI) | Oven-dried at 100°C, ground and treated successively with NaOH and HNO3. Maximum adsorption capacity at pH 2.0: 29 mg g-1 |
| Maize cob | Cr(VI) | Untreated material [oven-dried (110°C) and sieved]. Maximum adsorptive capacity: 13.8 mg g-1 dried cob ([Me]i, 300 mg dm-3; pH 1.5; 25°C) |
| Rice bran | Cu (II), Cr (III), Zn, Co, Ni | Defatted, extrusion-stabilized bran. Maximum adsorption capacity (mg g-1): 38.4 (Cu), 32.9 (Cr), 24.5 (Zn), 9.4 (Co), 6.8 (Ni) |
| Exhausted coffee grounds | Hg (II) | Pretreatment with 0.5 M NaOH and 0.5 M HCl, successively, then oven-drying at 105°C. Maximum sorption capacity (pH 3-11): ca. 80 mg g-1 |
| Palm pressed fibres | Cr(VI) | Oven-dried at 100°C, ground and treated successively with NaOH and HNO3. Maximum adsorption capacity at pH 2.0: 14 mg g-1 |
| Sugar cane bagasse | Cr(VI) | Untreated material {oven-dried (110°C) and sieved}. Maximum adsorptive capacity:13.4 mg g-1 dried bagasse ([Me]i, 500 mg dm-3; pH 2.0; 25°C) |

*…………Continue*

| | | |
|---|---|---|
| Sugar-beet pulp | Cu (II). Pb, Cd, Zn, Ni, CaCr (VI) | Sugar-free pulp dried by solvent exchange and air-drying.<br>Maximum binding capacity a of the acidic form (mg g-1 pulp) in 0.1 M NaNO3: 19.7 (Cu), 60.1 (Pb), 26.4 (Cd), 16.0 (Zn), 10.6 (Ni)<br>([Me]i = 10 mM, 14.55 g pulp dm-3, initial pH 7.2, 25°C Untreated<br>material oven-dried (110°C) and sieved].<br>Maximum adsorptive capacity: 17.2 mg g-1 dried pulp ([Me]i, 500 mg dm-3; pH 2.0; 25°C) |
| Apple residues<br>- raw<br>- phosphated | Cu (II), Zn, Ni | Saturation capacity (mg g-1 dry residues): 12.7 (Cu), 9.8 (Zn), 9.1<br>(Ni), 51.2 (Cu), 46.7 (Zn), 39.3 (Ni) |
| Marine macroalgae (brown algae: A. nodosum, Sargassum natans, Fucus vesiculosus, ...) | CoCdPb, Ni | Biosorption capacity of Ascophyllum nodosum > 160 mg g-1 (25°C, pH 4)Maximum adsorption capacity a of A. nodosum (raw biomass): 215 mg Cd g-1 dry weight (26°C, pH 4.9). Crosslinked biomass: 117-149 mg g-1, depending on the crosslinking agentMaximum adsorption capacity a (mg g-1) of native A. nodosum biomass (pH 3.5, 25°C):272 (crosslinked: 177-359) mg Pb g-1; 41 (crosslinked 24-30) mg Ni g-1. Corresponding data for F.vesiculosus: 229 (crosslinked 301-363) mg Pb g-1; 23 (crosslinked 31) mg Ni g-1 |

One such possibility would be the use of 'combo' biosorbents consisting more than one type of biomass (Hani Abu Qdais and Hassan Moussa, 2004). Although 'combo' biosorbents would tend to further complicate characterization of these biosorption systems, it may represent a more realistic approach to the design of biosorbent systems (Sandhya Babel and Tonni Agustiono Kurniawan, 2003). Activated carbon (AC) is perhaps one of the most widely used adsorbents in industry for environmental applications. Activated carbons are carbons of highly microporous structure with both high internal surface area and porosity, and commercially the most common adsorbents used for the removal of organic and inorganic pollutants from air and water streams. Any cheap and locally available biomaterial with a high carbon content, lowinorganics can be used as a raw material for the production of activated carbon (Fourest and Roux, 1992; El-Sikaily *et al.*, 2006; Abdelwahab *et al.*, 2006 and Karadag, 2007). Activated carbon is an excellent and versatile adsorbent and its main applications include the adsorptive removal of color, odor, taste, and other undesirable organic and inorganic impurities from drinking waters; in the treatment of industrial waste water; air purification in food processing and chemical industries; in the purification of many chemical, food and pharmaceutical products; in respirators for work in hostile environments; and in a variety of other gas-phase applications. Nearly 80% of the total activated carbon is consumed for liquid phase applications where, both granular and powdered activated carbons can be used (Karanfil *et al.*, 2006).

## Advantages

Overall, compared with the conventional heavy metal removal methods, the potential advantages of bio materials (By activated carbon) process includes (Zümriye, 1997):

- Use of naturally abundant renewable biomaterials that can be cheaply produced;
- Ability to treat large volumes of wastewater due to rapid kinetics;
- High selectivity in terms of removal and recovery of specific heavy metals;
- Ability to handle multiple heavy metals and mixed wastes;
- High affinity, reducing residual metals to below 1 ppb in many cases;
- Less need for additional expensive reagents which typically cause disposal and space problems;
- Operation over a wide range of physiochemical conditions including temperature, pH, and presence of other ions (including Ca 2+ and Mg 2+);
- Relatively low capital investment and low operational cost;
- Greatly improved recovery of bound heavy metals from the biomass;
- Greatly reduced volume of hazardous waste produced.

## Conclusion

So far, biosorption (by using activated carbon) research has mainly aimed for the removal of pollutants such as heavy metals and organics. However, precious metal resources are getting paid attention because of their price increases and limited deposits. For the recovery of precious metals such as gold, platinum, palladium, ruthenium, etc. the performance-effectiveness would be more important property of sorbents than cost-effectiveness. With the purpose of their recovery, the recovery efficiency and purity of finally recovered products would be additional criteria for evaluating biosorbents and related processes. But, the removal of inorganic pollutants from waste water by using activated carbon is some less effective compare to the removal of organic pollutants from waste water. We expect that high performance activated carbon will be used for the removal of inorganic pollutants effectively and one of these techniques will be better to commercialize to provide potable water to even common society in the near future.

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