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HEAVY METALS, CONVENTIONAL METHODS FOR HEAVY METAL REMOVAL, BIOSORPTION AND THE DEVELOPMENT OF LOW COST ADSORBENT

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ABSTRACT

The heavy metal pollutants include lead, cadmium, zinc, mercury, arsenic, silver, chromium, copper, iron and platinum group of metals arises from the natural and anthropogenic activities in the nature. Various methods cited in the literature for the removal of heavy metals from waste water are chemical precipitation, ultra filtration, ion exchange, reverse osmosis, electro winning, carbon adsorption, phytoremediation and biosorption. Among these biosorption is relatively new and efficient method for the heavy metal removal. The present paper is a review of literature on various aspects of biosorption. An attempt has been made to cover the literature and introduction of heavy metals, conventional methods for heavy metal removal and recent studies on biosorption.

KEYWORDS: Heavy metals, sources, removal methods, biosorption, low cost adsorbents.

INTRODUCTION

The number of naturally occurring elements in the nature[1] is 92 and among these 68 belongs to the group of metals, 6 metalloids and 18 to non metals.[2] Metals are the elements which conduct electricity, have a metallic luster, malleable and ductile, form cations and have basic oxides".[3] Based on individual properties these are classified as – metal, semimetal (metalloids), light metal, heavy metal, beneficial metal, toxic metal, abundant metal, available metal and trace metal or micronutrient.[4,5] Heavy metals may defined as metal with a density[6-9] greater than 4 gm/cm^3 or metals with a high atomic weight[10-12] or metals commonly used in industry and toxic to man and other organisms in the environment.[13-16] Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), copper (Cu), iron (Fe) and platinum group of metal.[17] The various anthropogenic activities that introduce the heavy metals in the environment are mining[18-22] and smelting of ores[23], municipal waste [24], burning of fossil fuels[25], industrial effluents[26-28] and agricultural activities.[29]

CONVENTIONAL METHODS FOR HEAVY METAL REMOVAL

Over the last few decades, several methods have been used for the removal of heavy metals from water and waste water. The commonly used procedures for removal of heavy metals from contaminated waste water are chemical precipitation, ultra filtration, ion exchange, reverse osmosis, electro winning, carbon adsorption and phytoremediation.[27]

Chemical precipitation

Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage. Precipitation is used as the treatment method to extract metals ions from solutions by almost 75 percent of plating companies. The most common precipitation methods used by industries are carbonate precipitation, sulphide precipitation and sodium hydroxide precipitation.[27]

Ultra filtration

Ultra filtration is pressure driven membrane operation that uses porous membranes for the removal of heavy metals. The main disadvantage of this process is the generation of sludge. Trivunac and Stevanoic [30] reported that at the best operating condition (pH 9.0) using diethylaminoethyl cellulose, the removal of Cd (II) and Zn (II) more than 95 and 99 %, respectively have been achieved.

Ion-exchange

Ion exchange technologies have been successfully applied by metal finishing industries from several decades. In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. The disadvantages include, high cost and partial removal of certain ions. For large quantities of competing mono and divalent ions Na (I) and Ca (II), ion exchange is almost totally ineffective [27].

Reverse osmosis

Reverse osmosis is usually used in desalination of the water. However, in the past decades a particular effort has been made for the application of reverse osmosis in recovery of concentrated solution of metal salts and to clean up water. In this process heavy metal ions are separated by a semi-permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in the wastewater. The disadvantage of this method is that it is expensive [27, 31].

Electro winning

An electro winning design consists of a rectifier and a reaction chamber containing the electrolyte and electrodes [32]. Metal ions from solutions are reduced on the cathode at a rate that depends on the metal ion concentration in the electrolyte, the current, cathode area and the species of metal being recovered. There is no sludge generation but this technology suffers from many restrictions.

Carbon adsorption

The carbon adsorption method removes the metal contaminants from single phase liquid streams by using granular activated carbon as an adsorbent [33]. Activated carbon consists of amorphous form of carbon that has been treated to increase the surface area or volume ratio of the carbon. Granular activated carbon have some limits such as high cost, water soluble component are not absorbed well and streams with high suspended solids may cause fouling of the carbon and may require a pretreatment.

Phytoremediation

Phytoremediation is the use of certain plants to clean up soil, sediment and water contaminated with metals. Aquatic plants in fresh water, marine and estuarine systems act as receptable for several metals. Gymnosperm, aquatic macrophytes, bryophytes and tree crops exhibiting resistance to metals and with potential to clean up toxic metals in all compartment of atmosphere [34-40]. The disadvantages of phytoremediation methods is that it takes a long time for the removal of metals and the regeneration of the plant for further biosorption is difficult.

Biosorption

The conventional methods include chemical precipitation, ultra filtration, ion exchange, reverse osmosis, electro winning, carbon adsorption and phytoremediation appear to be ineffective or extremely expensive or take long time for heavy metal ion removal from water and industrial waste water. Efforts are presently being made to develop novel technologies that are low cost, eco-friendly and can efficiently remove the metal ions. Alternative technologies termed biosorption have been used in the last twenty years and are based on the metal sorption potential of certain natural and cheap biomasses like algae, fungi, bacteria and waste plant materials.

The biosorption can be defined as the ability of biological material to accumulate heavy metals from waste water through metabolically mediated or physicochemical pathways of uptake. The major advantages of biosorption over conventional treatment methods are low cost, high efficiency, minimization of chemicals, no additional nutrient requirement, regeneration of biosorbent and possibility of metal recovery [41-44]. Recent biosorption experiments have focused attention on waste materials from large scale industrial operations [45-47].

RECENT STUDIES ON THE DEVELOPMENT OF LOW COST ADSORBENTS

Many reports have appeared on the development of low – cost adsorbents prepared from cheaper and readily available materials [48-55]. Solid substance with large surface area, micro porous character and chemical nature of their surface have made them potential adsorbents for the removal of heavy metals from industrial waste water [56]. A number of materials such as leaf mould [57], rice husk [58], groundnut husk [59], coconut husk and palm pressed fibers [60], coconut shell [61], coconut jute [62], coconut tree sawdust [63], cactus, olive stone cake and wool and pine needles [64] have been used as an adsorbent for the removal of the heavy metal ions. Mise and Rajamanya [65] reported the activated carbon derived from *Sorghum vulgare* can be used as an efficient adsorbent for the removal of Cr (VI). Alam [28] et al. studied the removal of copper ion from electrochemical wastewater using economically feasible material (Sand) as an adsorbent. This method of heavy metal removal proved highly effective. The removal efficiency of copper achieved more than 97 percent in the adsorption experiment.

Ayyapan [66] et al. used the batch adsorption study on agro waste for removal of Pb (II). The high removal efficiency of the metal ion is achieved at optimized conditions such as high dose of adsorbent, high pH and low initial concentration of metal ions. The adsorption study of Pb (II) ions from aqueous solutions on wheat bran (WB) as a function of initial concentration, adsorbent dose, adsorbent particle size, agitation speed, temperature, contact time and pH of solution has been investigated by Bulut and Bayasal [67]. The equilibrium process was described well by the Langmuir isotherm model with maximum sorption capacities of 69.0, 80.7 and 87.0 mg /g of Pb (II) on wheat bran at 20, 40 and 60 °C, respectively.

Wantanaphong [68] et al. carried out the biosorption study of copper, lead, zinc and cadmium by using a range of waste products and natural materials including chitin, fly ash, clay soil, cocoa shell, calcified seaweed and the natural zeolite clinoptilolite under batch experiments. All had ability to remove more than 70 % of metals from solution. Dupont [69] et al. studied the biosorption of Cu (II) and Zn (II) onto a lignocellulosic substrate extracted from wheat barn. The sorption capacity of this material was investigated through batch and column experiments. Batch adsorption capacity of lignocellulosic substrate was found 0.20×10^{-3} mol/g at pH 4.5 for the copper and 0.24×10^{-3} mol/g for the zinc.

The tobacco (*Nicotiana tobaccum*) root activated carbon has been prepared from tobacco roots impregnated with 20 percent $ZnCl_2$ and carbonized at 600 °C by Seth and Soni [50]. Its adsorption capacity has been tested for the treatments of waste water containing hexavalent chromium. The removal of chromium in the process has been found to increase with increase in adsorbent dose and contact time. The adsorption data were fitted to Langmuir isotherm model.The copper and zinc sorption on oxidized wheat lignocellulosic extracted from wheat barn is reported by Jolly and coworkers [70]. Oxidizing agents, such as potassium permagnate ($KMnO_4$) or sodium peroxide ($NaIO_4$) create oxygenated functions e.g. alcoholic and carboxylic acid, which increase the density of functional sites and the binding capacity of lignocellulose towards copper and zinc. Oxidized lignocellulose is thus a promising, efficient and cheap biomaterial for the decontamination of wastewater. Devaprasath [71] et al. carried out the adsorption of Cr (VI) on characterized *Prosopis spicegera* as an efficient low cost adsorbent. The removal of the chromium was maximum at pH 2. The equilibrium adsorption data showed significant correlation to Langmuir and Freundlich adsorption isotherm and supported the adsorption of Lagergren first order kinetics.

Aydin [72] et al. has been reported the use of low cost adsorbents for the removal of Cu (II) from aqueous solution. Removal of copper from aqueous solution by different adsorbents such as shell of lentil (LS), wheat (WS), and rice (RS) has been investigated. The maximum adsorption capacities for copper on LS, WS, and RS adsorbents at 293, 313, and 333K temperature was found 8.977, 9.510 and 9.588; 7.391, 16.077, and 17.422 ; 1.854, 2.314 and 2.954 mg/g respectively. An adsorbent prepared from sour sop seeds has been used by Oboh and Aluyor [82] for the removal of Cu (II), Ni (II), Zn (II) and Pb (II) ions. The results obtained for removal of Cu (II), Ni (II), Zn (II) and Pb (II) ions after contact time 120 minutes are 77.6, 68.5, 56.4 and 40.6 percent respectively. Meena [73] et al. reported the removal of Cr (VI), Pb (II), Hg (II) and Cu (II), by treated sawdust (*Acacia arabica*) and the process is found concentration, pH, contact time, adsorbent dose and temperature dependent. Adsorption capacity for treated sawdust recorded for metal ions on treated saw dust are Cr (VI) (11.61 mg/g), Pb (II) (52.38 mg/g), Hg (II) (20.62 mg/g) and Cu (II) (5.64 mg/g), respectively.

Sivamani and Prince [56] considered the adsorption of hexavalent chromium on Pongamia (*Pongamia pinnata*) leaf powder. Crude Pongamia leaf powder (CPLP) and nitric acid treated Pongamia leaf powder (APLP) were used as adsorbents. APLP has remarkable capability for metal uptake than CPLP. The best contact time for both adsorbents was 165 minutes and removal efficiency was best at initial concentration 5 mg/L. The Teak leaves (*Tectona grandis*) are excellent adsorbents for lead removal [83]. These leaves are abundantly found in India as waste material. Adsorption of lead ions was found pH and temperature dependent. Maximum adsorption occurred at pH 5. Batch and packed bed continuous biosorption studies were conducted by Nedumaran [74] and Velan to investigate the kinetics and isotherms of Cu (II) ions on the biomass of blue green alga *Azolla ronpong*. It is observed that the biosorption capacity of algae depends on initial pH and dosage. The biosorption capacity increases with increasing concentration and follows Freundlich isotherm model well with k and n values 0.06223 and 0.949 respectively. The optimum pH of 3.5 with an algae dosage of 1 g/L was observed. Alam [84] et al carried out the batch adsorption study of Zn (II) and Cu (II) on to Clove leaves (*Syzygium aromaticum*). The maximum removal efficiency achieved at optimized conditions of high pH, lower concentration of metal ions and high dose of adsorbent.

The ability of white-rot fungus, *Pycnoporus sanguineus* to adsorb copper (II) ions from aqueous solution was investigated by Yahaya [75] et al. in a batch system. The live fungus cells were immobilized into Ca-alginate gel to study the influence of pH, initial metal ions concentration, biomass loading and temperature on the biosorption capacity. The optimum uptake of Cu (II) ions was observed at pH 5 with a value of 2.76 mg/g. Riaz [76] et al. carried out the studies on biosorptive ability of *Gossypium hirsutum* (Cotton) waste biomass. The smaller size of biosorbent (0.355 mm), higher biomass dose (0.20 g), pH 5 and 100 mg/L initial Pb (II) concentration are found more suitable parameters for increased Pb (II) biosorption from aqueous medium. Mousavi and Seyedi [77] considered the nettle ash as an alternative adsorbent for the removal of nickel (II) and cadmium (II) from wastewater. Batch experiments conducted to determine the factors affecting the adsorption of nickel (II) and cadmium (II). The optimum pH required for maximum adsorption was found to be 6. The data were fitted well to the Langmuir isotherm. The adsorption kinetics was best represented by the pseudo second order model.

The biosorption potential of dried activated sludge as a biosorbent for zinc (II) removal from aqueous solution was investigated by Yang and coworkers [78].The monolayer adsorption capacity of dried activated sludge for zinc (II) was found to be 17.86 mg/g at pH of 5 and 25°C. Yusoff [79] has reported the durian tree dust (DTS), coconut coir (CC) and oil palm empty fruit bunch (EFB) are the efficient adsorbents for the removal of lead from waste water. A good adsorption potential was observed for these adsorbents to remove lead. The constituents of egg shell powder are good adsorbents for the removal of copper and zinc [80]. About 99 percent of copper and zinc are removed by these constituents. Pan [81] considered the leachate of litchi pericarp is an efficient adsorbent for the removal of lead. A high removal efficiency was observed at a temperature 25^0C, a pH of 6-7 and adsorbent dose 10g/L.

CONCLUSIONS

In recent times, attention has been focused on various natural solid supports, which are able to remove heavy metal pollutants from contaminated water at low cost. Cost is actually an important parameter for comparing the abundant materials. Certain waste product from the industries, agricultural operations and natural materials such as leaf mould, coconut husk and palm pressed fibers, coconut tree saw dust and pine needles represents potentially economical alternative.

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