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Heavy Metals Removal from Wastewater using Low-Cost Adsorbents-A Review

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Abstract: Heavy metals toxicity caused by industrial waste water and other natural sources has become threat to environment and ecosystem for the past many decades. Very small concentration of metallic ions present in water increases health problems to living organisms. Although there are various conventional treatment methods such as chemical precipitation, ion exchange, coagulation, flocculation, electrochemical technique, adsorption and co-precipitation are available for removal of heavy metals from aqueous solution. A number of researchers paid their attention towards highly effective and economical biosorption technique for the removal of heavy metals using various inexpensive adsorbents such as agricultural waste material, waste by products of food processing, fruit waste and dead microbial biomass. The use of low cost adsorbents is highly preferable due to the reduced cost of waste disposal and thus leads to environmental protection. In the present review paper, available research work related to use of various adsorbents for the removal of commonly occurring heavy metals have been reported.

Keywords: Biosorption, Heavy metals, Adsorbents, Adsorption.

Introduction

Water is an important source of life, energy and thus is essential element to all living things on earth. The purest form of water is colorless, odorless and tasteless in nature. The level of contaminants has increased due to discharge of industrial effluents in aquatic ecosystems which pollute and contaminate water streams naturally [1]. Water pollution raises a great concern now a days due to rapid industrialization e.g. domestic water, sewage, alley metal mining operations, agricultural waste, fertilizers, feather industries and pesticides which have largely discharged various types of pollutants into environment and cause disorder into ecosystem. However millions of people worldwide are suffering from shortage of fresh and clean drinking water chemicals, paper, petroleum and primarily metal sectors cause about 97% of water contamination. Heavy metal pollution caused by industrial activities and technological development is posing significant threats to environment because of its toxicity, non biodegradability, bioaccumulation and persistent tendency through food chain.

Heavy metals refer to any elements with high atomic weights and high density. These metals are highly toxic even at low concentration. They cause serious problem to human life and to aquatic, vegetation cover [2]. These heavy metals get adsorbed and accumulated in human body causing serious health diseases such as cancer, damaging of nervous system, organ damage and even death. Metals like cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver and titanium are generally found in industrial waste water effluents [3]. These metals get bioaccumulated in the auatic environment and tend to biomagnified along the food chain. As a result, organisms at higher trophic levels are more vulnerable to their toxicity. There are about twenty metals which are almost persistant and cannot be degraded or destroyed. From ecological point of view, mercury (Hg), lead (Pb), cadmium (Cd), chromium (Cr [VI]), Zinc (Zn), arsenic (As), nickel (Ni) etc., are toxic heavy metals [4]. Hence, there is a need to treat heavy metal contaminated water before discharging it into environment. The objective of this review paper is to provide fundamental information about adsorption of heavy metals from aqueous solution on various types of low cost adsorbents including agricultural waste biomass, microbial, synthetic, natural and industrial waste by products etc.

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Methods for Removal of Heavy Metals

Various techniques including precipitation, ion exchange, adsorption, filtration, electrodialysis, reverse osmosis etc. methods are available in literature for removal of heavy metals [5]. These methods are reliable but having certain disadvantages such as use of toxic reagents, high energy requirements, non selective, generation of toxic waste and also require large settling tanks for precipitation of voluminous sludges. Ion exchange method has advantage of allowing recovery of metallic ions, but it is expensive [6]. So, there is a need of safe and economical method for removal of toxic metals. For this purpose, adsorption process is one of the easiest, safest and cost effective processes [7]. Adsorption is a mass transfer process in which a substance is transferred from the liquid phase to the solid surface, and becomes bound by physical and/or chemical interactions [8]. Adsorption is primarily due to attractive interfaces between a surface (adsorbent) and the group being absorbed (adsorbate). Depending upon the nature of intermolecular attractive forces, there could be of physical or chemical adsorption. Physical adsorption involves binding of adsorbate on the adsorbent surface as a result of van der Waals forces of attractions. The electronic structure of the atom or molecule is hardly disturbed upon physical adsorption. On the other hand, chemical adsorption involves chemical reaction between adsorbent and adsorbate which leads to the formation of new ionic and covalent bonds [4]. Therefore this process led to the use of various adsorbents which have been found significant popularity because of their lower production costs, abundance of their ingredients in nature, low cost of their regeneration and further that they can be simply discharged after expiration. Various low cost adsorbents used for removal of heavy metals are described below:-

Adsorption on Natural Materials

Zeolites

These are naturally occurring crystalline alumino silicates minerals. Ion exchanging capacities of zeolites make them a suitable candidate for removal of heavy metals. Among the different varieties of zeolites such as clinoptilolite and chabazite, clinoptilolite has been extensively studied and was shown to have high selectivity for Pb (II), Cd (II), Zn (II) and Cu (II) metals. These zeolites can be modified to enhance their absorption efficiency [9].

Clay

Clays are divided into three categories: kaolinite, montmorillonitesmectite, and mica. The highest cation exchange capacity is found in montmorillonite, which is 20 times less expensive than activated carbon. Their capacity to remove heavy metals is lower than that of zeolites, but their ease of availability and cost-effectiveness compensate for this. Clay-polymer composites could be modified to improve the efficiency of heavy metal removal by clay. [10-12].

Peat Moss

It is complex organic substance which is obtained from residue of sphagnum moss & other water logged plants when partially decomposed. Peat moss was found to be one of effective natural adsorbent for heavy metals. Peat moss plays vital role in removal of heavy metals from industrial waste water like Zinc, copper, chromium [13]. It has been notified by researchers that maximum adsorption efficiency was observed with Peat moss for Cd and Cu it was 39.8mg/g & 1.2mg/g [14].

Adsorption on Industrial waste

There are various industrial waste materials that remove heavy metals from aqueous solution. These are quite easily available as by product of many industries. These industrial wastes are known to be effective adsorbents. Adsorptive capacity of these wastes could be improved by minor processing. Various industrial adsorbents such as fly ash, tea waste, saw dust, blast furnace sludge, lignin- a waste of paper industry, iron (III) hydroxide and red mud have been explored for their efficiency to remove toxic heavy metals from contaminated water. Other industrial wastes including coffee husks, sugar beet pulp, wasted pomace of olive oil, waste biogas residual slurry and grape stalk wastes have been utilized as low-cost adsorbents for the removal of toxic heavy metals from wastewater [4]. Tea waste has gained much attention as tea is second most used beverage in world after water. The cell wall material of tea consists of cellulose, lignin carbohydrates that have hydroxyl, oxyl and phenolic groups and could be a good bio sorbent material for heavy metals. Tea waste is shown to have 7.1% adsorption capacity during removal of Cu metal [15]. Flyash

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is one of residues produced in coal combustion that composed of fine particles that are driven out with flue gases. It is potentially used for water treatment process due to its chemical composition like silica, alumina, and ferric oxide. It is major air pollutant and water pollutant that disturb ecological balance & causes environmental hazards [16]. It has been reported that flyash is one of industrial waste that serves as better adsorbent for removal of Cu with 70% adsorption efficiency & removal of Ni with 68% adsorption efficiency [17].

Adsorption on Agricultural waste
Agricultural residues can be used as adsorbent material in removal of heavy metals as they are less costly, require little processing & possess good adsorption capacity [18]. Some of the agricultural waste adsorbents are discussed below:-

Rice straw
Rice straw is one of the agricultural waste materials used as low cost adsorbent material. Rice straw consists of cellulose (32-47%), hemicelluloses (19-27%), lignin [19] (24%). It is basically left residue in agricultural land during harvesting time which is burnt leading to emission visibility and even causes breathing problems. Rice straw serves as potential adsorbing material possessing efficient binding sites that are capable to remove toxic metals from waste effluents [20].

Sugarcane baggase
It is a waste product obtained from sugar refining industry that has been tested as adsorbent material for heavy metal removal. It consists of cellulose, lignin and pentosan. The negative charge of baggase makes it capable to absorb the postitively charged heavy metal ions. It has been reported that sugarcane baggase was found to be efficient adsorbent for removal of Cu and Ni heavy metals with greater adsorption efficiency about 87%-95% [21, 22].

Banana Peel
Fruit peels like orange peel and banana peel are capable in adsorption of heavy metals as their cell walls are rich in polysaccharides that mainly composed of cellulose and pectin compounds which get ionized on alkaline treatment & generate negative charges which bind metal cations [23]. Annadurai et al., (2003) reported that cellulose based fruit peels like banana and orange peels are (acid and alkali treated) are adsorbent material in adsorption of Cu+2, Zn+2, Co+2, Pb+2 and Ni+2. Banana peel exhibits maximum adsorption capacity for heavy metal removal in comparison to orange peel [24].

The advantages of using agricultural wastes for wastewater treatment include ease of use, minimal processing requirements, superior adsorption ability, selective heavy metal ion adsorption, low cost, cheap availability, and quick regeneration. On the other hand, using untreated agricultural wastes as adsorbents can result in a variety of issues, including low adsorption capacity, increased chemical oxygen demand (COD) and biological chemical demand (BOD), and total organic carbon (TOC) due to the discharge of soluble organic compounds contained in plant materials. Increases in COD, BOD, and TOC can reduce the amount of dissolved oxygen (DO) in water, posing a threat to aquatic life. As a result, plant wastes must be processed or modified before being used for removal of metals [4]. Chemically modified agricultural wastes have been reported to have enhanced chelating efficiency. Wheat bran has been found good adsorbent for removal of heavy metal ions like Cu, Cd. It has been reported that wheat bran on treating with strong dehydrating agent like H2SO4 shows 5% adsorption efficiency for Cu ions, in 51.5mg/g in 30 min at pH value 5, whereas, it was found 12% for Ni ions [25, 26]

Biosorbents
Biosorbents are quite advantageous because of their high effectiveness in heavy metal removal. These can be derived from following sources:

Algae Biosorbent
Algae are one of the autotrophic organisms that has been tested and used as biosorbent material to adsorb toxic heavy metals. Its low cost easy availability with more metal sorption capacity makes it more beneficial biosorbent. It has been reported that with use of spirogyra sp. of algae 14% removal efficiency was observed

for lead [27]. Celekli et al., (2010) observed that spirulina platensis showed 7% removal efficiency for copper metal ion [28].

Bacteria Biosorbent

Bacteria are one of the other categories that have been used as biosorbent material because of its size, ability to grow under controlled conditions [29]. Many bacterial species have been tested for heavy metal removal as they have excellent sorption capacity because of their surface to volume ratio and their active chemosorption sites [30]. The removal efficiency for Cu metal ion was found to be 32.5% with *Enterobactor* species and 17.87% with *Arthrobacter sp*. of bacteria [31]. For the removal of nickel metal ion *E. coli* has been tried out with removal efficiency of 6.9% [32].

Fungal Biosorbents

The fungal kingdom is very diverse, with species growing as unicellular yeasts and or branching hyphae that produce a remorbable array of spores and other reproduction structures. The shape and integrity of gungus is dependent upon mechanical strength of cell wall. The fungal cell wall can make up 30% or more of dry weight of gungus. Fungi can be grown easily and produces large biomass. It shows good metal binding property because of presence of cell wall material in large a quantity Alkali treated biomass of *Aspergillus niger* was used to remove Cd2+, Cu2+, Zn2+, Ni2+ with uptake capacity of upto 10% of its weight [33]. About 4% of Cr (VI) has been removed by using fungi *pencillium purpurogenum* [34]

Conclusion

A review of various low-cost adsorbents presented in this paper showed the effectiveness and potential of the adsorption process by using low-cost adsorbents derived from agro-industrial, dead microorganisms, food processing, and municipal wastes, etc. The use of waste materials as low-cost adsorbents for removing various pollutants from aqueous solutions presents many features, especially their contribution in the reduction of cost for waste disposal, therefore contributing to environmental protection. Technical applicability and cost-effectiveness are the two significant key factors for choosing an effective low-cost adsorbent for heavy metal removal. Although the amount of available literature data on use of low cost adsorbents in water treatment is increasing at tremendous pace, there are still several gaps that need to be filled.

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