

Review Article

A Review on Elimination of Heavy Metals from Wastewater Using Agricultural Wastes as Adsorbents

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Abstract: In this article, the potential of various low-cost adsorbents for the removal of heavy metals from contaminated water has been reviewed. There are various conventional methods for heavy metal removal from wastewater such as precipitation, evaporation, electroplating and also ion-exchange have been applied since previous years. However, these methods have several disadvantages such as only limited to certain concentrations of metals ions, generation large amount of toxic sludge and the capital costs are much too high to be economical. Adsorption is the alternative process for heavy metal removal due to the wide number of natural materials or agricultural wastes gathering in abundance from our environment. In this review, a list of adsorbent has been compiled to provide available information on a wide range of low cost adsorbents for removing heavy metals from wastewater.

Keywords: Adsorption Heavy, Metals Removal, Conventional Methods, Low Cost Adsorbent

1. Introduction

Environmental pollution is currently one of the most important issues facing humanity. It was increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures. Toxic heavy metals are considered one of the pollutants that have direct effect on man and animals. Excessive intake of chromium by human's leads to hepatic and renal damages, capillary damage, and sources is presented by highlighting the applicability of gastrointestinal irritation and central nervous system adsorbents [1].

Water of high quality is essential to human life and water of acceptable quality is essential for agriculture, industrial, domestic and commercial uses. The requirement for water is increasing while slowly all the water resources are becoming unfit for use due to improper waste disposal. The task of providing proper treatment facility for all polluting sources is difficult and also expensive, hence there is pressing demand for innovative technologies which are low cost, require low maintenance and are energy efficient. Various conventional treatments have been applied for removing heavy metals such

as precipitation, ion exchange, and filtration and electrochemical.

The recent worldwide trend to achieve higher environmental standards favors the usage of low cost systems for treatment of effluents. In the meantime various low cost adsorbent derived from agricultural waste or natural products have been extensively investigated for heavy metal removal from contaminated wastewater. It has been found that after chemical or thermal modifications, agricultural waste exhibited tremendous heavy metal removal capability. Concentration of adsorbate, extent of surface modification and adsorbent characteristics are the factors responsible for metal adsorption capability. Cost effectiveness and technical applicability are the two important key factors for selecting effective low cost adsorbent for heavy metal removal [2]. In this article, the technical feasibility of various low-cost adsorbents for heavy metal removal from contaminated water has been reviewed.

2. Relevant Literature

The idea of using various agricultural products and

byproducts for the removal of heavy metal from wastewater has been investigated by number of authors. The advantage of this method compared to other is lower cost involved when organic waste materials are used. Activated carbon adsorption appears to be a particularly competitive and effective process for the removal of heavy metals at trace quantities. However, the use of activated carbon is not suitable for developing countries because of its high cost [3].

2.1. Industrial Wastewater and Heavy Metals

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb). Heavy metals are natural components of the Earth's crust and they cannot be easily degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning [4].

Heavy metals are commonly released in the wastewater from various industries. Electroplating and surface treatment practices leads to creation of considerable quantities of wastewaters containing heavy metals. Apart from this wastewater from leather, tannery, textile, pigment and dyes, paint, wood processing, petroleum refining industries and photographic film production contains significant amount of heavy metals. These heavy metal ions are toxic to both human beings and animals. The toxic metals cause physical discomfort and sometimes life threatening illness and irreversible damage to vital body system [5].

2.2. Adsorption

Adsorption is basically a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions [6]. It is a partition process in which few components of the liquid phase are relocated to the surface of the solid adsorbents. The adsorption procedure can be batch, semi-batch and continuous. Depending upon the types of intermolecular attractive forces adsorption could be of following types:

Physical adsorption- is a process in which binding of adsorbate on the adsorbent surface is caused by van der Waals forces of attraction. The electronic structure of the atom or molecule is hardly disturbed upon physical adsorption. Physical adsorption can only be observed in the environment of low temperature and under appropriate conditions, gas phase molecules can form multilayer adsorption.

Chemical adsorption- it is a kind of adsorption which involves a chemical reaction between the adsorbent and the adsorbate. The strong interaction between the adsorbate and the substrate surface creates new types of electronic bonds. Chemical adsorption is also referred as activated adsorption. The adsorbate can form a monolayer. It is utilized in catalytic

operations.

2.3. Low Cost Adsorbents

In general, an adsorbent can be assumed as "low-cost" if it requires a little bit processing, is abundant in nature, or is a by-product or a waste from an industry. Natural material or certain waste from industrial or agricultural operation is one of the resources for low cost adsorbents. Generally, these materials are locally and easily available in large quantities [7].

Seeds as Biosorbent

Litchi chinensis seeds were indicated as an effective biosorbent for Ni removal from aqueous solutions [8]. *Jantrophia curcas L.* Seed's hull has been investigated for Cd(II) and Zn(II) metals ions' removal from aqueous solution [9]. *Strychnos potatorum* seeds have been investigated by [10] to remove Cd(II) from aqueous solution.

Shells and Husks as Biosorbent

Chromium adsorption in water was studied by [11] using *Moringa oleifera* husks. The husk of a black gram (*Cicer arietinum*) was investigated as a new biosorbent of Cd(II) from low concentration aqueous solutions [12]. Moreover, the removal and recovery of Cd(II) from waste waters using a rice husk have studied by [13].

2.4. Some Agricultural Adsorbents for the Removal of Heavy Metals from Wastewater

2.4.1. Rice Husk

Rice husk is an agricultural waste material generated in rice producing countries, especially in Asia. The annual world rice production is approximately 500 million metric tons, of which 10-20% is rice husk. Dry rice husk contains 70 - 85% of organic matter (lignin, cellulose, sugars, etc) and the remainder consists of silica, which is present in the cellular membrane [14]. The rapid uptake and high adsorption capacity make it a very attractive alternative adsorption material. The high removals for red dyestuff-treated husk are on lead (II) and cadmium (II) at 99.8% and 99.2% respectively, for yellow dyestuff-treated husk are on lead (II) and mercury (II) at 100% and 93.3% respectively. At optimal conditions, chromium, zinc, copper and cadmium ion removals from aqueous solution are 79%, 85%, 80% and 85% respectively [15]. The kinetic removal in batch experiment shows that the net uptake of Pb, Cd, Cu, and Zn was 54.3%, 8.24%, 51.4% and 56.7%, respectively whereas using rice husk carbon, while it varied as 74.04%, 43.4%, 70.08% and 77.2% for the same dosages of rice husk ash [16].

2.4.2. Sugarcane Bagasse

Bagasse pitch is a waste product from sugar refining industry. Removal of Cd(II) and Zn(II) is found to increase as pH increases beyond 2 and at pH > 8.0 the uptake is 100% [17]. It is also evident that the sorption affinity of the derived activated carbon towards Cd(II) and Zn(II) is comparable or better than other available adsorbents. According to [18] reported that at an adsorbent dose of 0.8 g/50 ml is sufficient to remove 80-100% Cr(VI) from aqueous solution having an initial metal concentration of 20 mg/l at a pH value of 1 and

less than 15% at pH 3.

Table 1. Types of rice husk as adsorbent for heavy metal removal.

adsorbent	Removal Efficiency (%)				Reference
	Cr(VI)	Cu(II)	Zn(II)	Cd(II)	
Rice husk carbon	>90	-	-	-	[19]
Rice husk (water and HCl washed)	79	80	85	85	[15]
Phosphate treated rice husk	-	-	-	>90	[13]
Raw rice husk	66	-	-	-	[20]

2.4.3. Saw Dust

Phosphate treated showed remarkable increase in sorption capacity of Cr (VI) as compared to untreated sawdust. The adsorption process was found to be pH dependent. Total (100%) adsorption of Cr (VI) was observed in the pH range < 2 for the initial Cr (VI) Concentration of 8-50 mg/l. The adsorbed Cr (VI) on phosphate treated saw dust was also recovered (87%) using 0.01 M sodium hydroxide [21]. A research group has carried out a comprehensive study on treated and untreated saw dust and the initial adsorption was observed to be very fast. Popular Romanian fir tree sawdust (*Abies alba*) was investigated as biosorbant for Cd (II) removal from synthetic aqueous solution and showed good results [22].

2.4.4. Mangifera Indica (Mango)

Mango seed and seed shell powders were studied for their possible application in the removal of Cu(II) from wastewater. The adsorption of Cu(II) on the powder of mango seeds and seed shell was found maximum at pH 6. The total adsorption on each adsorbent increased with the increase in temperature between 30-50°C and then decreased up to 60°C. Moreover, it was found that the seed shell of mango had higher sorption capacity than that of the seed powder for Cu(II) [23].

2.4.5. The Fruit Peel of Orange (Citrus Reticulate)

The extent of removal of Ni(II) was found to be dependent on sorbent dose, initial concentration, pH and temperature. The adsorption followed first order Kinetics. The process was found to be endothermic showing monolayer adsorption of Ni (II) with a maximum adsorption of 96% at 50°C for an initial concentration of 50 mg/l at pH 6 [24].

Table 2. Types of agricultural waste adsorbent and its removal efficiency (%).

Adsorbent	Removal Efficiency (%)						Reference
	Cd(II)	Cr(VI)	Hg(II)	Pb(II)	Ni(II)	CU(II)	
Silk cotton carbon	-	-	100	-	64	-	[25]
Maize cob carbon	-	-	100	-	84	-	[25]
Banana pitch carbon	-	-	100	-	100	-	[25]
Coconut husk	-	>80	100	-	-	-	[26]

Table 3. Types of agricultural waste adsorbent and its adsorption capacity (mg/g).

Adsorbent	Adsorption capacity(mg/g)					Reference
	Cd(II)	Cr(VI)	Hg(II)	Pb(II)	CU(II)	
Waste tea	1.63	1.55	-	-	-	[27]
Walnutshell	1.5	1.33	-	-	-	[27]
Redwood bark	27.6	-	250	6.8	-	[28]
Dry redwood leave	-	-	175	-	-	[28]
Moss	46.5	-	-	-	-	[29]
Rice husk ash	20.24	-	66.66	-	-	[30]

3. Conclusion

A review of various agricultural adsorbents presented herein shows a great potential for the removal of heavy metals from wastewater. The sorption capacity is dependent on the type of the adsorbent investigated and the nature of wastewater treated. The use of commercially available activated carbon for the removal of the heavy metals can be replaced by the utilization of inexpensive, effective, and readily available agricultural by-products as adsorbents. As presented above various agricultural adsorbents show a high degree of removal efficiency for heavy metals such as chromium, nickel, lead, copper, mercury, zinc, cadmium etc.

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