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# Heavy Metal Removal from Wastewater Using Low Cost Adsorbents

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## Abstract

With the onset of industrialization mankind has witnessed various environmental issues in the society. This industrialization has not only brought development and prosperity but eventually disturbed the ecosystem. One of the impacts is visible, in form of water pollution. In the present study heavy metal contamination of water bodies has been discussed. Effluents from large number of industries viz., electroplating, leather, tannery, textile, pigment & dyes, paint, wood processing, petroleum refining, photographic film production etc., contains significant amount of heavy metals in their wastewater. The conventional methods of treatment of heavy metal contamination includes chemical precipitation, chemical oxidation, ion exchange, membrane separation, reverse osmosis, electro dialysis etc. These methods are costly, energy intensive and often associated with generation of toxic byproducts. Thus, the adsorption has been investigated as a cost effective method of removal of heavy metals from wastewater. In the present study various low cost adsorbent has been reviewed as an abatement of heavy metal pollution from wastewater. These adsorbent includes materials of natural origin like zeolites, clay, peat moss and chitin are found to be an effective agent for removal of toxic heavy metals like Pb, Cd, Zn, Cu, Ni, Hg, Cr etc. Apart from these various agricultural wastes like rice husk, neem bark, black gram, waste tea; Turkish coffee, walnut shell etc. were also established as a potent adsorbent for heavy metal removal. Beside that low cost industrial by products like fly ash, blast furnace sludge, waste slurry, lignin, iron (III) hydroxide and red mud, coffee husks, Areca waste, tea factory waste, sugar beet pulp, battery industry waste, sea nodule residue and grape stalk wastes have been explored for their technical feasibility to remove toxic heavy metals from contaminated water.

**Keywords:** Agricultural waste; Heavy metal; Low cost adsorbent; Wastewater; Toxicity

## Introduction

Water pollution caused due to addition of heavy metals resulting from the industrial activities is increasing tremendously and is a matter of global concern. Mining, mineral processing and metallurgical operations are generating effluents containing heavy metals. The heavy metals present in the wastewater is persistent and non degradable in nature. Moreover, they are soluble in aquatic environment and thus can be easily absorbed by living cells. Thus, by entering the food chain, they can be bioaccumulated and biomagnified in higher trophic levels also. The heavy metals, if absorbed above the permissible labels, could lead to serious health disorders. In light of the facts, treatment of heavy metals containing industrial effluent becomes quite necessary before being discharged into the environment. The scientists and environmental engineers are therefore facing a tough task of cost effective treatment of wastewater containing heavy metals. The conventional methods for heavy metal removal from wastewater includes chemical precipitation, chemical oxidation, ion exchange, membrane separation, reverse osmosis, electro dialysis etc. These methods are not very effective, are costly and require high energy input. They are associated with generation of toxic sludge, disposal of which renders it expensive and non ecofriendly in nature. In the recent past, number of approaches has been investigated for safe and economical treatment of heavy metal laden wastewater. Adsorption has emerged out to be better alternative treatment methods. It is said to be effective and economical because of its relatively low cost. Authors have claimed adsorption to be easiest, safest and most cost-effective methods for the treatment of waste effluents containing heavy metals [1,2]. The key benefit of adsorption method for heavy metal removal is less initial as well as operation cost, unproblematic design and less requirement of control systems [3]. Generally the heavy metals are present in the wastewater at low concentrations and adsorption is suitable even when the metal ions are present at concentrations as low as 1 mg/L. This makes adsorption an economical and favorable technology for heavy metal removal from wastewater. The adsorbent may be of mineral, organic or biological origin. It could be zeolites, industrial byproducts, agricultural waste, biomass and polymeric material. One of the conventional adsorbent, activated carbon has been extensively used in many applications. However, the high cost effectiveness of activation processes limits its usage in wastewater treatment processes. The present research activity aims toward contributing in the search for cost effective or low cost adsorbents of natural origin and their applicability in recovery as well as removal of heavy metals from the industrial wastewater.

## Industrial Wastewater and Heavy Metals

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 (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver and titanium). Apart from this wastewater from leather, tannery, textile, pigment & 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 [4]. The metals get bioaccumulated in the auatic environment and tend to biomagnified along the food chain.

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Thus, the organisms at higher trophic level are more susceptible to be affected by their toxicity. There are 20 metals which are almost persistant and cannot be degraded or destroyed. Mercury (Hg), lead (Pb), cadmium (Cd), chromium (Cr [VI]), Zinc (Zn), Arsenic (As), Nickel (Ni) etc., are toxic heavy metals from ecotoxicoligal point of view. The table below shows Maximum Contaminant Level (MCL) standards for some heavy metals established by USEPA [5]. These heavy metals can lead to serious effects such as stunted growth, damage to vital organs, damage to brain, cancer and in some cases death also. Health hazard related to heavy metal toxicity are not new. Human diseases like minamata, itai itai, fluorosis, Arsenicosis etc. are due to heavy metal ingestion above permissible levels. Treating the industrial effluents contaminated with heavy metals within the industrial premises before being discharged is efficient way to remove heavy metals rather than treating high volumes of wastewater in a general sewage treatment plant. Thus it is advantageous to develop separate handling modus operandi for removal of heavy metals from the industrial effluents. The current work focuses on study of natural coagulants as an effective and economical alternative treatment process for heavy metals removal from industrial wastewater. (Table 1)

## Adsorption

As discussed earlier, adsorption has emerged out as effective, economical and ecofriendly treatment technique. It is a process potent enough to fulfill water reuse obligation and high effluent standards in the industries. 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 [5]. It is a partition process in which few components of the liquid phase are relocated to the surface of the solid adsorbents. All adsorption methods are reliant on solid-liquid equilibrium and on mass transfer rates. The adsorption procedure can be batch, semi-batch and continuous. At molecular level, adsorption is mainly due to attractive interfaces between a surface and the group being absorbed. Depending upon the types of intermolecular attractive forces adsorption could be of following types:

### Physical adsorption

It is a general incident and occurs in any solid/liquid or solid/gas system. 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. Van der Waals forces originate from the interactions between induced, permanent or transient electric dipoles. Physical adsorption can only be observed in the environment of low temperature and under appropriate conditions, gas phase molecules can form multilayer adsorption. Commercial adsorbents utilize physical adsorption for its surface binding.

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

**Table 1:** The MCL standards for the most hazardous heavy metals [5].

### 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 (Covalent, Ionic). Chemical adsorption is also referred as activated adsorption. The adsorbate can form a monolayer. It is utilized in catalytic operations.

In general, the main steps involved in adsorption of pollutants on solid adsorbent are:

Transport of the pollutant from bulk solution to external surface of the adsorbent.

Internal mass transfer by pore diffusion from outer surface of adsorbent to the inner surface of porous structure.

Adsorption of adsorbate on the active sites of the pores of adsorbent.

The overall rate of adsorption is decided by either film formation or intra particle diffusion or both as the last step of adsorption are rapid as compared to the remaining two steps.

### Low Cost Adsorbents

The removal of heavy metals by using low cost adsorbent is found to be more encouraging in extended terms as there are several materials existing locally and profusely such as natural materials, agricultural wastes or industrial by-products which can be utilized as low-cost adsorbents [6]. To be commercially viable, an adsorbent should have high selectivity to facilitate quick separations, favorable transport and kinetic characteristics, thermal and chemical stability, mechanical strength, resistance to fouling, regeneration capacity and low solubility in the liquid in contact. Adsorption process has several advantages over the conventional methods of heavy metal removal. Some of the gains of adsorption process are: (I) Economical, (II) metal selectivity, (III) Regenerative, (IV) Absence of toxic sludge generation (V) metal recovery and most importantly (VI) effective. Various low cost adsorbent derived from various natural as well as anthropogenic sources have been implemented for treatment of waste water contaminated with heavy metals. The adsorbents mostly used are agricultural waste, industrial byproducts, natural materials or modified biopolymers.

## Adsorption by Natural Materials

### Zeolites

They are naturally occurring crystalline alumino silicates consisting of a skeleton of tetrahedral molecules, connected with each other by mutual oxygen atoms. Ion exchanging capacities of zeolites make them a suitable candidate for removal of heavy metals. Adsorption in zeolites is in fact a choosy and reversible packing of crystal cages, so surface area is not a significant aspect. Zeolites consist of a wide variety of species such as clinoptilolite and chabazite. Among the different zeolites, clinoptilolite has been extensively studied and was shown to have high selectivity for metals like Pb (II), Cd (II), Zn (II)

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and cu (II). Several zeolites are modified during the past few years to increase their efficiency. Clinoptilolite was found to be more effectively removing heavy metals owing to its ion exchange capability, followed by pretreatment [5,7].

### Clay

There are three main groups of clays: kaolinite, montmorillonite-smectite, and mica. The montmorillonite has the highest cation exchange capacity and its recent market price is found to be 20 times cheaper as compared to activated carbon. Their heavy metals removal capacity is less as compared to zeolites but their easy availability and economical properties give back their less efficiency. Efficiency for heavy metal removal by clay could be improved by modifying them to clay-polymer composites [8-10].

### Peat moss

Abundant in nature and has a very high organic content. Its large surface area (≥ 200 $m^2/g$) and high porosity makes it an effective agent for heavy metal removal from wastewater. It was observed that peat moss plays an important role in treatment of metal-bearing industrial effluents such as $Cu^{2+}$, $Cd^{2+}$, $Zn^{2+}$ and $Ni^{2+}$ [11]. The adsorption capacity of sphagnum peat moss was found to be 132 mg of $Cr^{6+}$/g at a pH range of 1.5-3.0. The most striking benefit of this adsorbent in treatment is the easiness of the system, low cost, and the capability to acknowledge a wide variation of effluent composition [12].

Chitin: It is the second most abundant natural biopolymer followed by cellulose. Chitin is a long-chain polymer of a *N*-acetylglucosamine, a derivative of glucose. It is the main component of the cell walls of fungi, the exoskeletons of arthropods such as crustaceans (e.g., crabs, lobsters and shrimps) and insects, the radulas of mollusks, and the beaks and internal shells of cephalopods, including squid and octopuses. It has been used for removal of several heavy metals in the past. Currently, chitosan, which is produced by alkaline N-deacetylation of chitin, is drawing an increased amount of research interest for its heavy metal removal capability due to chelating property. It can be made by treating shrimp and other crustacean shells with the alkali sodium hydroxide. Chitosan has been used for treatment of $Hg^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Cr^{6+}$, $Cd^{2+}$ and $Pb^{2+}$.

## Adsorption by Agricultural Wastes

Use of agricultural byproducts as adsorbents for heavy metal removal from industrial waste water has been increasing nowadays. Most of the studies were focused on plant wastes such as rice husk and neem bark [13,14], Black gram husk [15], Waste tea, Turkish coffee, Walnut shell [16] etc. Some more adsorbents like papaya wood [17], maize leaf [18], teak leaf powder [19], coraindrum sativum [20], lalang (Imperata cylindrica) leaf powder [21], peanut hull pellets [22], sago waste [23], saltbush (Atriplex canescens) leaves [24,25], tree fern [26-28], grape stalk wastes [29], etc. are also studied in detail. The benefits of using agricultural wastes for wastewater treatment include easy technique, needs modest processing, superior adsorption ability, selective adsorption of heavy metal ions, economical, easy availability and easy regeneration. On the other hand, the use of untreated agricultural wastes as adsorbents can also fetch a number of problems such as small adsorption ability, elevated chemical oxygen demand (COD) and biological chemical demand (BOD) as well as total organic carbon (TOC) due to discharge of soluble organic compounds contained in the plant materials [30,31]. The increase of the COD, BOD and TOC can cause diminution of dissolved oxygen (DO) content in water and can make threats to the aquatic life. Consequently, plant wastes require to be modified or treated ahead of being applied for the cleansing of heavy metals.

New products such as jackfruit, rice husk, pecan shells, hazenut shell, maize cob or husk are also used for adsorbent for heavy metal elimination after chemical modifications. Chemically modified agricultural wastes have been found to have enhanced chelating efficiency. Wheat bran, a by-product of wheat milling industries proved to be a good adsorbent for removal of many types of heavy metal ions which eventually results in better efficiency of adsorption of copper ions as reported by O zer et al. [32]**.** Orange peel has been used for Ni (II) removal from simulated wastewater [33]. Similarly, Adsorption of divalent heavy metal ions particularly Cu2+, Zn2+, Co2+, Ni2+ and Pb2+ onto acid and alkali treated banana and orange peels was performed by Annadurai et al. in 2002 [34]. Activated Coconut shell carbon powder (ACSCP) and Activated charcoal powder (ACP) is used as adsorbent for removal of Lead from electrochemical industry effluent [35]. There are several other examples of chemically modified agricultural wastes also. Moreover, factors like pH, temperature, contact period, initial concentration of metal, agitation rate, dosage of adsorbent etc. affects the adsorption capacity [36].

## Adsorption by Industrial Wastes

Various industrial wastes have also got adsorption capacity and can be used for adsorbing heavy metals from wastewater. These industrial wastes are produced as a by-product and are used rarely for any purpose. The by-product nature renders it to be easily available and very economical also. These industrial wastes are found to have good application as adsorbent. Adsorptive capacity of these wastes could be increased followed by slight processing. Industrial by-products such as fly ash [37,38], blast furnace sludge [39,40], waste slurry, lignin-a black liquor waste of paper industry [41,42,43], iron (III) hydroxide [44,45] and red mud [46,47] have been explored for their technical feasibility to remove toxic heavy metals from contaminated water. Other industrial wastes, coffee husks [48], Areca waste [49], tea factory waste [50], sugar beet pulp [51], waste pomace of olive oil factory waste [52], battery industry waste, waste biogas residual slurry [53], sea nodule residue [54] and grape stalk wastes [29] have been utilized as low-cost adsorbents for the removal of toxic heavy metals from wastewater. Several adsorbents have been used for adsorption of Zinc from waste water. Some of the highest adsorption capacities reported for Zn2+ are 168 mg/g powdered waste sludge, 128.8 mg/g dried marine green macroalgae, 73.2mg/g lignin, 55.82mg/g cassava waste, and 52.91mg/g bentonite [55].

## Conclusion

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.

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