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Adsorption of Heavy Metals: A review

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ABSTRACT

This study reviews, available technologies that can help small scale industries to remove heavy metals from industrial wastewater, different plant materials used as natural, easily available, low cost adsorbents, factors which affects adsorption process and acid or alkali modified adsorbents to enhance adsorption. The literature survey reveals that low cost plant materials are widely used for removal of heavy metals from aqueous solution and industrial wastewater. This review also gives some outlines of basic principles of adsorption technique and the adsorption process.

Keywords: Adsorption, Heavy metals, Low cost materials, Industrial wastewater.

INTRODUCTION

Water is the principal need of life on earth, and is an essential component for all forms of lives, from micro-organism to man. The unplanned urbanization and industrialization [1] has resulted in over use of environment in particular of water resource[2]. A kind of crises situation has made getting clean water a serious problem. It is a known fact that when pure water is polluted its normal functioning and properties are affected [3]. It has been also estimated that only 0.00192% of the total water on the earth is useful for human consumption Hence for highlighting the issue UNGA (United Nations General Assembly) celebrated the decade 1981-1990 as “International Drinking Water Supply and Sanitation Decade” [4,5**].** International World Water Day is held annually on 22nd March as a means of focusing attention on the importance of freshwater and advocating for the sustainable management of freshwater resources. An international day to celebrate freshwater was recommended at the 1992 United Nations Conference on Environment and Development (UNCED). The United Nations General Assembly responded by designating 22nd March 1993 as the first World Water Day. Each year, World Water Day highlights a specific aspect of freshwater.

The objective of World Water Day was to focus international attention on the impact of rapid urban population growth, industrialization and uncertainties caused by climate change, conflicts and natural disasters on urban water systems. The theme, Water for cities: responding to the urban challenge, aimed to spotlight and encourage governments, organizations, communities, and individuals to actively engage in addressing the challenges of urban water management.

Water quality assessment is one of the prime concern and a major challenge in all over the world. Needless to say water quality criteria is directly related to the health factors. Water quality determines the 'goodness' of water for particular purposes. Water quality tests gives information about the health of the waterway [6].

Several states in the India are facing problems due to over exploitation of ground water resources and pollution of surface water. Its manifestations are declining per capita water availability, falling water tables and deterioration of water quality. Unfortunately, the inability of the authorities to keep a check on the issue is also to blame for this state of affairs. In Maharashtra state of India there is acute scarcity of water due to drought and can also be attributed to the steep growth in population due to rapid urbanization and industrial development of cities has increased the demand of water manifold. As pollutants, heavy metals were intensively studied due to their significance from the point of view of persistence and toxicity. These toxic metals can cause accumulative poisoning, cancer and brain damage when found above the tolerance levels [7]. The agencies for the environmental monitoring have set permissible limits for heavy metals levels in drinking water because of their harmful effects. The removal and rapid decontamination of heavy metals (Cd, Pb, Cu, and Hg) become very important for the environmental remediation. Many processes have been used for the removal of heavy metals from waste waters, such as chemical precipitation, coagulation, solvent extraction, membrane separation, ion exchange and adsorption [8].

For dilute metal concentrations, ion exchange, reverse osmosis and adsorption can be applied [9]. However, the common use of ion exchange and reverse osmosis is restricted by the high operating cost. As an alternative to chemical precipitation, membrane filtration, or ion exchange, adsorption processes with wide variety adsorbents have been tested. The adsorbents used should have some specific properties, such as a high ability to reduce the concentration of heavy metals below the acceptable limits, high adsorption capacity and long lifetime [10]. Thus, it is a continuing need to identify and develop low-cost and efficient adsorbents for facile and efficient removal process. Heavy metal adsorption was studied on various adsorbents such as activated carbon [11]. fly ash [12] and bioadsorbents (adsorbents from plant and animal-origin materials, for example bark/tannin-rich materials, humus, peat moss, modified cotton and wool, chitin, chitosan, seaweed, and biopolymers) [13-15].

Generally we use very small water for drinking and cooking and remaining water for other purposes like bathing, cleaning, flushing toilets etc. So the use of recycled wastewater for irrigation, industry, landscaping and toilet flushing is a good way to conserve our fresh water resources. Recycled wastewater can also be used for recharging ground water and for ecosystems. The most concerned environmental pollutions are air pollution and wastewater pollution. Wastewater pollution comes from the industrial effluent and also from the domestic sewage etc. The presence of toxic metals ions in industrial waste has attracted worldwide attention. Heavy metals when discharged into water bodies through wastes also affects the aquatic life and destroy their self-purification power [16].Hence it is necessary to remove these heavy metals from industrial wastewater before discharging into water bodies. Many researchers are working on to develop suitable technologies either to prevent heavy metal pollution or to reduce it to very low level. Some heavy metals which are generally found in Industrial wastewater are discussed in Table1. Heavy metal pollution can be controlled by controlling discharge into water bodies like rivers, lakes etc.or by their removal from wastewater by different techniques. Many methods are available for the removal of heavy metals from wastewater. The methods are classified into biological, chemical and physical. The major method of wastewater treatment involves physical and chemical processes. They have advantages and disadvantages because of high cost and disposal problems. A combination of different processes is often used to achieve the desired water quality in the most economical way [24]. Chemical methods involve electro flotation, conventional oxidation methods by oxidizing agents, irradiation, electro chemical processes, coagulation and electro kinetic coagulation. These chemical methods are very costly and have disposal problems. So these methods are commercially unattractive even though they are efficient for removal of heavy metals from the contaminated water. The high consumption of chemical reagents and high electrical energy requirement are the common problems for these methods.

Table1.

Heavy metal	**MPL ($mg\ L^{-1}$)**	**Source**	**Adverse effects**	**Reference**
Chromium	0.05	Leather,tanning,textile, dyeing, electroplating industries	Carcinogenic, liver damage, skin irritation,ulcer,edema	[17]
Lead	0.05	lead paint, Batteries manufacturing, printing , glass industries	Destruction in kidney, reproductive system, liver, brain and central nervous system, anemia, headache	[18]
Arsenic	0.06	Pesticides, fertilizers, metallurgical, dyes, detergents,glasswares, ceramic industries	Vomiting , diarrhea, black foot disease, cancer	[19]
Copper	2.0	Electroplating, PCB designing, as contaminant in food especially shellfish, liver, mushroom, nuts chocolate	Carcinogenic, Hemochromatosis , gastrointestinal problems, accumulation in the kidneys, brain, skin, heart	[20]
Nickel	0.1	Electroplating, Batteries manufacturing,mining,metal finishing and forging	Damage to lungs,kidneys,vomiting, diarrhoea,skin dermatitis	[21], [22]

Mercury	0.1	Paints, pulp and paper, oil refining, rubber processing, fertilizer batteries, thermometers, fluorescent light tubes, high intensity street lamps, pesticides, cosmetics and pharmaceuticals industries	Teratogenic effects, Children suffer from mental retardation, cerebral palsy and convulsions, genetic defects causing chromosome breaking, chest pain	[23]

Physical methods involved are membrane filtration and adsorption. Membrane filtration methods are reverse osmosis, nanofiltration, electro dialysis etc. Limited lifetime of membrane is major disadvantage of this method. Following are the physicochemical and biological techniques have been studied for the removal of heavy metals from industrial wastewater(table2) [25, 26].

Table 2.

Technique	**Disadvantages**	**Advantages**
Ion exchange	Expensive, Sensitive to particles	Effective, Metal recovery
Reverse Osmosis	High pressures, Membrane scaling, Expensive	Pure effluent
Chemical precipitation	For high concentrations, Difficult separations, Generates sledges	Simple, Cheap
Evaporation	Expensive, Generates sludge's	Pure effluent
Chemical oxidation/reduction	Chemicals required	Mineralization
Electrochemical	For high concentrations, Expensive	Metal recovery

Electrodialysis	Formation of metal hydroxides which clog the membrane, Expensive	Pure effluent

Adsorption: The phenomenon of accumulation of chemical substances at the surface of a solid is called adsorption. The process of removal of an adsorbed substance from the surface is known as desorption. It is the reverse of adsorption. Adsorption is one of the most popular techniques for the removal of heavy metals from wastewater. As the proper design of the adsorption process will produce high quality treated water. This method provides an important and attractive alternative for treatment of wastewater, when the adsorbent is cheap (low cost) and does not require any additional pretreatment step before application. Adsorption has been found to be superior method as compared to the other methods for the removal of heavy metals from the wastewater due to- Low cost, Regeneration of adsorbent, High efficiency, Minimization of chemical and/ or biological sludge, Possibility of metal recovery [27]. The process is suitable even when the metal ions are present in concentration as low as 1mg L^{-1} [16]. Flexibility and simplicity of design, Easy to operate and Insensitivity to toxic pollutants.

The attachment of atoms or molecules of adsorbate on the surface of solids and liquids may be through two types of forces, physical or chemical. Depending upon the types of forces involved in adsorption, it may be divided into two types- Physical adsorption or physisorption and Chemical adsorption or chemisorption.

Theories of adsorption:

(1) Langmuir isotherm: Langmuir supposed that because of rapid failing of intermolecular forces with distance, it is probable that adsorbed layer is no more than a single molecule in thickness. The view is extensively accepted for adsorption at low pressures or at moderately high temperatures. For the solid-liquid interface the saturated monolayer can be represented by the following expression:

$$\frac{C_e}{Q_e} = \frac{1}{Q^o b} + \frac{C_e}{Q^o} \qquad \text{………. (1)}$$

Where Q_e is the adsorbed at equilibrium (mg/gm), Q^0 and b are Langmuir constants related to capacity (mg/gm) and energy of adsorption (L/gm) respectively. The values of Q^0 and b are calculated from the slope and intercept of plot of Ce/Q_e vs. Ce, respectively [28]. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter R_L which is defined as [29].

$$R_L = \frac{1}{1+bC_o} \qquad \text{………. (2)}$$

Where C_o is initial concentration in ppm and *b* is Langmuir constant. R_L is indicative of the nature of the isotherm and is enlisted below as [30],

R_L Value	Type of Isotherm
R_L>1	Unfavorable
R_L = 1	Linear

O < R_L<1	Favorable
R_L = O	Irreversible

(2) Freundlich isotherm: It can be expressed by a general form of the adsorption equation [29],

$$\frac{v}{v_m} = bp^{1/n} \quad .... (3)$$

This is known as the Freundlich equation, which is followed only at medium pressures. The equation is of greater significance for chemisorptions although some Physical adsorption has also been explained using this equation. For adsorption from solution phase, the equation can be written as,

$$\frac{v}{v_m} = \frac{x}{m} = k_f c_e 1/n = \pi r^2 \quad .... (4)$$

Where c_e is the equilibrium concentration (mg/L), k_f is the adsorption capacity (mg/gm (L/gm))$^{1/n}$ and x/m is the amount adsorbed per unit mass of the adsorbent. The constant n is the Freundlich equation constant (adsorption intensity) that represents the parameter characterizing quasi-Gaussian energetic heterogeneity of the adsorption surface. The equation can be written in the linear form as, [31]

$$ln\,\frac{x}{m} = lnk_f + \frac{1}{n} lnc_e \quad .... (5)$$

A plot of $\ln \frac{x}{m}$ against $\ln c_e$ gives a straight line with an intercept on the ordinate axis. The values of *n* and k_f can be obtained from the slope and the intercept of the linear plot. The value of n is greater than unity (1< n < 10), that mean favorable adsorption [32].

Thermodynamic parameters: The thermodynamic parameters, such as Gibbs energy *(*ΔG), the enthalpy change (ΔH) and the entropy change *(*ΔS) for the adsorption were calculated by using the following equations [33],

$$\Delta G = -RTlnk_d \quad .... (6)$$

$$\text{Where } \Delta G = \Delta H - T\,\Delta S \quad .... (7)$$

After integration and rearrangements the above equation gives,

$$lnK_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad .... (8)$$

Where *T* is the absolute temperature in Kelvin (*K*), *R* is the gas constant (8.314 J/ mol) and K_d is distribution coefficient for the adsorption (cm^3/ gm). The values of ΔH and ΔS were determined from the slopes and intercepts of the plots of *log* K_d versus *1/T* [34].The Gibbs free energy change indicates the degree of spontaneity of the adsorption process; the negative value of ΔG suggested that adsorption is a spontaneous process [30]. The positive value of ΔH suggest the endothermic nature of adsorption, while the negative value of ΔH shows the exothermic nature of adsorption [30].

Factors affecting on adsorption of Heavy Metals: The adsorption is affected by several factors such as contact time, amount of adsorbent, temperature, concentration of adsorbate, pH of solution, etc.

Effect of amount of adsorbent: Effect of amount of adsorbent plays an important role in standardizing the adsorption process with quantification of adsorbate solution and the adsorbent. With increase in the amount of adsorbent the removal efficiency increases rapidly which may be attributed to the greater availability of the exchangeable sites or surface areas at higher concentration of the adsorbent [35].

Effect of contact time: Contact time is very important parameter for the application of adsorption process. Kinetics of the adsorption process is studied with the help of this parameter.

Effect of pH: The removal of heavy metals from wastewater by adsorption is dependent on the pH of solution; the variation of pH can affect the surface charge of the adsorbent, the degree of ionization and species of adsorbate [36].

Effect of Initial Concentration of metal ions: The efficiency and feasibility of a adsorption not only depends on the properties of the adsorbents but also on the initial concentration of the metal ion solution. The initial concentration of metal ions provides an important driving force to overcome all the mass transfer resistances of the metal between aqueous and solid phase [37]. The decrease in the adsorption capacity with increase in the concentration of metal ion may be attributed to the availability of smaller number of surface sites on the adsorbents for a relatively larger number of adsorbing species at higher concentration. The increase in metal ion concentration, also increases electrostatic interaction between the metal ion and adsorbent active sites and can be explained by the fact that more adsorption sites were covered as the metal ion increases [37].

Effect of temperature: With increase in temperature metal removal increases. This may be probably due to a decrease in the escaping tendency of the adsorbate species from the surface of the adsorbent. With the purpose of understanding the effect of temperature on adsorption process, thermodynamic parameters such as change in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) should be determined. ΔH and ΔS can be calculated from the slope and intercept of Van't Hoff, the plot *ln K* versus *1/T* [38].The positive value of ΔH, indicating the process of metal adsorption is endothermic in nature. While the positive value of ΔS suggests an increase in disorder at the solid–liquid interface [39].

Adsorbents: Variety of adsorbents can be used for the removal of heavy metals from aqueous solution and industrial wastewater. In general, adsorbent should be low cost, abundantly available, environmental friendly. A byproduct or waste material from another industry, which has lost its economic or further processing values, is a good alternative to costly adsorbents which are available in the market. Several low cost adsorbents have been used for the removal of heavy metal. Cost is an important parameter for comparing the adsorbent materials. However, cost of adsorbents vary depending on the degree of processing required and local availability. Research related to low cost absorbents is gaining importance these days though most of the work is at laboratory levels. Literature survey reveals that variety of plant materials have been used as low cost adsorbents for heavy metal removal from aqueous solution and industrial wastewater; some are listed in table 3.

Table3.

Name of Plant/adsorbent	**Name of heavy metal removed**	**Reference**
Date tree leaves	Pb(II)	[40]
Coffee, Green tea	Cd(II),Pb(II)	[41]
Syzygium cumini	Cu(II)	[42]
Algae	Cd,Hg,Pb,As,Co	[43]
Tea waste	As(III)	[19]
Jambhool	Cr(VI)	[30]
Ashoka leaf	Ni(II),Cu(II),Fe(II)	[44]
Potato husk	Pb(II)	[18]

Syzygium cumini	Fe(II)	[35]
Jute & Sunnhemp	Fe(II)	[45]
Almond husk	Cr(VI),Cd(II),Cu(II)	[46]
Ratrani leaf	Ni(II),Cu(II),Fe(II)	[47]
Prosopis spicegera	Cr(VI)	[48]
Cashew nut shells	Cr(III)	[49]
Jute stick	As(III),As(V)	[50]
Coconut husk	Cu(II),Fe(III),Pb(II)	[51]
Cassia Siamea	Cu(II)	[20]
Apple Pomace	Pb(II)	[52]

There are a lot of other kinds of materials applied for adsorption of heavy metals from aqueous solutions. Activated carbon has been used for the removal of Pb, Cd and other heavy metals. Hydroxides of aluminium, iron have been used as adsorbents for the removal of heavy metals [16].But the cost of adsorbent become relatively high when pure adsorbents are used.Some inorganic and organic adsorbents like ores, activated red mud, oxidized anthracite have been used for the removal of heavy metals. Other adsorbents which have been used are wool, albumin, feathers, waste rubber, hair and bagasse [16].

Effect of pretreatment of adsorbents on the adsorption of heavy metals: Pretreatment of adsorbents can enhance metal adsorption efficiency and chelating efficiency. Pretreatment can be carried out by using base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate), mineral acid solutions (hydrochloric acid, nitric acid, sulfuric acid), etc. Pretreatment of adsorbents in general improved the adsorption capacity of adsorbents probably due to higher number of active binding sites, better ion-exchange properties and formation of new functional groups that favors metal adsorption. Although pretreatment of adsorbents can enhance the adsorption of heavy metals, the cost of chemicals used and methods of pretreatment also have to be taken into consideration in order to produce 'low-cost adsorbents'. Many researchers reported that the heavy metal adsorption increased by pretreating the adsorbents with acids (like HNO_3, H_2SO_4 and HCl) and alkalies (like NaOH). Some are listed in table4.

Table 4

Metal	**Adsorbent**	**% Removal**	**Reference**
Pb	Untreated Rice husk	54.3	[53]
	Acid treated Rice husk	74.04	
Cd	Untreated Rice husk	8.24	
	Acid treated Rice husk	43.4	
Cu	Untreated Rice husk	51.4	
	Acid treated Rice husk	70.08	
Zn	Untreated Rice husk	56.7	

	Acid treated Rice husk	77.2	
Cu,Ni,Zn, Cd,Pb	Untreated peanut shells	5.7	[54]
Cu,Ni,Zn, Cd,Pb	Acid treated peanut shells	19-34	
Cu	Untreated Nerium Indicum	71	[20]
	HCl & NaOH treated Nerium Indicum	80	
	Untreated Cassia Siamea	42	
	HCl & NaOH treated Cassia Siamea	60	
Cr	Untreated Jambhool leaf powder	69.2	[30]
	HNO_3 treated Jambhool leaf powder	98.4	
Fe	Untreated Syzygium cumini	73.62	[35]
	HNO_3 treated Syzygium cumini	94.21	

Muthusamy P.et al. [55] also reported that H_2SO_4 and NaOH treated Maize Cob strongly enhance the adsorption capacity of Ni (II).

APPLICATIONS

This technique has found different uses, clarification of sugar liquid, removal of impurities from petroleum oils and motor sprits, recovery of dyes from dilute solution, inactivation of bacteria toxin, hormone or a mineral or as antidote in cast of poisoning, gas masks are containing adsorbents to purify the air from poisonous gases and vapors and purification of enzymes [56]. Softening of hard water, separation of gas mixture, drying gases, in chromatographic analysis, decolourisation, and purification [57].

CONCLUSIONS

Adsorption is a useful alternative to conventional systems for the removal of heavy metals from the industrial wastewater. Adsorption power can be enhanced by using acid or alkali treated adsorbents. By using low cost plant materials as adsorbents the adsorption process can be made economical. The wastewater after the adsorption process can be recycled and used for irrigation, industry, landscaping and toilet flushing as a solution to water scarcity and to conserve our fresh water resources. Recycled wastewater can also be used for recharging ground water to increase water level and for ecosystems.

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