REVIEW ARTICLE

FREE for Reading & Publication
Diamond Open Access

A Review on Removal of Heavy Metals from Water by Adsorption

Ayesha Dhawas[1,*], Dhananjay Bhatkhande[1], Shraddha Khamparia[2], Priya Nakade[3]

[1]Department of Chemical Engineering, Vishwakarma Institute of Technology, Pune, India
[2]Department of Water, Sanitation and Hygiene, Vishwakarma University, Pune, India
[3]Department of Chemical Engineering, Vishwakarma Institute of Technology, Pune, India

***Corresponding author: E-mail: ayesha.dhawas18@vit.edu**

DOI: 10.5185/amp.2020.030403

Substantial contamination of heavy metals in drinking water has been an issue to consumers since long. The persisting contamination level has been monitored by various agencies and researchers, which direct towards constant deterioration of water quality. The quality of water is degrading exponentially from rural to urban areas in a significant manner. Industrial effluents, sewage and agricultural waste are the prime sources of contamination of water resources. Various heavy metals such as nickel, chromium, lead, arsenic, cadmium, mercury and copper may be present in industrial effluents. Though different methods such as chemical precipitation, ion exchange, membrane filtration, coagulation – flocculation and electro dialysis are known, amongst which adsorption being the most versatile and economically viable has been extensively adopted by various researchers for trace level of concentrations. In this review, several low cost adsorbents are reported in the literature have been studied at length. Different types of adsorbents like nanosorbent, biosorbents, carbonaceous material and metal based adsorbents have been considered for the review paper. The review paper evaluates the possibilities of utilizing various adsorbents for efficient removal of different heavy metals from water. Study reflected towards remarkable adsorption capacity, efficiency and cost effectiveness of adsorbents utilized by researchers. The boundless use of low cost adsorbents for treatment of wastewater are strongly recommended due to their availability, applicability, technical feasibility and cost effectiveness.

Introduction

Fresh potable water sources are the most important reservoirs in the world. It is essential for all living organisms on earth to have access to sufficient clean water. Due to increase in population, developing industries and water scarcity the water resources are decreasing day by day. The pollutants discharging from industries leads to water shortage even in rich water content area. It is feasible to store rain water to control shortage of fresh water for some duration. However the best way to get rid of this problem is to treat wastewater and reuse it.

Wastewater contains toxic pollutants coming from anthropogenic activities which include industrial processes such as mining, petrochemical manufacturers, oil and gas refineries, dyes, pharmaceuticals, agrochemicals, etc. Natural activities like volcanoes, earthquakes or storms are the other factors contributing towards the contamination of water in ecosystem. These pollutants are classified into three different groups that are organic, inorganic and biological particles. The aim of this study is focused on inorganic group containing heavy metal ions. As these heavy metals are toxic and carcinogenic in nature this should not be discharged in water directly as it is hazardous for the environment [**1**].

Heavy metal ions are elements from 4th period of periodic table are commonly chromium (Cr), nickel (Ni), copper (Cu), cadmium (Cd), arsenic (As), lead (Pb) and mercury (Hg) are naturally found in environment, but nowadays their concentration is getting higher due to increase in industrial waste. The toxic ions enters the food chain and then to the human body. Once they are accumulated by the human more than there standard limits, they cause serious health diseases. Wastewater being the main source of diseases and hinders the sustainable growth of human population; it needs to be treated to degrade the pollutants to less toxic forms. [**2**] The concentration limits given by Bureau of Indian Standards (BIS) is listed below in **Table 1**.

Table 1. Drinking Water standards for contaminants in mg/L [3].

Contaminants	Acceptable limits (mg/L)	Permissible limits (mg/L)
Arsenic (As)	0.01	0.05
Cadmium (Cd)	0.003	No relaxation
Chromium (Cr)	0.05	No relaxation
Copper (Cu)	0.05	1.5
Mercury (Hg)	0.001	No relaxation
Nickel (Ni)	0.02	No relaxation
Lead (Pb)	0.01	No relaxation

Sources and health effects

Arsenic

Arsenic is one of the contaminants found in the environment which is notoriously toxic to man and other living organisms. It is generally accepted that the inorganic species, arsenite [As^{+3}] and arsenate [As^{+5}], are the predominant species in most environments, although the organic ones might also be present. Although As^{+5} tends to be less toxic compared to of As^{+3}, it is thermodynamically more stable due to it predominates under normal conditions and becomes the cause of major contaminant in ground water. The occurrence of arsenic in natural waters is usually associated with sedimentary rocks of marine origin, weathered volcanic rock, fossil fuels, geothermal areas, mineral deposits, mining wastes, agricultural use, and irrigation practices. Anthropogenic sources of arsenic include nonferrous metal mining and smelting, pesticide application, coal combustion, wood combustion, and waste incineration. Most anthropogenic releases of arsenic are due to land or soil, primarily in the form of pesticides or solid wastes. Chronic intake of inorganic arsenic being present in concentrations above 50 µg/L in drinking water, different kinds of skin lesions (e.g., hyperpigmentation, hyperkeratosis) and cancers (e.g., skin, lung, kidney, bladder) can develop, which are collectively termed as arsenicosis.

Cadmium

It is divalent metal and has +2 oxidation states. The average concentration of cadmium in earth's crust is found to be 0.1-0.5 ppm. Cadmium is insoluble in water and non-flammable. Cadmium is a toxic metal which has hazardous effect on environment as well as human beings. Cadmium is widely used in making nickel-cadmium batteries, pigments, phosphate fertilizers, alloy and metal plating. Runoff from waste batteries and paints, corrosion of galvanized pipes, and discharge from metal refineries are sources of cadmium discharge in water. Natural emission of cadmium in water is by volcanic eruptions and in form of ores of zinc, lead and copper, and coal. As per the drinking standards given by Bureau of Indian Standards the limit in drinking water is from 0.003mg/L to 0.005mg/L [**3**]. High concentration of cadmium in drinking water causes serious poisoning in human beings. Cadmium affected humans has a risk of cancer, cardio vascular diseases, and osteoporosis.

Chromium

About 60% of the chromium produced goes into chromium-based alloys, 20% into chemical use including electroplating, and most of the remainder into furnace bricks and other refractory products. At many locations, chromium has been released into the environment via leakage, poor storage or improper disposal practices. Sources of chromium waste include metal plating, steel fabrication, paint and pigment production, wood treatment, leather tanning, and chromium mining and milling. Chromate is also an important constituent of waste streams from coal-burning power plants. Chromium and its salts are used in the leather tanning and textile dyeing industries, the manufacture of catalysts, laundry chemicals, pigments and paints, fungicides, the ceramics and glass industry, and in photography, and for chrome alloy and chromium metal production, chrome plating and corrosion control. Chromium has oxidation states from -2 to +6; however mostly trivalent and hexavalent occurs in water.

Chromium toxicity is dependent on chemical speciation and thus associated health effects are influenced by chemical forms of exposure. Cr (VI) compounds are much more soluble than Cr (III) and are much more toxic (mutagenic and carcinogenic) to microorganisms, plants, animals and humans. Cr (VI) is toxic, producing liver and kidney damage, internal haemorrhage and respiratory disorders. An oral dose of 2–5 g of a soluble hexavalent chromium compound can be fatal to an adult human. Ingesting less than 2 g of hexavalent chromium compound can result in kidney and liver damage after 1–4 days of exposure. Sub-chronic and chronic effects include dermatitis and skin ulceration. Cr (VI) has been shown to cause cancer in humans and animals through inhalation exposure, but has not been shown to be carcinogenic through ingestion exposure. Cr (VI) compounds have been associated with lung cancer in humans.

Copper

In nature, copper occurs in a variety of minerals, including native copper, copper sulphides such as chalcopyrite, bornite, digenite, covellite, and chalcocite, copper sulfosalts such as copper (II) oxides such as cuprite and tenorite, respectively. Copper has +1 and +2 oxidation states. Copper enters in the environment through natural and anthropogenic sources. The contamination of air and water by copper is contributed from mining, milling, refining of copper ores, electroplating, petroleum and refinery industries. Copper is discharged in water effluent of various industries like chlor alkali, electroplating, paints, dyes, fertilizer, mining and metallurgy, explosives, pesticides, iron and steel industries etc. Copper is a toxic metal which is hazardous for flora, fauna, and human beings. Ingestion of 15-75 mg of copper causes gastro intestinal diseases. Excessive intake of copper may cause haemolysis, hepatotoxic and nephron toxic. Its toxicity leads to widespread capillary damage, hepatic and renal damage, and also central nervous system irritation followed by depression.

Mercury (Hg)

Mercury is a naturally occurring metal that is present in several forms. Mercury is a persistent environmental pollutant with bioaccumulation ability in fish, animals, and human beings. Mercury salts and organo mercury compounds are among the most poisonous substances in our environment. The mechanism and extent of toxicity depend strongly on the type of compound and the redox state of mercury. Environmental contamination due to mercury is caused by several industries, petrochemicals, mining's, painting, and also by agricultural sources such as fertilizer and fungicidal sprays. Mercury and its compounds are cumulative toxins and in small quantities are hazardous to human health. The major effects of mercury poisoning manifest as neurological and renal disturbances as it can easily pass the blood-brain barrier and has effect on the brain.

Nickel

It has +1 and +2 oxidation state. Nickel is resistant to corrosion by air, water and alkali. It is used in many manufacturing process like stainless steel, metallic alloys, super alloys, coin, nonferrous metals, batteries, copper sulphate, electroplating, forging, porcelain enamelling, mineral processing, paint formulation and steam-electric power plants. At non-dangerous level nickel may be beneficial as an activator of some enzyme systems and participating in important metabolic reactions. Excessive intake of nickel beyond its permissible limits causes severe damage to lungs (pulmonary fibrosis and cancer), renal edema, gastro intestinal distress, skin dermatitis, chest pain, shortness of breath, etc.

Lead

It has two oxidation states i.e. +2 and +4. Soil and plants can be contaminated by lead from car exhaust, dust, and gases from various industrial sources. Pb^{+2} were found to be acute toxic to human beings when present in high amounts. Since Pb^{+2} are not biodegradable, it remains a long-term source of Pb^{+2} exposures. Metal pollution has a harmful effect on biological systems and does not undergo biodegradation. Lead contamination in the environment exists as an insoluble form, and the toxic metals pose serious human health problem, namely, brain damage and retardation.

Adsorbents and removal of heavy metals

Arsenic

G. N. Manju *et. al.*, (1998) [**4**] Copper-impregnated coconut husk carbon can be used as an adsorbent for the active removal of As (III) from aqueous solutions. The removal of As (III) was found to depend on adsorbent dose, time and initial concentration of the sorbate. The process is endothermic and the maximum uptake occurs at pH 12. Quantitative removal of As (III) from synthetic and industrial wastewater confirms the validity of results obtained in the batch mode studies. Adsorbent would be useful for the economic treatment of wastewater containing As (III) as the carbon is easily prepared from the agricultural waste product.

E. Diamadopoulo *et. al.*, (1993) [**5**] Arsenic (V) adsorbs strongly on fly ash. Equilibrium is practically achieved in less than 72 h, while most of adsorption takes place in less than 24h. Equilibrium studies of As (V) on fly ash show that arsenic adsorbs more strongly at pH 4 with complete removal of arsenic at high concentration.

K.K. Pant *et. al.*, (2004) [**6**] Activated alumina is found to be a suitable adsorbent for the removal of As (III) from drinking water. A maximum of 96.2% As (III) removal could be achieved at pH 7.6. Low adsorption was observed at higher pH values. The pH of the solution determines the concentration distribution of the ionic forms of the As (III). The adsorption process was spontaneous and decreased with increase in temperature showing exothermic nature of the adsorption.

A.K. Gupta *et. al.*, (2006) [**7**] Adsorption of as (III) onto IOCC (iron oxide coated cement) studied is not strongly dependent on pH. The adsorption is influenced by the degree of agitation. But above 150 rpm, the mass transfer effect is negligible and below 150 rpm the adsorption process was external mass transfer limited. The equilibrium adsorption capacity increased with increase of the initial concentration. The adsorbed As (III) is desorbed quantitatively by 10% NaOH solution and the adsorbent can be efficiently reused for three cycles consecutively.

H. S. Altundogan *et. al.*, (2000) [**8**] Red mud is formed during the digestion in the Bayer Process which is practiced for alumina production from bauxite. Red mud consists mainly of different forms of iron and aluminium oxide minerals, calcium and sodium aluminium silicates, various titanium compounds, etc. As(III) and As(V) adsorptions are equilibrated within 45 and 90 min respectively, at 10mg/L concentration and 20g/L of red mud dosage. For As(III) and As(V), favourable adsorptions take places at pH 9.5 and 3.2, respectively. Thermodynamic calculations based on the data from the study on temperature indicate that As(III) adsorption reaction is exothermic and that of As(V) is endothermic. However, red mud is a very economical material since it is a waste product and is very fine grained. In addition, arsenic adsorbed red mud may be reused in some red mud usable metallurgical processes which are recommended to utilize red mud as an iron source. Since red mud is a waste, is fine grained and inexpensive it can be economically used for the removal of arsenic from wastewaters. Its adsorption capacity may be increased by activation.

Cadmium

A. F. Tajar *et. al.*, (2009) [**9**] Activated carbon from nut shells is a low cost adsorbent, which had high capacity to adsorb cadmium ions. The adsorbent was modified with SO_2 gas as a sulphurizing agent to introduce sulphur on carbon surface. This modification has led to modification of physico-chemical properties of material which has increased the adsorption capacity of Cd^{2+} ions. The removal of cadmium ions is concentration-dependent, so that the removal efficiency decreases with an increase in the concentration. The maximum adsorption has occurred in the pH range of 8-12.

V. K. Gupta *et. al.*, (2003) [**10**] Adsorption of cadmium by using bagasse fly ash which is obtained from sugar industry. This is an efficient and effective adsorbent for removal of cadmium from wastewater. The results showed that the saturation has reached from 0.64 to 1.18 mg/g with increase in adsorbent dose from 2 to 10 g/L; which indicates that the dosage 10g/L of adsorbent is sufficient for optimum removal of cadmium. The increase in adsorption with increase in temperature indicated endothermic nature of adsorption process.

A. K. Bhattacharya *et. al.,* (1984) [**11**] Rice husk a low cost adsorbent has studied for removal of cadmium. The rice husk was modified by pyrolyzing it at 550° C in a fixed bed reactor enveloped by furnace followed by its exposure to high pressure steam at 700° C for 100 min and subsequent drying at 100° C. The results showed that as compared to coal activated rice husk has 94.4% removal of Cd^{2+} ions. At pH 10 there was increase in adsorption to about 80%. Decrease in sorption beyond pH 10 was due to the formation of soluble hydroxy complexes.

T. K. Sen *et. al.,* (2010) [**12**] Castor (Ricinus communis) seed hull (CSH), is an agricultural residue obtained during processing of castor seeds before oil extraction. The castor seed hull is high in fiber content that is expected to provide ample negatively charged sites for capturing positively charged species. Experimental studies have been done in this work on the batch kinetics and adsorption equilibrium of Cd^{2+} in order to determine the uptake capacity of castor hull, kinetic rate constants, and equilibrium adsorption isotherm parameters under different process conditions. The results from this study clearly stated that castor hull from castor oil industry is a low cost, potentially attractive adsorbent as compared to activated carbon for the removal of cadmium (Cd^{2+}) ions from aqueous solution.

K. Pyrzynska (2010) [**13**] Comparative study was done between activated carbon (AC), carbon nanotubes (CNT); carbon encapsulated magnetic nanoparticles (CEMNP). All these particles were prepared under similar conditions by nitric acid treatment. The results concluded that activated carbon and carbon nanotubes has very similar results than carbon encapsulated magnetic nanoparticles which has much higher affinity for Cd(II) ions. Hence, cadmium retention is more dependent on the concentration of specific active sites on the surface than the total area available.

Chromium

S. A. Khan *et. al.,* (1995) [**14**] Bentonite is a clay mineral which is used in geological disposal for high level radioactive wastes. The soil and clay minerals has variations in their compositions is been used for the back fill of radioactive wastes into the ground. In this study the adsorption capacity was found to be 0.063mmol/100g at 20 °C which is being increased to 1.1mmol/100g at 40 °C. These results showed that bentonite can be effectively used for removal of chromate ions from waste water effluents if the metal concentration is low and the pH of the waste effluents is adjusted to about 2.

X. S. Wang *et. al.,* (2009) [**15**] Walnut hull is a good adsorbent for removal of chromium from aqueous solution. The removal efficiency was 97.3% at 1 pH. The removal increased with the increase in the adsorbent concentration and the decrease in adsorbate concentration. An increasing equilibrium adsorption capacity with the rise in temperature indicated that the nature of adsorption process is endothermic, which is further supported by the thermodynamic parameters calculated from the Langmuir isotherm at various temperatures.

X. Wang *et. al.,* (2009) [**16**] Adsorption of Cr (VI) on oxidized MWCNTs (Multiwalled carbon nanotubes) is strongly dependent on pH values and independent on ionic strength. Adsorption of Cr (VI) on oxidized MWCNTs decreases with increase in pH value. It takes long time for removal of Cr (VI) from waste water by using multiwall carbon nanotube as adsorbent. The high preconcentration and solidification capacity of multiwalled carbon nanotube makes the possibility of removal of metal ions in polluted wastewater treatment. As the preparation cost is higher so it cannot be applied in commercial water treatment.

I. Marzouk *et. al.,* (2012) [**17**] Activated alumina was found to be the significant adsorbent for removal of chromium from wastewater. The effect of parameters showed that the adsorption was dependent on adsorbent dosing and pH. A maximum 97% removal of chromium was achieved at pH 5-6.

A. Belgic *et. al.,* (2019) [**18**] The modification of silica gel was done by using 3-chloropropyltrimethoxysilane (CPTS) and 4-acetyl-3-hydroxyaniline (AHAP) and was characterized by using FT-IR and SEM. Different parameters were used based on these results, the best chromium removal was carried out at pH 2, with 0.05 g of adsorbent, at a temperature of 323.15 C, at a concentration of 20 mg/L for a contact time of 180 min. Thermodynamic parameters calculated for the adsorption of Cr(VI) metal ions to the Si-CPTS-AHAP adsorbent surface are endothermic and spontaneous. The adsorption of heavy metal ions on the Si-CPTS-AHAP adsorbent is higher at higher temperatures, meaning that it has a high adsorption capacity to remove Cr (VI) ions from wastewater.

S. O. Owalude *et. al.,* (2010) [**19**] Carbon nanotubes are found to be most efficient adsorbent for removal of chromium from wastewater. The adsorbent was characterized by transmission electron microscope (TEM) and field emission scanning electron microscope (FE-SEM). At optimum pH 7, 6% removal of Cr (III) ions by using unmodified CNTs and 10% of Cr (III) ions by using modified CNTs from aqueous solution was studied. With an increase in agitation speed from 50 to 150 rpm, in which 150 rpm gave slightly higher removal for chromium.

K. K. Pant *et. al.,* (2006) [**20**] Eucalyptus bark is a naturally occurring bio-sorbent. Eucalyptus bark was found to be the most effective adsorbent with 99% removal of chromium amongst bagasse, charred rice husk and activated charcoal. Higher sorption capacity of this sorbent indicates that eucalyptus bark can be used for the treatment of chromium effluent.

Copper

Z. Kovacova *et. al.*, (2019) [**21**] Sawdust is an agricultural waste material that is available in large quantities, has a low cost, and is easily regenerated after use**.** This adsorbent was characterized by FTIR to determine the changes after the adsorption. In 24 hours experiment the efficiency of saw dust for removal of copper was 85% at 5.3 pH. The change in pH due to ion exchange between the ions in model solutions and functional groups of spruce wood sawdust has resulted in retention of copper by saw dust. This study has been done for higher environmental standards to use the cheap, inexpensive and environment friendly materials should be used for the removal of heavy metal ions from water.

G. V. S. R. P. Kumar *et. al.*, (2019) [**22**] The aim of this paper was to access the low cost adsorbents that is groundnut seed, sesame seed and coconut seeds. These biosorbent were crushed to get homogeneous powdered size particles. This study has shown 99.7% removal of copper ion in 30 min of contact time. From the results, it was clear that the removal of copper ion from aqueous solution decreases as the metal ion concentration increases. It is due to the absence of adsorption sites in the adsorbent. The maximum removal of copper using the adsorbents was found at a metal concentration of 10 mg/L.

M. A. Hossain *et. al.*, (2012) [**23**] Banana peel is a high capacitate, economically viable and low cost adsorbent for copper removal. The results were good at optimum pH 6 while at higher pH, the removal was also low compared to the optimum condition as the binding site may not activate in basic condition. Highest copper removals were 85 and 88 % for the initial copper concentration of 5 and 10 mg/L, respectively at the adsorbent dose of 5 g/L. This study is favourable alternative of copper removal from water.

I. G. Díaz *et. al.*, (2018) [**24**] Carbon nanofibers was used as adsorbent. The results obtained in this research prove that helical carbon nanofibers are a potential adsorbent of copper ions from wastewaters. pH has the greatest influence on copper adsorption capacity, reaching a maximum value of around 8.80 mg/g at a pH value of 10. An increase in the temperature does not influence the adsorption capacity; however, the equilibrium is reached in less time.

N. H. Yarkandi (2014) [**25**] Alumina is mostly used for removal of metal ions as it has high adsorption capacity. In this study percentage removal of copper ions decreases with the increase in initial concentration due to lack of sufficient active sites on alumina to adsorbed more metal ions available in the solution. The effect of contact time reveals that the adsorption rate slowly decreases and reaches equilibrium at 60 min at the beginning the adsorption rate was high due to presence of more active sites available in sorption.

Mercury

A. K. Sen *et. al.*, (1987) [**26**] Fly ash adsorption is more sensitive to pH than on activated charcoal. The performance of coal fly ash as adsorbent was found to be significant when compared with that of activated powdered charcoal. Coal fly ash is a promising adsorbent for the removal of mercury(II) from waste water.

M. Zabihi *et. al.*, (2000) [**27**] Wall nut shell is agricultural waste which is used as carbonaceous material for adsorption of mercury. This study was carried out under different temperature among which 29 ^{0}C was effective for adsorption. The experimental data shows that solution concentration of Hg (II) ions reduces with temperature increase, indicating an endothermic nature of the sorption processes. Further increase in the contact time has a negligible effect on the sorption amount of metal ion. The maximum adsorption capacity was found on initial concentration of 107mg/L.

H. S. Silva *et. al.*, (2010) [**28**] Activated carbon from carbonized eucalyptus wood is an adequate adsorbent for mercury removal from aqueous solutions and its adsorbent efficiency can be enhanced by the modifications of its surface chemistry. The surface sulphurization treatments produce important variations in the zero charge point, in the textural properties of the solid basically specific surface and pore size distribution and in the number of acid and basic surface groups. The temperature of the adsorption tests does not influence the adsorption capacity of the studied adsorbents. If the heat of adsorption of a solute molecule is similar to desorption of the solvent molecule, the whole process will not be influenced by the temperature.

Nickel

T. Jesionowski *et. al.*, (2015) [**29**] Peat is a brown deposit resembling soil, formed by the partial decomposition of vegetable matter in the wet acidic conditions of bogs and fens, and often cut out and dried for use as fuel and in gardening. In this study peat was a potential adsorbent for removal Ni (II) from wastewater. The physicochemical characteristic of peat confirmed that it contains numerous numbers of functional groups in its structure that can easily adsorb positively charged metal ions. From the study it was noted that increasing the contact surface between adsorbent and adsorbate solution the efficiency of metal ions removal can be easily improved. The most important factor determining the successful removal of nickel(II) and lead(II) ions onto peat was pH, which influence both adsorbent surface functional groups as well as metal ions form. The advantage of this material is its availability and low extraction cost for its application in the purification of waste waters containing different types of metal ions.

K. Srinivasan *et. al.*, (2015) [**30**] Citrus Limettioides is one of the low cost nutritious fruit variety consumed in rural areas of India and belongs to Rutaceae family.

Extracted acid from these fruits are used as flavouring and preservative in food and beverages, especially in soft drinks and the peel and seeds are disposed of as waste materials. The citrus limettioides fruit is mainly composed of D-limonene, myrcene, citronellal and β-citronellol. In this study the maximum removal efficiency of Ni (II) ions onto CLPC (Citrus Limettioides peel carbon) and CLSC (Citrus Limettioides seed carbon) was found to be 99% at an adsorbent dose of 1.5 g/L. The increase in removal efficiency of Ni (II) ions can be attributed to the increase in surface area resulting from the increase in adsorbent mass or greater availability of the exchangeable sites for adsorption. Removal of Ni (II) ions decreases with the increase in temperature due to decrease in surface activity suggesting that the adsorption between Ni (II) and CLPC, CLSC is an exothermic process. The activated carbon prepared from Citrus Limettioides peel (CLPC) and seed (CLSC) has considerable potential for the removal of Ni (II) ions from aqueous solutions.

M. N. Zafar *et. al.*, (2007) [**31**] Bran is a by-product from the milling of rice, consisting of the large kernel with a part the germ. It is used in some applications mainly as a fertilizer or fuel. Rice bran contains different vitamins, carbohydrates, potassium, nitrogen and phosphorus compounds, which induce to water to contact with it. Therefore, the use of bran to eliminate pollution from water reveals the significance of the bran or natural products. Rice bran was protonated by using three acids that is hydrochloric acid (HCl), sulphuric acid (H_2SO_4) and phosphoric acid (H_3PO_4). The adsorption capacity for untreated rice bran was found to be 39.76mg/g. The adsorption capacity treated with HCl, H_2SO_4 and H_3PO_4 were 68.7mg/g, 79.3mg/g and 101.9mg/g respectively. Analysis of biosorption capability of rice bran possessed maximum sorption capacity for cationic metal ion with 0.250mm biosorbent size. Hence rice bran was selected for studying biosorption due to its originality as well as to access the possibility of utilizing a waste biomass to eradicate the metal pollution.

M. Saleem *et. al.*, (2015) [**32**] Coconut copra meal (CCM) was used as natural biosorbent. It is the waste material from coconut oil extracting industry. On a large scale the CCM is generated as a waste. The major components in CCM are polysaccharides and minor composition is lipids, proteins, and dietary fibers. This adsorption study of Ni (II) on CCM was accomplished within 2 h at pH 5. This biosorption of Ni (II) by CCM as a sorbent provides a potential inexpensive method to remove Ni (II) ions from wastewater.

S. Gupta *et. al.*, (2019) [**33**] Aloe barbadensis Miller leaves (Aloe Vera) is a biosorbent which is increasingly used as a raw material in food, pharmaceutical and cosmetic industries due to its medicinal properties. Maximum removal of nickel ions 42.2% was achieved at 7 pH but decrease in pH values removal decreases due to competition between hydrogen and nickel ions on the sorption site. This study helps in designing the biosorbers used in the industry for removal of Ni (II) ions from their effluents. The use of aloe vera leaves waste shall minimize the use of activated carbons, which are usually obtained from wood, thus protecting our environment.

M. Rafatullah *et. al.*, (2009) [**34**] Saw dust is generally used in heating the boiler. Sawdust has received particular attention as an economical adsorbent for removing heavy metals from wastewater due to its abundance, easily available and low cost. The results showed that the amount of nickel ions adsorbed increased with increase in concentration and dosing of adsorbent. The rate of reaction of adsorbent increases with increase in temperature.

Lead

P. Bartczak *et. al.*, (2015) [**35**] Peat is a brown deposit resembling soil, formed by the partial decomposition of vegetable matter in the wet acidic conditions of bogs and fens, and often cut out and dried for use as fuel and in gardening. The physicochemical characteristic of peat confirmed that it is very good material containing different functional groups that can easily adsorb positively charged metal ions. The most important factor determining the successful removal of nickel(II) and lead(II) ions onto peat was pH, which influence both adsorbent surface functional groups as well as metal ions form. The undoubted advantages of this material include its availability and low extraction costs, which may be of fundamental importance for its application in the purification of waste waters containing different types of metal ions.

M. Momcilovic *et. al.*, (2011) [**36**] Activated carbon obtained from cones of European Black pine was employed as an adsorbent for removal of lead(II) ions from aqueous solution. Increase in the adsorbent concentration, from 0.5 to 2.5 mg/L, increases removal of lead (II) ions from 23.95% to 43.72%. The removal of lead (II) ions is not increased considerably when adsorbent concentrations are higher than 2.0 mg/L. Thus, optimum dosage of adsorbent for adsorption of lead (II) ions is found to be 2.0 mg/L. All active sites on the adsorbent surface are then occupied and increase in adsorbent dosage do not provide higher uptake of lead (II) ions. Activated carbon from pine cones can be considered as a potential adsorbent used for the elimination of lead (II) ions from wastewater, since it is a low-cost and locally available adsorbent.

F. Zhang *et. al.*, (2009) [**37**] Biochars is a charcoal like substance obtained by burning organic material from agriculture and forestry waste. Lead adsorption onto the biochars was strongly influenced by the solution pH. The adsorption was a physical endothermic process. The removal capacity is very little at pH below 2.0 and increases along with the increase of pH, reaching a plateau value at pH 5.0. Adsorption studies were carried out at three temperatures 298, 308 and 318K from which maximum adsorption capacity was found on 318 K.

Conclusion

This review is based on removal of heavy metals based on their adsorption capacities and its efficiency of various adsorbents such as natural materials, industrial by products, agricultural and biological waste. The widespread uses of low-cost adsorbents in industries for wastewater treatment applications today are strongly recommended due to their local availability, technical feasibility, engineering applicability, and cost effectiveness. Many varieties of low-cost adsorbents such as agricultural and industrial solid wastes, natural materials and bio sorbents have been developed and tested as effective and economic adsorbents for the removal of low concentration of copper, nickel(II) ions and lead from water and wastewater. Activated carbon and carbon nanotubes shown similar results, while carbon-encapsulated magnetic Nano-particles exhibit much higher affinity for Cd (II) despite of almost the same surface acidity. Thus, cadmium retention is more dependent on the concentration of specific active sites on the surface than the total area available.

Acknowledgement

I would like to thank Wilo Foundation-Vishwakarma University Water Quality Centre of Excellence for their support.

Conflicts of interest

"There are no conflicts to declare".

Keywords

Heavy metal, adsorption, low cost adsorbents, wastewater treatment

References

1. Khulbe, K. C.; Matsuura, T.; *Applied Water Science*, **2018**, *8*, 19.
2. Arora, R.; *Materials Today*, **2019**, *18*, 4745.
3. "Drinking Water – Specification", Second Revision of IS 10500, **2012**.
4. Manju, G. N.; Raji, C.; Anirudhan, T. S; *Water Resources*, **1998**, 32, 332.
5. Diamadopoulos, E.; Ioannidis, S.; Sakellaropoulos, G. P.; *Water Resources*, **1993**, 27, 73.
6. Singh, T. S.; Pant, K.K.; *Separation and Purification Technology*, **2004**, 36, 139.
7. Kundu, S.; Gupta, A.K.; *Separation and Purification Technology*, **2006**, 51, 165.
8. Altundogan, H. S.; Altundogan, S.; Tumen, F.; Bildik, M.; *Waste Management*, **2000**, 20, 761.
9. Tajar, A. F.; Kaghazchi, T.; Soleimani, M.; *Journal of Hazardous Materials*, **2009**, 165, 159.
10. Gupta, V. K.; Jain, C.K.; Ali, I.; Sharma, M.; Saini, V.K.; *Water Research*, **2003**, 37, 38.
11. Bhattacharya, A. K.; Venkobachar, C.; *J. Environment*, **1984**, 110, 33.
12. Sen, T. K.; Mohammod, M.; Maitra, S.; Dutta, B. K.; *Clean – Soil, Air, Water*, **2010**, 38, 850.
13. Pyrzynska, K.; *Microchim Acta*, **2010**, 169, 7.
14. Khan, S. A.; Rehman, R.; Khan, M. A.; Waste Management, **1995**, 15, 271.
15. Wang, X. S.; Li, Z. Z.; Tao, S. R.; *Journal of Environmental Management*, **2009**, *90*, 721.
16. Hua, J.; Chena, C.; Zhub, X.; Wang, X.; *Journal of Hazardous Materials*, **2009**, *162*, 42.
17. Marzouk, I.; Hannachi, C.; Dammak, L.; Hamrouni, B.; *Desalination and Water Treatment*, **2012**, *26*, 279.
18. Bilgiç, A.; Çimen A.; *Royal Society of Chemistry*, **2019**, *9*, 403.
19. Atieh, M. A.; Bakather, O. Y.; Tawabini, B. S.; Bukhari, A. A.; Khaled, M.; Alharthi, M.; Fettouhi, M.; Abuilaiwi, F. A.; *Journal of Nanomaterials Volume*, **2010**, *55*, 232.
20. Sarin, V.; Pant, K.K.; *Bio Resource Technology*, **2006**, *97*, 15.
21. Kovacova, Z.; Demcak, S.; Balintova, M.; *Proceedings*, **2019**, *33*, 16.
22. Kumar, G. V. S. R. P.; Malla, K. A.; Yerra, B.; Rao, K. S.; *Applied Water Science*, **2019**, *9*, 201.
23. Hossain, M. A.; Ngo, H. H.; Guo, W. S.; Nguyen, T. V.; *Int. J. of GEOMATE*, **2012**, *2*, 227.
24. Díaz, I. G.; Lopez, F. A.; Alguacil, F. J.; *Metals*, **2018**, *8*, 811.
25. Yarkandi, N. H.; *International journal of Current Microbiology and Applied Science*, **2014**, *3*, 415.
26. Sen, A. K.; De, A. K.; *Water Resources*, **1987**, *21*, 885.
27. Zabihi, M.; Ahmadpour, A.; Asl, A. H.; *Journal of Hazardous Material*, **2009**, *67*, 230.
28. Silva, H. S.; Ruiz, S. V.; Granados, D. L.; Santangelo, J. M.; *Materials Research*, **2010**, *13*, 129.
29. Bartczak, P.; Norman, M.; Klapiszewski, Ł.; Karwanska, N.; Kawalec, M.; Baczynska, M.; Wysokowski, M.; Zdarta, J.; Ciesielczyk, F.; Jesionowski, T.; *Arabian Journal of Chemistry*, **2015**, *117*, 115.
30. Sudha, R.; Srinivasan, K.; Premkumar, P.; *Ecotoxicology and Environmental Safety*, **2015**, *143*, 478.
31. Zafar, M. N.; Nadeem, R.; Hanif, M. A.; *Journal of Hazardous Materials*, **2007**, *13*, 194.
32. Saleem, M.; Wongsrisujarit, N.; Boonyarattanakalin, S.; *Desalination and Water Treatment*, **2015**, *10*, 187.
33. Gupta, S.; Kumar, A.; *Applied Water Science*, **2019**, *9*, 201.
34. Rafatullaha, M.; Sulaimana, O.; Hashima, R.; Ahmad, A.; *Journal of Hazardous Materials*, **2009**, *170*, 969.
35. Bartczak, P.; Norman, M.; Klapiszewski, Ł.; Karwanska, N.; Kawalec, M.; Baczynska, M.; Wysokowski, M.; Zdarta, J.; Ciesielczyk, F.; Jesionowski, T.; *Arabian Journal of Chemistry*, **2015**, *10*, 187.
36. Momčilović, M.; Purenović, M.; Bojić, A.; Zarubica, A.; Ranđelovic M.; *Desalination*, **2011**, *276*, 53.
37. Liu, Z.; Zhang, F.; *J. of Hazardous Materials*, **2009**, *167*, 933.

Authors biography

Ayesha Dhawas is student in Vishwakarma Institute of Technology, Pune pursuing Masters in Chemical Engineering. She has completed her graduation that is B.Tech Chemical Engineering from Priyadarshini Institute of Engineering and Technology, Nagpur. At present she is doing internship in Wilo-Vishwakarma University Water Quality Centre of Excellence in Vishwakarma University. Her research project is related to waste water treatment and management

Dr. Dhananjay Bhatkhande is the director in state of art Wilo-Water quality Center of Excellence in Vishwakarma University and professor in Vishwakarma Institute of Technology, Pune. He is involved in several research projects related to wastewater treatment, e-waste management, mathematical modeling of LLE and heat transfer at boiling, meta selective hydrogenation, biogas generation and optimization. He is chairman in syllabus committee of University of Pune and referee for International journal of catalyst and chemosphere.

Dr. Shraddha Khamparia is the Deputy Director in the state of the art Wilo-Water Quality Centre of Excellence in Vishwakarma University. She is actively involved in several research projects related to water treatment Water and Waste Water Treatment, Adsorption Technique, Modelling and Simulation. Dr. Khamparia is having several international and national journal papers of high repute and two book chapters in her credit. She has presented and attended various conferences and workshops. She has received her doctoral degree from Symbiosis International University, Pune.

Ms. Priya Nakade is Assistant Professor in Chemical Engineering Department, Vishwakarma Institute of Technology, Pune. She is actively involved in various research projects related to Water Treatment, Water Quality Survey, Adsorption Techniques, Phase Transfer Catalysis and Chemical Reaction Engineering. She is having two international journal paper of high repute and many more inline. She is pursuing Ph.D. in Savitribai Phule Pune University, Maharashtra.

SUPPORTING INFORMATION

Table: Different adsorbents used for heavy metal removal from water.

Heavy metal	Adsorbent	Type of adsorbent	pH	Temperature ^{0}	Dosage (g)	Adsorption capacity (mg/g)	References
Arsenic	Copper impregnated coconut husk carbon	Natural (carbon based)	12	30	2	20.35	**[4]**
	Fly ash	Industrial waste	4	20	1	30	**[5]**
	Activated alumina	Metal based	7.6	25	1-13	0.18	**[6]**
	Iron oxide coated cement(IOOC)	Metal based	7	30	15	0.73	**[7]**
	Red mud	Mineral based	9.5	25	20	-	**[8]**
Cadmium	Sulphurised activated carbon	Carbon based	12	25	0.1	15.7	**[9]**
	Bagasse fly ash	Carbon based	6	50	10	1.2	**[10]**
	Activated rice husk	Natural	10	27-28	1	-	**[11]**
	Castor hull seeds	Bio sorbents	6	23	0.15	5.5	**[12]**
	Activated carbon Carbon nanotubes Carbon encapsulated magnetic nanoparticles (CEMNP)	Carbon based Nano sorbents	5-9	25	0.05	12 14 18	**[13]**
Chromium	Bentonite	Mineral based	2	30	0.5	-	**[14]**
	Walnut hull	Natural	1	30	5	59.2-90.8	**[15]**
	Multiwalled carbon nanotubes	Carbon based nanosorbent	2	20	1.25	-	**[16]**
	Activated alumina	Metal based	5-6	25	1	10	**[17]**
	Silica gel	Metal based	2-7	323.15	0.05	-	**[18]**
	Modified carbon nanotubes	Carbon based nanosorbent	7	25	0.15	-	**[19]**
	Eucalyptus bark	Bio sorbent	2	32	5	45	**[20]**
Copper	Spruce saw dust	Natural	5.3	-	-	-	**[21]**
	Groundnut seed cake	Biosorbent	5	40	0.75	4.82	**[22]**
	Sesame seed cake	Biosorbent	5	40	1	4.24	**[22]**
	Coconut seed cake	Biosorbent	5	40	1	4.32	**[22]**
	Banana peel	Biosorbent	6	25	5	-	**[23]**
	Carbon nano fibre	nanosorbent	10	25	0.1	8.77	**[24]**
	Alumina	Metal based	6	25	0.1-1	-	**[25]**
Mercury	Coal fly ash	Industrial waste	3.5-4.5	30	1-1.1	-	**[26]**
	Activated charcoal	Carbon based	3.5-5.5	30	1-1.1	-	**[26]**
	Wall nut shell	Carbon based	5	29	0.05	101	**[27]**
	Modified activated carbon	Carbon based	7	25	0.1	-	**[28]**
Nickel	Peat	natural	9	25	5	14	**[29]**
	Citrus limettiodies peel and seed carbon	Natural carbon based	5	27	1.5	38.46 35.54	**[30]**
	Protonated rice bran	biosorbent	6	30	0.25	101.9	**[31]**
	Coconut copra meal	biosorbent	5	26	1	3.77	**[32]**
	Aloe barbadensis miller leaves (aloe vera)	biosorbent	7	20-60	1	10	**[33]**
	Meranti Saw dust	Natural	6	30	10	35.97	**[34]**
Lead	Peat	Natural	5	25	0.5	82.31	**[35]**
	Pine cones carbon	Carbon based	5.2	25	2	27.53	**[36]**
	Biochars	Natural	5	24.8	-	-	**[37]**