

Review

Choice of Suitable Economic Adsorbents for the Reduction of Heavy Metal Pollution Load

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Abstract

Heavy metals e.g., Hg, Cd, Cr, Pb, Zn, As and Ni etc are a major sources of pollutants which enter into the food chains and cause serious health impairments, carcinogenicity and mutagenesis. They have adverse effects on blood composition, lungs, energy level, kidneys, central nervous system, liver, and other vital organs of the body. Heavy metals can be successfully removed by easily available, eco-friendly and low-cost adsorbents which include the wastes/products of natural (chitin, silicate porous material, clay and zeolites, vermiculite, cyclodextrin, chitosan, starch and its derivatives, alginates, fly ash), agricultural (walnut shell, Turkish coffee, waste tea, black gram, neem bark, coconut shell, coconut husk, coal, oil palm shell, sugarcane bagasse, rice, wool, waste tea, peat moss, Turkish coffee, exhausted coffee, crop biomass, rice straw, rice hulls, rice husk, rice, soybean hull, papaya wood, peanut shell, peanut, citrus fruits, palm date pits, black gram, wool, cassava waste, carrot residues, banana and orange peels, sugar-beet pectin gels, black gram husk) and industrial (waste rubber tire, waste slurry, lignin, fly ash, red mud)) origin. The adsorption efficiency is affected by functional groups and particle/pore size of the adsorbent, speed of agitation, biosorbent dose, initial concentration and molecular size of metal ions, temperature and pH.

Keywords: heavy metals, adsorbents, agricultural, natural, industrial

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Introduction

Water is necessary for human beings, plants and animals. However, water pollution has become a major issue these days due to mixing of urban, agricultural and industrial wastes in it [1, 2]. Tremendous quantities of wastewater containing heavy metals (like Cu, Hg, As, Cd, Cr, Pb, Zn and Ni etc.) are released by industries (like photographic film production, petroleum refining, wood processing units, electroplating, paint, dyes, pigments, textile, tannery, leather) into the aquatic environment and enter into the food chains resulting in carcinogenicity, mutagenesis and many other adverse effects [3-6]. Their toxicity and mobility in an aqueous system greatly affect vegetation, animals and human beings [7]. So it has become necessary to adopt appropriate strategies for the reduction of heavy metal's concentration in water to an acceptable level [8]. Although different procedures e.g., ion exchange, reverse osmosis, electro-dialysis, membrane separation, chemical oxidation, chemical precipitation [9], anaerobic biotechnology [10], membrane filtration, evaporation and precipitation [11] are applied to remove the heavy metals, the adsorption has attracted greater attention due to its low-cost, high efficiency, design flexibility, eco-friendly nature and easy availability of adsorbents [12].

Current studies were performed to overview various adsorption strategies that are applied to eliminate heavy metals from wastewater.

Pollution Load of Heavy Metals and Its Hazardous Effects

Heavy metals are essential nutrients and play a vital role in healthy lives of people; however, they are toxic in excessive concentrations. The heavy metals are generally present in vegetables, fruits and in multivitamin products. They are also part of residual wastes of batteries, pesticides, alloys, textile dyes, steel [13]. Their higher concentrations may lead to allergies and cancer and also causes adverse effects on blood composition, liver, lungs, energy level, kidneys, central nervous system etc. Long-term exposure to heavy metals may lead to neurological, physical and muscular degenerative processes which may result in Alzheimer's disease, muscular dystrophy, Parkinson's disease, multiple sclerosis etc. [13]. Table 1 summarizes some sources and toxic effects of common heavy metals.

Adsorption Processes

Adsorption is a renowned equilibrium separation process which involves the adsorbents of biological, organic or mineral nature [20]. These adsorbents include clays, zeolites, silica beads, activated carbons, biomass, agricultural wastes, industrial by-products and numerous polymeric materials [21]. Based upon the nature of intermolecular forces, adsorption is classified into physical and chemical categories.

Table 1. Sources of heavy metals and their toxicological effects.

Heavy metals	MCl* (mg/L)	Sources	Toxicity	Ref No.
Arsenic (As)	0.05	Pesticides, fungicides, metal smelters, tobacco smoke, combustion of coal, production of steel and iron, nickel and copper	Bronchitis, dermatitis gastrointestinal damage, severe vomiting, diarrhea, death	[4, 14]
Cadmium (Cd)	0.01	Production of steel and iron, sludge, paints, incinerations, combustion of coal and fuel	Reproductive system, fertility, kidney damage, renal disorder, carcinogenic	[15]
Lead (Pb)	0.006	Mining and burning of coal, emissions from automobile, pesticides, paint	Mental illness in children, gastrointestinal problems, liver and kidney damage	[6]
Chromium (Cr)	0.05	Steel and textile industry	Headache, diarrhea, nausea, vomiting, carcinogenic	[14]
Mercury (Hg)	0.00003	Pesticides, batteries, paper, pulp, solid waste combustion, smelting, mining, fossil fuel combustion	Nervous system is affected badly	[16]
Zinc (Zn)	0.80	Metal plating, brass manufacture, refineries	Effects on nervous system. Zinc fumes cause skin problems	[17]
Copper (Cu)	0.25	Copper water heaters, water pipes, alcoholic beverages from copper brewery equipment, copper in canned greens and frozen greens to produce ultra-green color	Liver damage, Wilson disease, Insomnia, gastrointestinal problems	[18]
Nickel (Ni)	0.20	Effluents of silver refineries, storage battery industries, electroplating, zinc base casting	Dermatitis, nausea, chronic asthma, coughing, human carcinogen, reproductive effects, respiratory cancer	[19]

*MCl = Metal chloride

Physical adsorption involves the binding of adsorbates on to the surface of adsorbents by van der Waals forces. The electronic structures of atoms and molecules are almost not disturbed in physical adsorption. Physical adsorption is favored at specific pH conditions under the low-temperature atmosphere [9, 14]. In chemical adsorption (also called activated adsorption), the adsorbent and adsorbate chemically react with each other resulting in a strong interaction (covalent or ionic) between both. The adsorbate which has the ability to make a monolayer is used in the catalysis. Generally, a pollutant is adsorbed on to the solid adsorbent in 3 main steps: (i) Transfer of pollutants to external surface of an adsorbent from bulk solution (ii) Mass transfer by pore diffusion to inner surface of porous structure from outer surface of adsorbent (iii) Adsorption of adsorbate on to active sites of adsorbent pores [9, 14]. Adsorption is associated with several advantages which include: (a) metal recovery (b) absence of toxic sludge generation (c) regenerative (d) metal selectivity (e) inexpensive and (f) most significantly effective. The wastewater contaminated with heavy metals can be treated by applying low-cost adsorbents (e.g., modified biopolymers, natural materials, industrial byproducts or agricultural wastes) [9].

Natural Materials as Adsorbents

Natural materials are considered as low-cost adsorbents; they are environment-friendly and available in large quantities [22]. Biosorption by plant leaves is an environment-friendly technique for elimination of heavy metals from an aqueous environment and is applied worldwide [23]. The adsorbents of natural origin e.g., chitin, peat moss, clay and zeolites show an efficient removal of toxic heavy metals including Cd, Cr, Hg, Ni, Zn, Cu, Pb [9]. Recently attempts are being made to develop more effective and cheaper adsorbents containing natural polymers for example cyclodextrin [24], chitosan [25], starch and its derivatives [26], alginates [27] etc. The natural polymers like polysaccharides are biodegradable, renewable and abundantly available and have natural ability to associate physically or chemically with a large variety of molecules. Hence polysaccharides are considered as excellent low-cost adsorbents for water decontamination. Alginates are commercially attractive polysaccharide biopolymers due to their excellent potential for the formation of complexes with various metals [28]. There are many other natural biosorbents which have tendency to eliminate heavy metals from wastewater. Tea is the mostly consumed beverage

Table 2. Low-cost natural adsorbents used to remove metals.

Natural adsorbent	Metals removal capacity
Peat moss-derived biochars	Cu (18.2 mg/g), Cd (39.8) and Pb (81.3 mg/g) [30]
Zeolite	Pb ²⁺ and Cd ²⁺ (175 and 137 mg/g, respectively) [31] For cobalt – 0.011 mg-equ/L; for nickel – 0.020 mg-equ/L; for iron – 0.021 mg-equ/L; for copper – 0.023 mg-equ/L [32]
Silicate porous material (SPM)	Cu ²⁺ , Cd ²⁺ and Pb ²⁺ (32.26 mg/g, 35.36 mg/g and 44.83 mg/g, respectively) [33]
Chitosan-based sorbents	(i) With functionalized chitosen (CH)-based biosorbent, Pb ²⁺ , Cd ²⁺ and Cu ²⁺ (1.60, 1.96, 2.82 mg/g, respectively) [34] (ii) With xanthated chitosen, the removal rate reached upto 99.1%, 100% and 100% for Cd ²⁺ , Cu ²⁺ and Cr ³⁺ , respectively [35] (iii) Arginine cross-linked chitosan-carboxymethyl cellulose beads can remove 168.5 and 182.5 mg g ⁻¹ of Cd(II) and Pb(II) ions, respectively [36] (iv) Chitosan-coated sour cherry kernel shell beads can remove 24.492 mg g ⁻¹ Cr(VI) [37]
Clay minerals and metal oxides	Cr, Ti, Th, Mo, Eu, V, Mn, Cs, Ga, Cr, Cd, As, In, Hg, Pb, V, Zn, Cu, Co, Ni, As, In [38]
Vermiculite	Cu(II) removal up to 67.6% at the agitation speed of 400 rpm and ambient temperature. It is about 42.5% at 60°C without agitation [39]
Sepiolite	Cd(II) < Mn(II) < Fe(III) < Co(II) ~ Cu(II) < Zn(II) with affinities of 0.445 × 10 ⁻⁴ , 0.979 × 10 ⁻⁴ , 1.193 × 10 ⁻⁴ , 1.865 × 10 ⁻⁴ , 1.870 × 10 ⁻⁴ and 2.167 × 10 ⁻⁴ mol g ⁻¹ respectively [40].
Pumice	1.15 mg/g of Zn uptake. The modified pumice (at 300°C and soaked with HCl) can remove zinc up to 1.24 mg/g [41].
Iron-ore-sludge	Adsorption was found in the order of Pb > As > Cd > Zn > Mn; it was ranging either from 0.370 mg/g to 1.059 mg/g with mixed-metal solutions or from 0.710 mg/g to 1.113 mg/g with single-metal solutions [42]
Other low-cost adsorbents	Chitosan (250, 273, 815 mg/g of Cd ²⁺ , Cr ²⁺ and Hg ²⁺ , respectively); zeolites (137 and 175 mg/g of Cd ²⁺ and Pb ²⁺ , respectively); waste slurry (540, 560, 1030 mg/g of Cr ⁶⁺ , Hg ²⁺ and Pb ²⁺ , respectively); Lignin (1865 mg/g of Pb ²⁺) [31]

worldwide. With greater production and consumption, a large quantity of tea is discarded in the environment. Tea waste is getting much attention from researchers these days because it is an excellent biosorbent for removal of iron, chromium, nickel and lead [29]. Table 2 shows some low-cost natural adsorbents used to remove metals by adsorption phenomenon.

Adsorption by Agriculture/Plant/Animal Wastes

The application of agricultural by-products in bioremediation of heavy metals is called biosorption [43]. Metal ions can be recovered from an aqueous environment by using agricultural-by-products which are biodegradable and have no adverse effects on the environment. The use of agro-products as alternatives to conventional adsorbents has been gaining popularity [44]. Such products also have the advantages of cost effectiveness, engineering applicability, technical feasibility and local availability [45]. The temperature, speed of agitation, biosorbent dose and initial concentration of the metal ions and pH are important parameters which significantly affect the biosorption capacity. Biomass can also be modified physically or chemically before its use as adsorbent. Moreover, the biosorbent can be reused after desorption of heavy metals from it; it makes this process economical [46]. Biosorbents have excellent ability to eliminate toxic heavy metals from effluents and also provide the means of usage of discarded open wastes in wastewater treatment. This procedure demands low investment, less labor and minimal energy input. The efficiency of adsorption is controlled by the particle/pore size of adsorbent, functional groups present on surface of adsorbent, temperature, initial pH and molecular size of metal ions [47]. Numerous agricultural wastes like walnut shell, Turkish coffee, waste tea, black gram, neem bark, rice husk etc. were investigated to be potent adsorbents of heavy metals [9]. The low-cost agricultural adsorbents like crushed coconut shell and Giridih coal were found suitable for successful elimination of cadmium(II) from aqueous environment depending upon the pH. The chemical interaction and electrostatic forces are responsible for adsorption when $\text{pH} > \text{pH}_{\text{zpc}}$ whereas ion exchange phenomenon occurs when $\text{pH} < \text{pH}_{\text{zpc}}$. However, when the soluble hydroxy complexes are formed above pH 10, the sorption capacity is lowered [48]. There is an extensive usage of activated carbon (AC) in wastewater treatment on commercial level; however AC remains an expensive material and require the formation of cheaper AC which are more efficient and environment-friendly [49]. The agro-based inexpensive adsorbents (e.g., coconut shell, rice husk, coconut husk, oil palm shell, rice, wool, waste tea, peat moss, Turkish coffee, exhausted coffee, wall nutshells, crop biomass, rice straw, rice hulls, coconut shell, soybean hull, papaya wood, peanut shell, citrus fruits and sugarcane bagasse) can be used as good alternatives

of AC [50, 51]. Palm date pits were found to be a cheaper source of activated carbon and were used to eliminate iron, hexavalent Cr and Cu from wastewater of an electroplating unit and a tannery. The adsorption of heavy metals took place very fast during first 30 minutes with achievement of equilibrium in 90 minutes. Important parameters include the optimum pH (4.5-6.5), particle size (0.5-0.75 mm) and depth of adsorbent layer (70-90cm). The removal efficiency and adsorption capacity were reached up to 89% Fe, 61.65% Cr^{+6} and 82.857% Cu for effluents collected of electroplating unit while they were found to be 87.03% Fe, 65.42% Cr^{+6} and 85.17% Cu for tannery wastewater [52]. Metal ions e.g., selenium, zinc, cadmium, lead etc can be significantly recovered from the waste-water by using agricultural-by-products like potato peels, sawdusts, corn cobs, yam peels, banana peels, plantain peels, orange peels, cassava peels, rice-husks as adsorbents [44]. Papaya seeds were tested to eliminate copper ions from aqueous environment; maximum adsorption (212 mg/g) was observed with the stirring rate of 350 rpm at pH 6 [53].

Zinc (II) and copper (II) can be eliminated from metal finishing wastewater by low-cost adsorbents including natural zeolite, fly ash and peanut husk charcoal at optimum pH of 6, 8 and 6, respectively. The natural zeolite required the adsorption time of three hours while fly ash and peanut husk charcoal took 2 hours for the removal of metal. The metal elimination capacity was found in the following order: fly ash < peanut husk charcoal < natural zeolite [54]. Zn^{2+} adsorption capacity was tested by using cheaper modified adsorbents e.g., byproduct adsorbents (rice husk ash, coal fly ash, lignin, sawdust etc.), biosorbents (marine green macroalgae, algal, algae, cassava waste, carrot residues, banana and orange peels, citrus peels, sugar-beet pectin gels, black gram husk etc.), natural source adsorbents (zeolite, bentonite, clay etc.) and activated carbon. The highest Zn^{2+} adsorption capacity was 52.91 mg/g with bentonite, 55.82 mg/g with cassava waste, 128.8 mg/g with dry marine green macroalgae, 73.2 mg/g with lignin and 168 mg/g with powdered waste sludge [55]. By using groundnut shells as adsorbent, the optimum Cr(VI) adsorption was observed to be at metal ion concentration of 25 mg/L, adsorbent dose of 2.0 g/L, temperature of 41.5°C, pH 8 and a contact time of 120 min [56]. The corncob and coconut shell have shown the adsorption in the order of $\text{Cu} > \text{Pb} > \text{Cr} > \text{Zn} > \text{Ni} > \text{Cd}$, as shown by Freundlich and Langmuir model [57].

Chitin from crab shells is an easily available, economical and efficient biosorbant which was used for adsorption of M(II) (zinc, cadmium, nickel, copper, lead) in batch system. The metal adsorption capacity was found to depend upon the initial concentration of M(II), biomass dose, contact time and initial pH. The adsorption capacities were found to be 38.46, 40, 43.4, 47.61 and 50 (mg L^{-1}) for Cd(II), Pb(II), Cu(II), Ni(II) and Zn(II), respectively. The positive enthalpy (ΔH°)

Table 3. Some low-cost agricultural adsorbents and the respective metals which can be removed.

Bio-adsorbents	Adsorbents performance
Rice husk and fly ash	Rice husk has the ability to remove simultaneously nickel, lead and iron whereas fly ash can eliminate Cd and Cu. They can eliminate heavy metals up to the concentration of 20-60 mg/L from wastewater. Fig. 1 represents a schematic diagram showing the step wise removal of Cu, Ni and Fe by rice husk and fly ash [60].
Byproducts of soybeans, cottonseed hulls, and rice straw	Their Zn(II) adsorption capacities (0.52 to 0.06 meq/g) are in the following order: soybean hulls>cottonseed hulls>rice straw>sugarcane bagasse. The sugarcane bagasse and rice straw have low adsorptive capacities (≤ 0.12 meq/g) [50, 61].
Groundnut husk	Groundnut husk oxidized with silver treatment, has higher chromium adsorption capacities [62].
Sawdust (a cheaper by-product of wood industry)	Sawdust is very efficient for elimination of Zn^{2+} and Cu^{2+} ions. The organic compounds (hemicelluloses, cellulose and lignin) present in saw dust have polyphenolic groups which can attach heavy metal ions by numerous mechanistic pathways. [63].
Waste tea leaves	Tea waste can remove 3 toxic metal ions like copper, cadmium and lead from aqueous medium. The elimination capacities of copper(II), cadmium(II) and lead(II) from aqueous water were observed to be 21.02, 16.87 and 33.49 mg/g, respectively [64].
Watermelon Shell (eco-friendly and cheaper biosorbent)	Watermelon shell was tested to eliminate copper (II) from an aqueous environment. The monolayer adsorption potential was observed to be 111.1 mg/g from aqueous media [65].
Peanut hulls	21.7 \pm 9.5% of arsenic and 88.6 \pm 1.9% of cadmium removal [66]
Peanut husk	Ultrasound assisted chemically activated peanut husk shows 19.6 mg/g of copper adsorption [67]

and negative free energy (ΔG°) showed the endothermic and spontaneous adsorption [58]. Cr(III) can be adsorbed up to 97.48% by using fly ash (the solid waste from coal-fired power plants) modified with 20 wt% of KOH at 15-20°C and a contact time of 120 min [59]. Table 3 displays some low-cost agricultural adsorbents and the respective metals.

Agricultural wastes can also be modified by chemical or thermal treatment and are abundantly applied as adsorbents due to their excellent potential for heavy metals removal. The metal adsorption capability majorly depends upon the adsorbent characteristics, adsorbate concentration and extent of surface modification. However, it is highly important to consider the key factors such as technical applicability and cost effectiveness during the selection of cheaper adsorbents [9]. The low-cost systems are favored to achieve higher environmental standards worldwide. Cu(II) is successfully eliminated from the wastewater by using sawdust (a cheap material) as an adsorbent. The elimination efficiency of Cu(II) is greatly affected by salinity, particle size of the adsorbent, dose, temperature, contact time, pH and concentration. This process is easier, economically feasible and can be utilized for the development of an appropriate wastewater treatment plant [68]. Desorption of Cr^{6+} , Zn^{2+} , Ni^{2+} and Cu^{2+} is pH dependent. For Cr^{6+} ions, desorption occurs with 0.01 M NaOH in electroplating wastes while desorption of Zn^{2+} , Ni^{2+} and Cu^{2+} ions was found to take place in the presence of 0.01 M HCl solution [69]. Metal ions can be successfully transferred from their aqueous solution into the Bran and hulls (rice milling byproducts). The Cr(III), Zn(II), Cu(II), Ni(II) and Co(II) ions are adsorbed up to 13–27% at metal ion

concentration of 100 mg/L. The defatted, extrusion stabilized rice bran (a byproduct of rice oil extraction) was found to be an excellent chelating agent (cation exchanger) for adsorption of Cr^{+3} , Zn^{+2} and Cu^{+2} ; the adsorption was lowered for Co^{+2} and Ni^{+2} ions. However, it is necessary to ensure the effectiveness of rice bran in column applications and its stability to harsh aqueous treatment before its use on industrial scale. Actually 50% of cation-exchange capacity of rice bran is lost when it is treated with α -amylase, SDS, EDTA and boiled for an hour. Under the same conditions, the carboxymethyl cellulose resin does not lose its cation-exchange ability so further investigations are needed to address such kinds of issues [70]. The arsenic and some other heavy metals can be eliminated from mining wastewater by applying simultaneously the horizontal-subsurface-flow constructed wetland (CW) with *Phragmites australis* (common reed) and adsorption (with modified iron-ore drainage sludge). A pilot-scale experiment was performed on real wastewater of a Pb–Zn mine in northern Vietnam for a period of 4 months with 5 m³/day constant flow rate. The average removal of Pb, Zn, Cd, Mn and As was found to be 38.7%, 52.9%, 79.6%, 96.9% and 80.3%, respectively during this period (4 months) by the combined system with limestone substrate. The removal efficiency of arsenic was further improved by using another constructed wetland substrate laterite. The laterite substrate was found more efficient for arsenic removal whereas limestone substrate in CWs exhibited greater elimination of Cd, Zn, Zn and Mn [71]. There were investigations on the sorption capacities, morphology properties and physicochemical characteristics of discarded mushroom-stick biochar (DMB) synthesized

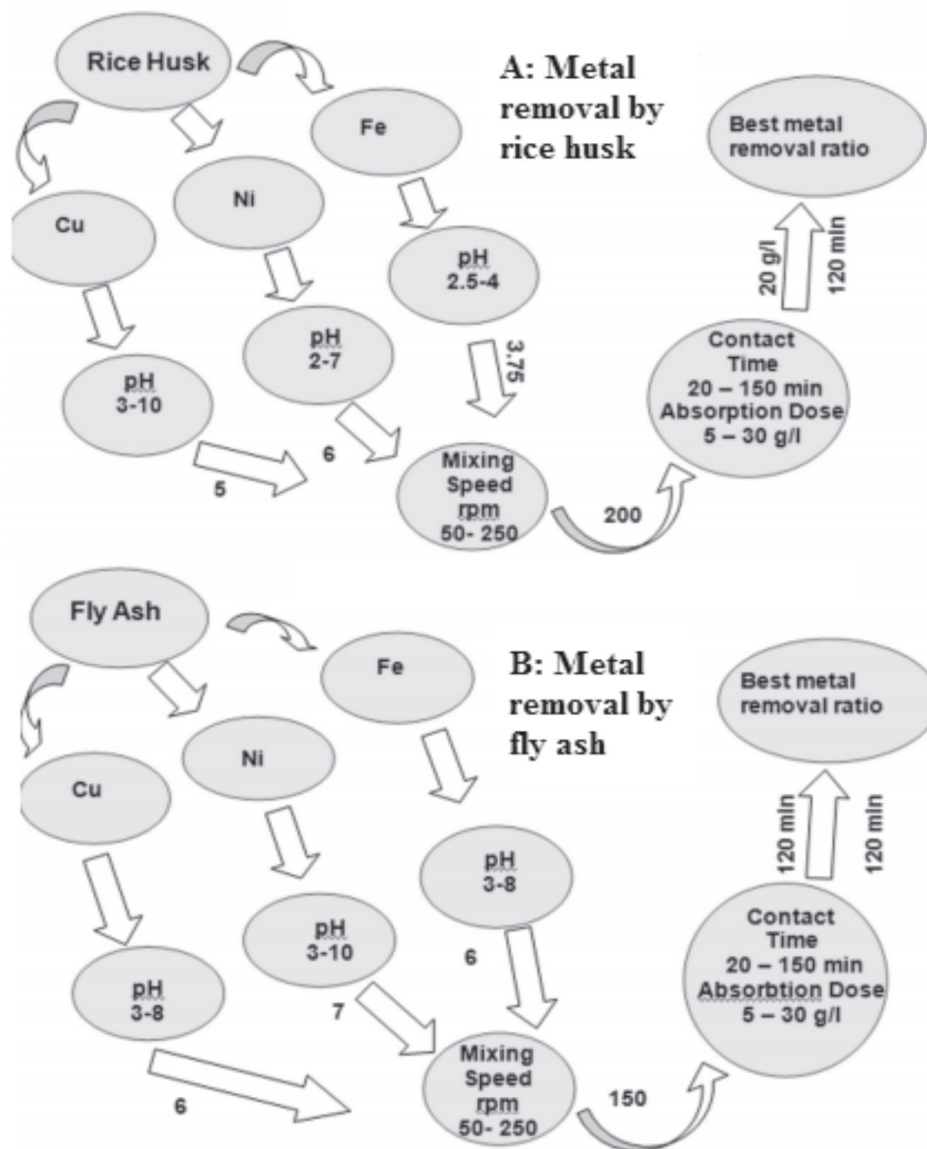


Fig. 1. Schematic Diagram showing the step wise removal of Cu, Ni and Fe by rice husk (A) and fly ash (B) under specific conditions [60].

under various pyrolysis temperatures (300°C to 800°C). The DMB3 (prepared at 300°C) has shown higher yield and surface oxygen-containing group content as compared to that prepared at higher pyrolysis temperatures (500°C and 800°C). The DMB8 (prepared at 800°C) has higher polarity, aromaticity, ash content, mineral element and pH. DMB3 has shown higher adsorption capacity (for heavy metals) as compared to DMB5. DMB8 has shown maximal sorption capacities of 21.0, 18.8, 11.2, and 9.8 mg g⁻¹ for Pb²⁺, Cu²⁺, Cd²⁺, and Ni²⁺, respectively. The heavy metal adsorption by DMB depends upon two dominant mechanisms of ion exchange and mineral precipitation and is monitored by the pyrolytic temperature. When pyrolysis temperature is enhanced, then effect of organic components on sorption of heavy metals is decreased whereas the effect of minerals is enhanced. The use of discarded mushroom-sticks in the production of efficient biochars provides

an efficient path of removing the mixed heavy metals from wastewater. The study provides the way of recycling of discarded mushroom-sticks and their conversion into efficient metal adsorbents and potential use of agriculture waste [72]. Mixed waste tea and coffee ground tea are excellent environment-friendly biosorbents for elimination of Cr(VI) from an aqueous medium [73]. The adsorption capacities with agricultural waste composite-activated carbon were observed to be 200 and 250 mg/g for As(III) and Pb(II), respectively with the BET surface area of 849.630 and 230.242 m²/g [74].

Adsorption by Industrial Wastes/Products

The toxic heavy metals can be successfully eliminated from the contaminated water by numerous low-cost industrial byproducts such as grape stalk

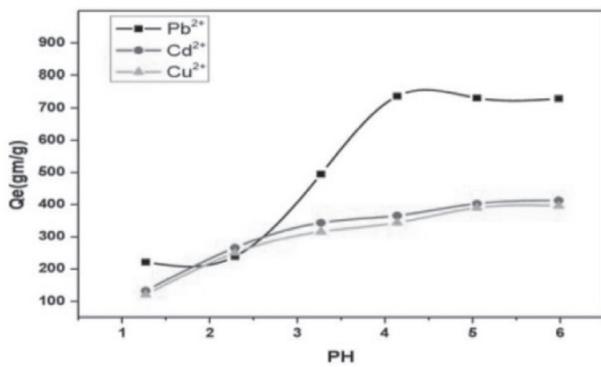


Fig. 2. Effect of pH on adsorption of Cu(II), Cd(II) and Pb(II) on modified PAN-g-GA [77].

wastes, sea nodule residue, tea factory waste, battery industry waste, areca waste, coffee husks, sugar beet pulp, red mud and iron (III) hydroxide, lignin, waste slurry, fly ash and blast furnace sludge [9]. Adsorption of Cu, Cd and Cr was investigated with various potential agricultural and commercial adsorbents. Maximum Cr removal potential is 201.2 mg/g (with α -ketoglutaric acid-modified magnetic chitosan), 160 mg/g (with PEI functionalized eggshell), 2,859.38 mg/g (with graphene sand composite) and 264.5 mg/g (with composite of activated alumina and carbon nanotubes); that for Cd was found to be 285.7 mg/g (with green coconut shell powder), 108.7 mg/g (with chitosan-coated ceramic alumina), 2838.7 mg/g (with NaX nanozeolite), 48.1 mg/g (with electrospun nanofibre membrane of PEO/chitosan), 256.41 mg/g (with chitosan/TiO₂ composite) and 200 mg/g (with succinic anhydride modified olive stones). The adsorption potential for Cu was found to be 1,602 mg/g (Paenibacillus polymyxa bacteria) and 285.7 mg/g (green coconut shell powder). The optimum pH values were observed to be in the ranges of 4.5-6, 4-7 and 1-2 for Cu, Cd and Cr, respectively; the

optimum contact time was 120 minutes - 12 hours for maximum copper removal, 5-120 minutes for Cd and 120-9,900 minutes for chromium. For adsorbent dose, the optimum value was lying in a range of 0.75-10 g/L [12].

Industrial electroplating wastewater was subjected to heavy metal removal (Zn, Fe, Cu, Ni, Cd, Cr, Pb and As) by using two nano-adsorbents namely polyhydroxybutyrate functionalized carbon nanotubes (PHB-CNTs) and purified carbon nanotubes (P-CNTs). The experiments were performed at a pH of 5.63-5.65, optimum dosage of 20 mg, equilibrium time of 70 minutes and optimum contact time of 10 minutes. The removal capacities of heavy metals were found in an order of PHB-CNTs > P-CNTs based on electrostatic forces and ion exchange mechanism [75]. Commercial sodium alginate can be acidified with alcoholic HCl to change into water-insoluble form which is used to remove Zn(II) ions from wastewater [20]. Copper is adsorbed to the extent of 4.24 mg/g by using bioadsorbents including coconut cake powders (1.0 g), sesame seed cake powder (1.0 g) and groundnut seed cake powder (0.75 g). The process was optimized at 40°C, 5 pH, 10 mg/L initial metal concentration and 30 minutes contact time [76].

The modified PAN-g-GA was investigated for adsorption of Cu(II), Cd(II) and Pb(II); the adsorption capacity was found to depend upon the pH (Fig. 2), contact time and initial concentration of metal ions. The PAN-g-GA was obtained by graft polymerization of polyacrylonitrile (PAN) with arabic gum (AG); it was chemically modified by treating with hydrazine hydrochloride followed by hydrolysis in the basic medium [77].

Table 4 shows some low-cost industrial adsorbents and the respective metals which can be removed. Table 5 compares the economic analysis of heavy metals removal technologies.

Table 4. Some low-cost industrial adsorbents and the respective metals which can be removed.

Adsorbent	Performance
Waste rubber tire	The mesoporous RTAC (a novel carbon prepared from waste tire rubber by physical activation) is very helpful due to its enhanced batch adsorption capacity for Ni and Pb ions as compared to microporous commercial carbon [78]. The waste tires (activated by thermally treatment) are used to manufacture activated carbon which acts as a potential adsorbent for Cr(III) under optimized conditions of pH, adsorbent dosage, contact time and initial concentration [79].
Waste slurry	Waste slurry is used to remove the metals ions like of Pb ²⁺ , Hg ²⁺ , and Cr ⁶⁺ (0.30, 560, 540 mg/g) [31]
Lignin-a black liquor waste of paper industry	Lignin can remove up to 63% Cr ⁶⁺ and 100% Cr ³⁺ from an aqueous medium [80]. Ni(II), Zn(II), Cd(II), Cu(II) and Pb(II) are adsorbed on lignin isolated from black liquor (a waste material formed in paper industry). The metal removal tendency of lignin is Pb(II) > Cu(II) > Cd(II) > Zn(II) > Ni(II) [81]
Coal fly	Coal fly can eliminate Cu, Mn, Cd, Pb and Zn from municipal solid leachate [82].
Red mud (an aluminum industry waste)	Red mud waste material is commonly used to eliminate copper ions from contaminated water [83]. It can be modified to eliminate zinc and cadmium ions from aqueous medium [84].

Table 5. The economic comparisons of heavy metals removal technologies [86].

Treatment	Advantages	Disadvantages from economic point of view
Ion exchange	High regeneration of material, Metal selective	High maintenance and initial capital cost
Chemical precipitation	Non-metal selective, simple operation	High cost of disposal sludge, Large production of sludge
Membrane filtration	Almost no chemical consumption, very little formation of solid waste	Low flow rate, High maintenance and initial capital cost
Electrochemical treatment	Metal selective, Potential treat effluent > 2000 mg dm ³	High initial capital cost
Adsorption	Low-cost, easy availability, high efficiency, design flexibility and eco-friendly nature	No cost disadvantages. It is cost affective process

Table 6. Cost comparison of various adsorbents used for the removal of heavy metals from wastewater [85].

Species	Type of adsorbent	Optimum dose g/L	Initial metal concentration mg/L	Optimum pH	Adsorption capacity mg/g	Retail price USS/kg	Ref.
Cr(VI)	AS-received CSC	24	20	6.0	2.18	0.25	[31]
	CSC coated with chitosan	18	20	4.0	3.65	0.25	
	HNO ₃ -treated CSC	12	20	4.0	10.88	0.25	
Cu (II), Cd(II), Zn (II)	Peanut hulls (agricultural waste)	10	32	N.A	10.17	2.0	[87]
Cu (II), Cd(II), Zn (II)	Peanuts hulls pellets (modified agricultural waste)	10	32	N.A	9.11	11.0-18.5	[87]
Cr (IV)	As-received Zeolite (natural material)	27	20	4.5	1.79	0.75	[88]
Ni (II)	Activated slug (Industrial by-product)	N.A	248	N.A	66	0.038	[89]

*N.A: Not Applicable

Economic Comparison of Adsorption with Conventional Treatment Methods

Adsorption is a cost effective method as compared to other conventional treatment methodologies. Table 5 represents an economic comparison between adsorption and other treatment procedures. Table 6 demonstrates cost comparison of various adsorbents used for the removal of heavy metals from wastewater [85].

Conclusions

Heavy metals e.g., Hg, Cd, Cr, Pb, Zn, As and Ni, etc. have a greater tendency to be accumulated in aqueous water and create disturbances in the food chain. They are highly difficult to remove and cause adverse effects on blood composition, lungs, energy level, kidneys, central nervous system, liver, and other vital organs. Adsorption is a cheapest and excellent technique for removal of heavy metal ions from

wastewater and is advantageous due to easily accessible favorable conditions as well as local and abundant availability of required resources. It involves low-cost adsorbents of industrial (e.g., waste slurry, fly ash, sugar cane bagasse, lignin, red mud, blast furnace slag, sugar beet pulp etc.), natural (e.g., zeolite) and agricultural (e.g., rice, wool, waste tea, coffee, crop biomass, waste tea, rice straw, rice hulls, coconut shell, soybean hull, papaya wood, peanut shell, and citrus fruits) origin. Adsorption may be classified into a continuous batch, semi-batch, and batch categories or into physical and chemical adsorption. The adsorbates bind on to the surface of adsorbents due to van der Waals forces in physical adsorption. In chemical or activated adsorption, adsorbent and adsorbates chemically react with each other.

Conflict of Interest

The authors declare no conflict of interest.

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