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The Quest for Active Carbon Adsorbent Substitutes: Inexpensive Adsorbents for Toxic Metal Ions Removal from Wastewater

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Due to overgrowth in population, industrialization and civilization, demands for water are increasing geometrically. Therefore, alternative sources of water are required and wastewater treatment and recycling may serve this purpose. Among various water treatment technologies, adsorption onto activated carbon is in the front line due to its universal nature. Activated carbon is the best adsorbent able to capture inorganic, as well as organic, pollutants that contaminate water resources. Inorganic pollutants, especially metal ions, are more dangerous due to their toxic and possibly carcinogenic natures. Also they are most often persistent and difficult to biodegrade. The present article describes the quest to find an economically viable substitute to active carbon adsorbent to remove toxic metal ions. A brief discussion of design of batch and column adsorption experiments, development of inexpensive adsorbents, and experimental conditions of metal ions removal by batch and column procedures is included. Efforts have also been made to differentiate adsorption versus speciation of metal ions.

KEYWORDS Wastewater, adsorption, removal, toxic metals, inexpensive adsorbents, active carbon substitutes

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INTRODUCTION

Water is the most important and essential component of this universe and plays a vital role in the proper functioning of the Earth's ecosystems. In spite of this, safe drinking water is not available in some parts of the world. The quality of water resources is deteriorating exponentially due to contamination. The geometrical growth of world population, modern industrialization and civilization, domestic and agricultural activities and other geological, environmental and global changes are responsible for water pollution. Nowadays, water pollution is a serious issue as it affects all living creatures, household, recreation, fishing, transportation and other commercial activities (1–3).

The importance of water quality preservation and improvement is essential in life and increasing continuously. In view of these facts, all water regulatory authorities and agencies are very serious on the pollution of water resources. More than 700 organic and inorganic pollutants have been reported in water. Among these pollutants, heavy metal ions are signaled as the most dangerous, due to their toxic and carcinogenic natures. Moreover, some metal ions are not biodegradable or bio-transformable and, hence, persist in the environment for a long time. The most toxic metals are in the 4^{th} period of the periodic table, namely cadmium, platinum, mercury, arsenic, antimony, etc. (4–8). In view of these points, the present review focuses on the removal of these toxic metal ions from wastewater.

With the development of science and technology various methods for water purification and recycling have been developed and used from time to time (9–25). These methods are classified on the basis of physical, chemical, electrical, thermal and biological principles. These methods include screening, filtration and centrifugation, micro- and ultra filtration, crystallization, sedimentation and gravity separation, flotation, precipitation, coagulation, oxidation, solvent extraction, evaporation, distillation, reverse osmosis, ion exchange, electrodialysis, electrolysis, adsorption etc. Among these methods, reverse osmosis, ion exchange, electrodialysis, electrolysis, and adsorption are excellent technologies.

The cost of water purification by these technologies, except adsorption, ranges from 10 to 450 US$ per cubic meter of treated water. Oppositely, the cost of water treatment using activated carbon adsorption ranges 5 to 200 US$ per cubic meter of water. Besides, adsorption is supposed to be the best wastewater treatment method, due to its wide range of applications and ease of operation. It is also considered as a universal water treatment and reclamation technology, as it can be applied for the removal of soluble and insoluble organics, inorganics as well as biological pollutants with removal efficiency up to 99%. At the industrial level, pollutants are removed from wastewater using columns and contractors filled with suitable adsorbents. Adsorption can also be used for source reduction, reclamation for potable, industrial and other water purposes. Due to wide applications of adsorption, much work has been carried on the removal of different pollutants and, hence, many review articles have been written on this issue (26–37). This article is limited to the applications of adsorption for the removal of metal ions using adsorption technology.

ADSORPTION ESSENTIALS

Adsorption is a surface phenomenon and defined as the increase in concentration of a particular component at the surface or interface between two phases. The compound (pollutant) that sticks or adheres to the solid surface is called as adsorbate, and the solid surface is known as adsorbent. The adsorption is affected by temperature, nature of adsorbates and adsorbents, presence of other pollutants, and other atmospheric and experimental conditions. In addition, the adsorption process is controlled by other factors such as pH, temperature, concentration of pollutants, contact time, and particle size of the adsorbent. The presence of suspended particles, oils, and greases reduces the efficiency of the process and, therefore, sometimes prefiltration is required. When a finely divided solid is shaken with the contaminated/polluted water, the pollutants adhere to the solid surface, and a stage of equilibrium is established. At this stage the amount of pollutants adsorbed and in wastewater becomes constant. The relationship, at given temperature, between the equilibrium amount of the pollutants adsorbed and those remaining in wastewater is called the adsorption isotherm. Langmuir, Freundlich and other models are well-known adsorption models by which the adsorption efficiency of the pollutants can be explained in a systematic and scientific way (23).

Design of Batch and Column Adsorption Experiments

The design of a batch adsorption process starts with plotting the isotherm (Figure 1). The loading (mg) amount of material adsorbed per gram of adsorbent is plotted versus the concentration of the solution at equilibrium. The design of a column for the adsorption starts with laboratory testing to determine the breakthrough capacity. A mass transfer zone is formed in the column bed by passing the contaminated water. The depth of this zone is controlled by the characteristics of the adsorbent and metal ions and hydraulic factors. The depth of mass transfer zone is a measure of physical and chemical resistance to mass transfer. This zone moves down and reaches to the bottom of the column where metal ion concentration in effluent becomes equal to the influent concentration and a breakthrough point of the column occurs.

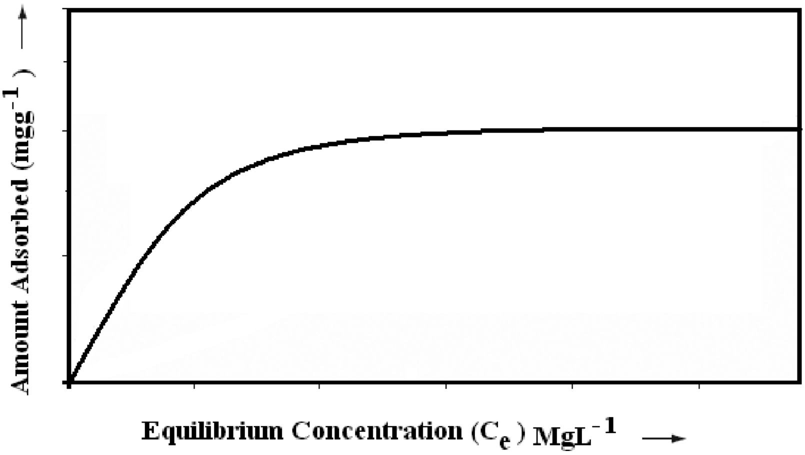

FIGURE 1 A typical batch adsorption isotherm indicating equilibrium stage at adsorption.

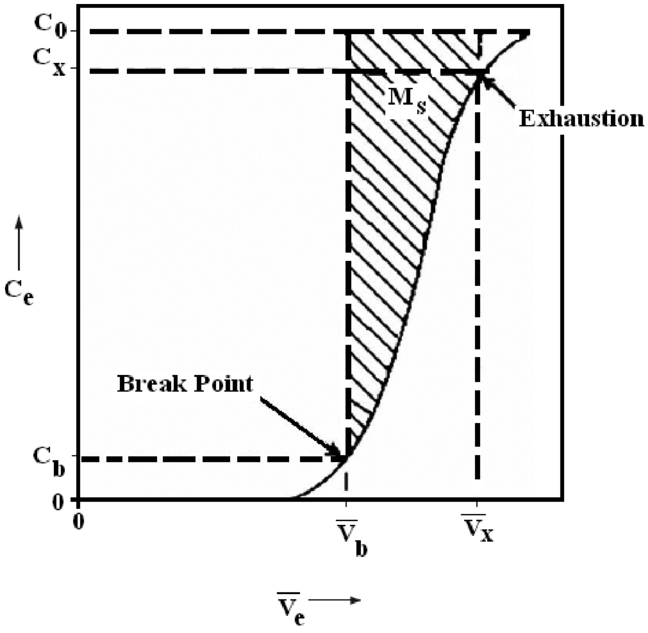

FIGURE 2 A typical column breakthrough curve. (Co = initial concentration of influent, Cx = concentration of effluent at exhaustion, Cb = concentration of effluent at breakpoint, Ce = equilibrium concentration effluent, Vb = volume of effluent at breakpoint, Vx = volume of effluent at exhaustion, Ve = volume of total effluent).

This situation is shown in Figure 2, and the breakthrough curve is idealized by the assumption that the removal of the solute is completed over the initial stages of operation. The break point is chosen arbitrarily at some low value, C_b, for the effluent concentration. At an arbitrarily selected effluent concentration, C_x closely approaching to C_0, the sorbent is considered to be essentially exhausted. The total volume of effluent V_b, passing per unit cross section at the break point and the nature of the breakthrough curve between the values of V_b and V_x are used for design purpose. The primary adsorption zone in the fixed bed adsorbent is that part of the bed where there is a concentration reduction from C_x to C_b. It is assumed to be of constant length (L in m).

The fractional capacity (*f*) of the adsorbent at break point may be calculated as follows:

$$f = \int_0^1 [1 - \frac{C}{C_0}]\, d\frac{(V_e - V_b)}{(V_x - V_b)} \qquad (1)$$

where C, C_0 and V_e are equilibrium concentration, initial concentration and volume of effluent at exhaustion, respectively.

The percent column saturation at break point is given by the following equation.

$$\%\ \text{Saturation} = \{[D + L(f - 1)]/D\} \qquad (2)$$

where D is the adsorbent bed depth.

Activated Carbon Adsorbents

Since its first introduction in the 1940s, activated carbon has been the main water industry's standard adsorbent for the reclamation of municipal and industrial wastewater to a potable water quality (10, 29). The use of carbon adsorption for the direct treatment of liquid industrial waste streams is a relatively recent practice but has been successfully utilized for the reclamation of metals from electro-plating wastewater (30). Activated carbon has been found as a suitable adsorbent due to its good capacity of adsorption because of small particle sizes and active free valences. In spite of this, it could not be used as the adsorbent for water treatment at large scale due in all cases due to its high cost of production. Moreover, the regeneration of activated carbon is difficult which involves the use of costly chemicals and, hence, its regeneration has also a limited viability at commercial scale.

DEVELOPMENT OF LOW-COST ADSORBENTS

The drawbacks associated with activated carbon have resulted into the growing research interest for the development of some low-cost alternatives using a range of carbonaceous and other precursors (26, 31). Many of the starting materials for these replacements are from agricultural or industrial by-products and, hence, their use as secondary adsorbents contributes to waste minimization with recovery and reuse. Many types of low-cost adsorbents have been developed and used for wastewater treatment. For the convenience of the readers we have categorized them into two classes: i.e., prepared from i) organic and ii) inorganic precursors. The absorbents obtained from both classes of precursors are used for water purification, especially for the removal of metal ions.

PREPARATION OF ADSORBENTS FROM ORGANIC PRECURSORS

The commonly used organic precursors are scrap tires, bark, tannin-rich materials, saw dust, petroleum wastes, rice hulls, fruit stones, coconut shell, fertilizer wastes, peat moss, chitosan, algae, seaweeds, seafood processing wastes, resins, fly ashes and wastes of some industries. Contrarily, inorganic precursors include metal oxides, hydroxides, clays, red mud, zeolites, blast furnace slag, sediment, soil, ore minerals etc.

Low-Cost Sources to Obtain Activated Carbon

Selected wastes are converted into activated carbons by some physicochemical processes. Activated carbon includes a broad range of carbonaceous materials, which exhibit a high degree of porosity and extended inter particle surface area (32). Typically activated carbons possess high surface areas (600–2000 m^2 g^{-1}) and well defined micro-porous structure (average pore opening is about 1.5 nm) (33). Activated carbon is prepared in a two-stage operation and involves carbonization of the raw material below 800°C in the absence of oxygen, followed by the activation at elevated temperatures using an activator (steam, carbon dioxide or air) or sometimes chemical catalysts. The heating rate, time for carbonization and activation are the most important factors that control the final pore structure, surface area and the chemistry of the carbon prepared (34–36).

Huge varieties of carbon containing feed stocks have been used to prepare activated carbon of different grades, preferably by the catalytic activation of an initially pyrolyzed char. The most commonly used feed stocks for the production of activated carbon at commercial scale are wood (generally pine, 130,000 tons per year), anthracite and bituminous coal (100,000 tons per year), lignite (50,000 tons per year), peat (50,000 tons per year) and coconut shell (35,000 tons per year). Other alternative feed stocks such as olive stones and almond shells account for ~10,000 tons per year (32, 37). The carbon contents of these precursors range from 40–90% (w/w) with a bulk density range of 0.40–1.45 g cm^{-3} . Principally, commercial carbon is prepared from pine wood and coal but still there is a continuous search for more inexpensive alternatives (26).

Carbonization and Activation

As discussed above, carbonization and activation are the most important processes in the development of low-cost activated carbon. During carbonization, pyrolytic decomposition of precursor occurs together with the concurrent elimination of many non-carbon species (H, N, O and S) (38). In this process, low molecular weight volatiles are first released followed by light aromatics and, finally, hydrogen gas (39), which resulted into a fixed carbonaceous char (40). The pores formed during carbonization are filled with tarry pyrolysis residues and hence, activation is required to increase the internal surface of the material.

Activation may be accomplished via a chemical or physical treatment. Sometimes, in chemical activation a catalyst is impregnated into the feedstock. The most widely used chemical activates are $ZnCl_2$, H_3PO_4, H_2SO_4, KOH, K_2S and KCNS (36). In this process an almost saturated solution of catalyst impregnated feedstock is dried to influence pyrolysis in such a way that tar formation and volatilization can be kept at minimum. The resulting product is then carbonized and activated in a single action at two different temperatures (41). The chemical carbonization is performed starting at 400°C followed by activation raising the temperature up to 800°C as used for the industrially wood based carbons.

The pore size distribution of the final product depends largely upon the degree of initial impregnation (32). Kadlec et al. (42) compared the chemically and physically activated carbons and found that the different mechanisms of activation are responsible for varying shapes and sizes. The porosity develops due to an increased burn-off of disorganized carbon (34). Steam, CO_2 and air are the most common activants and the mechanisms of these reactions are given in several articles (43–45). Many industrial and agricultural wastes are high in carbon content and, hence, offer a significant potential for the preparation of carbonaceous charcoals, which may be further activated to obtain porous adsorbents. Various such waste precursors are discussed herein.

Scrap Tires

The disposal and management of waste tires are of great concern as they pose serious fire risk. Their uncontrolled combustion may lead to the large volume release of oils, polynuclear aromatic hydrocarbons (PAH), phenols and heavy metals into the atmosphere (46). On the other hand, these waste tires have high carbon content and, thus, controlled pyrolysis has been employed to convert waste tires to semi-active carbon. The stripped tires have been used to obtain carbon using a moving bed reactor, at 400–700°C, and a variety of atmospheres. The surface area of the finished active carbon was found to be around 300 m^2 g^{-1} (47). For vapor phase applications, a highly active carbon of surface area 1260 m^2 g^{-1} was prepared using a wet thermal process (water/steam 700–900°C) (48). Another powdered activated carbon with a lower surface area of 193 m^2 g^{-1} was prepared from waste tires. It exhibited a considerable affinity for many pollutants (49). However these precursors could not achieve a good reputation in the development of low-cost charcoal alternative due to costly operations involved in their production.

Bark and Other Tannin-Rich Materials

Bark is a solid waste of timber industry and it can be used directly as a possible adsorbent due to its high tannin content. The polyhydroxy polyphenol groups of tannin are found to be the active species in the adsorption process. The uptake of cations takes place through ion exchange by displacing the adjacent phenolic hydroxyl groups forming a chelate (50, 51). The main problem associated with tannin containing materials is the development of coloration and toxicity in water due to soluble phenols. To overcome this problem, chemical pre-treatment of bark has been tried by a number of workers. Alves et al. (52) carried out formaldehyde pretreatment to diminish the bleeding of colored compounds without appreciably affecting capacity.

Randall et al. (50, 53) carried out a comparative study of bark adsorption to that of peanut skins, walnut expeller meal and coconut husks and found their adsorption capacities to be comparable. Furthermore, Randall et al. (54) also tried formaldehyde pre-treatment of peanut skins to prevent leaching of color and disintegration upon prolonged contact with water. The resulting product was quite stable in water and was efficient for uptake of Cd(II), Cu(II), Hg(II) and Pb(II). Orhan and Buyukgungor (55) observed the adsorption capacities of tannin containing products obtained from nut and walnut shell, waste tea and coffee and compared it with that of activated carbon. They demonstrated that the capacities of the tannin containing products are only slightly less than that of activated carbon.

Edgehill and Lu (56) determined the potential of carbonized slash pine bark as a suitable substitute for activated carbon. The bark was carbonized by slow heating in nitrogen for 6.5 h at 670°C. The surface area, average micropore and mesopore diameter, and micropore volume of the prepared adsorbent were 332 m^2 g^{-1} , 2.17 Å and 0.125 cm^3 g^{-1} , respectively. Al-Asheh and Duvanjak (57) evaluated cadmium ions adsorption onto carbonized pine bark. The maximum cadmium uptake was obtained using very fine particles of pine bark. Portuguese pine bark was shown to be a suitable precursor for activated carbon production by Guedes de Carvalho et al. (58). The carbonization of ground bark was carried out at 600°C for 1h under nitrogen atmosphere and then activated between 800–1000°C by partial CO_2 gasification. Aoyama et al. (59) studied the adsorption capacities of 34 conifer leaves with good adsorption capacities of *Ginkgo biloba*, *Taxus cuspidata*, *Cephalotaxus harringtonia*, *Taxodiaceae* and *Cupressaceae* species for Cr(III) metal ion.

The adsorption capacities of conifer leaves for were compared with those of commercial activated carbons. It is interesting to note that 3.12–5.09 mg g^{-1} Cr (III) was adsorbed on different conifer leaves, while the adsorption capacities of activated carbons were 1.23–2.75 mg g^{-1} for Cr(III). The larch (*Larix leptolepis*) bark was able to remove Cr(VI) from dilute aqueous solutions at pH 3. Bark and tannin rich materials are having high adsorption capacities but the preparation of activated carbon is costly. Moreover, coloration and toxicity are developed in water. Therefore, they could not be used extensively for the removal of toxic metal ions from wastewater.

Patil et al. (60) removed nickel metal ions by using powder activated charcoal and non-conventional adsorbents. Kalmykova et al. (61) used sawdust, pine bark and fiber sludge ash and some other biological materials (peat, shrimp shells and seaweed) for absorption of some metal ions from laboratory synthesized water and industrial landfill by using batch and column operations; with maximum adsorption on peat. The addition of 10% by weight of fiber ash to the peat resulted into higher adsorption capacities of Cd(II), Ni(II) and Pb(II) but lower for Cu(II) and Zn(II), respectively. Subbaiah et al. (62) achieved bio-sorption of Ni(II) ions from aqueous solution by Acacia leucocephala bark by varying pH, metal ion concentration, adsorbent dosage, contact time and temperature parameters. Khokhotva and Waara (63) compared adsorption of Cu(II), Ni(II), Zn(II) and Pb(II) metal ions on plain and urea treated pine bark (UTB) of Pinus sylvestris.

Sawdust, Lignin and Other Wood-Type Materials

Sawdust and other wood materials may be used as the alternatives of activated carbon. The adsorption capacities of these adsorbents are due to lignin or tannin components rather than the cellulose content (64). Sabadell and Krack (65) investigated several wood types for the adsorption of Pb(II), Cd(II), Cu(II) and Ni(II) metal ions. These wood materials were converted by heat into low-cost activated carbons. The average capacities for the woods used in these studies are 0.0982 meq g^{-1} for oak sawdust, 0.0721 meq g^{-1} for ash shavings and 0.0683 meq g^{-1} for cedar sawdust. Vaishya and Prasad (66) reported that rate of adsorption of cupric ions on saw dust was very high initially and maximum adsorption occurs within 1 h. The ability of sawdust to adsorb Cr(VI) from waste solutions has been investigated by Zarraa (67) in a batch reactor under forced convection conditions.

The removal of Cr(VI) was found to be significantly dependent on the weight of sawdust. The sawdust of a mango tree (*Mangifera indica*) was treated with 0.1 M disodium hydrogen phosphate for 24 h and then washed with distilled water followed by dying at 40°C by Ajmal et al. (68). A comparative study on the sorption capabilities of this phosphate treated and untreated sawdust, for the adsorption of Cr(VI), was carried out. Nearly 100% adsorption was observed below pH 2.0 for the initial Cr(VI) concentration of 8–50 mg $L.^{-1}$ The experiments, carried out with synthetic as well as actual electroplating industry wastewaters containing 50 mgL^{-1} Cr(VI) showed 100% adsorption.

For regeneration purposes, 87% desorption of Cr(VI) from phosphate-treated sawdust was achieved using 0.01 M NaOH. Raji and co-workers (69) determined the factors influencing uptake of Pb(II), Hg(II) and Cd(II) onto the activated carbon prepared from bicarbonate treated wood sawdust. The percent adsorption increases with decrease in initial adsorbate concentration, increase in adsorbent concentration and temperature. The maximum adsorption was observed in pH range of 4–8 for Pb(II) and Hg(II) and 5–9 for Cd(II). The adsorbent can be regenerated by using 0.2 M HCl. The lignin was extracted from black liquor, a waste product of paper industry and converted into a low-cost adsorbent for the removal of lead and zinc (70).

The adsorption capacity of lignin at 30°C was found to be 1587.0 and 73.0 mg g^{-1} for Pb and Zn respectively, which increased to 1865 and 95 mg g^{-1} respectively at 40°C. Masri et al. (71) carried out an adsorption study of Hg(II) and reported adsorption capacity 150 mg g^{-1} . Adsorption capacities of sawdust, lignin and other wood-type materials were quite high with short equilibrium time. The process development and regeneration of these adsorbents were quite costly. Moreover, the availability of these raw materials was not high at the commercial level and, hence, could not be used frequently.

Sulfur-containing groups on the adsorbents provide a high affinity for the adsorption of heavy metals but a low affinity for lighter metals. Some sulfur containing compounds include sulfides, thiols, dithiocarbamates, dithiophosphates and xanthates. Among them xanthates are highly insoluble and important precursors because they are easy to prepare with relatively inexpensive reagents (72). The ion exchange reaction method is used for heavy metal removal by xanthates. The sorptive capabilities of xanthates have been studied and the solidifications of xanthate sludges made these adsorbents effective (73). Adsorption capacity varied randomly due to variation in particle porosity and size. The sorption capacity of xanthates decreased with time (18% in 47 days) due to decomposition and air oxidation of sulfur atoms.

The adsorption capacity for Cd(II) ranged from 0.28–0.38 meq g^{-1} [15.7–21.4 mg g^{-1} of Cd(II)]. The adsorption capacities for Mn(II), Co(II), Ni(II), Ag(II), Zn(II), Hg(II) and Pb(II) ranged 0.3 to 0.4 meq g^{-1} . The soluble (SSX) and insoluble (ISX) starch xanthate were compared for their adsorption capacities (74,75). ISX forms were produced from corn starch by an extra cross-linking step. The experiments with ISX involved sorption process since solute molecules from an aqueous phase were transferred to an already existing solid phase. The experiments showed that ISX exhibited better properties than SSX in terms of metal removal capacities, reliabilities and ease of operation, however, SSX is more economical than ISX. The cost of ISX is US$ about $60 for 100 g and requires 90–110 h for preparation while the cost for SSX is only $10/100 g taking only 3–4 h for preparation. A preliminary estimated cost for ISX production was only $0.60/kg (76). Wing (77) presented several case studies demonstrating ISX effectiveness. ISX was used to remove heavy metals from plating rinse waters. The adsorption principle is ion exchange, which limits ease of their regeneration due to high cost. The probabilities of decomposition and air oxidation of these adsorbents are serious drawbacks. The adsorption capacities of xanthates are not quite good; especially for light metal ions and, hence, they could not be used at pilot scale for wastewater treatment.

Rice Hulls

Rice hulls or husks; agricultural wastes products; have been used for the production of low-cost adsorbents [rice husk carbon (RHC)]. Adsorption efficiencies of these adsorbents are quite encouraging, i.e., RHC has shown 94.4% w/w Cd(II) adsorption capacity (78). This efficiency was compared to Filtrasorb 400®, a commercial activated carbon, with 25.4% w/w removal capacity of Cd(II). However, the high cost of steam activation at 700°C remains a major problem with RHC. Srinivasan et al. (79) used RHC for Cr(VI) removal from industrial wastewater. The batch studies revealed that RHC was comparable to commercially available activated carbon. The column capacities for Cr(VI) uptake were found to be 8.9 and 6.3 mg g^{-1} of RHC and commercial carbon, respectively. The adsorbent was successfully used for the treatment of an actual wastewater from a real plating shop bearing Cr(VI) up to 300 mg L^{-1} . Roy et al. (80) investigated heavy metal uptake by rice hulls and adsorption capacities of rice hulls were quite good for Cr(VI) and Pb(II). Mostafa (81) prepared steam-activated and zinc chloride-activated carbons from rice husks and used for the removal of Hg(II), Pb(II) and Cd(II) ions from aqueous solution at 298°K. The uptake capacities of rice hulls were greater than commercially available activated carbons in both batch and column experiments.

Organic Waste from Paper Industry

Guo et al. (82) studied adsorption of Pb(II), Cu(II), Cd(II), Zn(II), and Ni(II) on a lignin isolated from black liquor; a waste product of the paper industry. It was observed that adsorption was strongly pH and ionic strength dependent. The authors carried out surface complexation modeling, which confirmed two main types of acid sites attributed to carboxylic- and phenolic surface groups responsible for adsorption; with maximum adsorption by phenolic. Similarly, Wu and co-workers (83) also used the same lignin for removal of Cr(III) from waters. The effect of pH, dosage, contact time, ionic strength and Cr(III) concentration were studied. The data followed pseudo–second-order and Langmuir models with maximum 17.97 mg/g. The authors reported ion-exchange mechanism for adsorption. They applied the developed method for removal of Cr(III) from real wastewater sample.

Pejic et al. (84) used waste short hemp fibers; after chemical removal of lignin and hemicelluloses; for adsorption of Pb(II), Cd(II) and Zn(II) metal ions from aqueous solutions. The effects of initial ion concentration, contact time and co-sorption were studied in batch sorption experiments. The obtained results showed when the content of either lignin or hemicelluloses was progressively reduced by chemical treatment; the sorption properties of hemp fibers were improved. Short hemp fibers were capable of sorbing metal ions with maximum total uptake capacities for Pb(II), Cd(II) and Zn(II) of 0.074, 0.035 and 0.035 mM L/g, respectively. Of course, the cost of processing was low in comparison to the ready-made activated carbon and, definitely, these raw materials have quite good scope in the wastewater treatment process.

Fruit Stones

The outside or inner side hard parts of certain fruits such as olive stones, almond shells, apricot and peach stones, palm fruit bunch, coconuts, etc. are the prevailing raw materials for the preparation of activated carbons. The oily part of these raw materials is removed by treating them under anaerobic conditions and the obtained residue is dried and washed with organic solvents. The solid part is roasted in a rotating metal cylinder until its color change from brown to black (85).

Generally, the developed material is economic with a cost of \$50/ton in comparison to granulated activated carbon having a \$4500/ton cost. Rodriguez-Reinso and coworkers (86) had optimized the activation procedures for activated carbon production using a variety of chemical and physical techniques. Consequently, high quality microporous carbons have been prepared and characterized having 90–1550 $m^2\ g^{-1}$ surface area. Ferro-Garcia et al. (87) tried a series of fruit pit carbons for the removal of Zn(II), Cd(II) and Cu(II) from metal finishing plant wastewaters. Adsorption capacities for three metal ions ranged 18–150 $\mu M\ g^{-1}$. The prepared adsorbents were subsequently recommended by the authors for the treatment of metal finishing plant wastewaters.

Namasivayam and Periasamy (88) prepared activated carbon from bicarbonate treated peanut hulls (BPHC) with 208 $m^2\ g^{-1}$ surface area and investigated the adsorption of Hg(II). Quantitative removal of 20 $mgdm^{-3}$ Hg(II) in 100 mL by 70 mg adsorbent was observed over a pH range of 3.5–10.0. A comparative study with a commercial granular activated carbon (GAC) showed that BPHC was 7.0 times more effective in comparison of GAC. Furthermore, Periasamy and Namasivayam (89) also investigated the removal of lead from aqueous solutions using peanut hull carbon (PHC) and coal based commercially activated carbon (GAC). PHC adsorbent was also used for the removal and recovery of cadmium from wastewater by the same authors (90). A comparative study with a commercial granular activated carbon (GAC) revealed that the adsorption capacity (K_f) of PHC was 31.0 times larger than that of GAC. An almost quantitative removal of 20 mg L^{-1} Cd(II) by 0.7 g of PHC/L of aqueous solution was observed in the pH range of 3.0–9.5. A range of chemically activated tamarind nut carbons were prepared by using a variety of treatments adapted from the carbon literature (91, 92).

Coconut shell is a well-known precursor for the production of high-quality granular activated carbons. Currently it is responsible for ~9% w/w global production of commercial activated carbon. It has been considered as an inexpensive raw material due to its wide spread distribution in the developing countries. Banerjee et al. (93) prepared activated carbon by heating $ZnCl_2$ impregnated crushed coconut shells at 700°C. The resulting charred intermediate was activated in steam or air at 900°C. The black carbon obtained had a surface area of 800 $m^2\,g^{-1}$ with high adsorbing properties.

Alaerts et al. (94) reported the removal efficiencies of commercial carbons having surface area similar to activated coconut based carbon for the removal of aqueous Cr(VI). Coconut based carbon was found to be highly effective as 94% (w/w) of a 20 mgL^{-1} Cr(VI) solution was removed in 4 h contact time during equilibrium batch studies. Mortley et al. (95) characterized activated carbon from materials of varying morphology including coconut husks and shells and compared them with commercially available carbons. The precursors with higher activation energies yielded higher surface areas and developed micro porosities on account of the lesser degree of lignocellulosic breakdown. Laine and co-workers (96) prepared Venezuelan coconut carbons by chemical activation. The shells were impregnated with H_3PO_4 followed by a one step carbonization/activation at 450°C. The surface area of the product was 1200 $m^2\,g^{-1}$. Manju and coworkers (97) evaluated the efficiency of copper impregnated coconut husk carbon (CuCHC) for the removal of arsenic from water and wastewater.

Coconut husk carbon (CHC) was prepared by treating one part of coconut husk with 1.8 parts by weight of concentrated sulfuric acid (18 M) and keeping it in oven at 150°C for 24 h. The carbonized CHC material was washed with distilled water to remove free acid and dried at 105°C. The studies showed that CuCHC is 5 times more effective than CHC for the removal of As(III) and the maximum adsorption capacity of the prepared adsorbent was 158 mg g^{-1} at 60°C. The batch operation was also carried out for the removal of As(III) from actual industrial waste collected from one fertilizer industry in Cochin city (Kerala, India) using CuCHC. The results showed that the CuCHC can be used as an adsorbent for the effective removal of As(III) from water and wastewaters.

Rao (98) investigated the kinetics of Cr(VI) removal on prepared activated coconut shells. The activated carbons were prepared by physical and chemical activation using H_2SO_4, H_3PO_4 and $ZnCl_2$ activating agents of different impregnation ratio. The adsorption was maximum at pH 1.0 and increased with increase in impregnation ratio due to increase in surface area of coconut shell carbon. The developed activated carbons from these raw materials were quite good having high surface area, activation energies and adsorbing properties. These adsorbents have been used under a wide range of experimental conditions with up to 31 times higher efficiencies than the commercial available activated carbon. But low abundance restricts their use at pilot scale.

Peat Moss

During the past few decades, peat moss is advocated as an inexpensive and easily available adsorbent material, having high adsorption capacities for a variety of pollutants. Peat is mined and processed for fuel in Ireland and Northern Europe and as a soil conditioner in the United States (99). Peat is a complex soil material with lignin and cellulose as the major constituents. Lignin contains polar functional groups that can be involved in chemical adsorption phenomenon. Because of these properties, peat mosses tend to have a high cation adsorption capacity and can be effectively used for the removal of a variety of metal ions (100).

Peat is highly porous (95%) and possess a large specific surface area (>200 m^2 g^{-1}) (101). There are different types of peats available with varying chemical and physical properties. Chen et al. (102) reported the complexation and ion exchange facilitating adsorption of Cu(II) onto eutrophic and oligotrophic peat. The efficiency of these adsorbents had been reported up to six times for Cr(VI) in comparison to activated carbon (103).

Kertman et al. (104) examined the efficacy of modified peat to adsorb different heavy metals with the adsorption capacity of 90–230 mg g^{-1} for lead. Acid treated peats had higher adsorption capacities than the normal ones for uptake of Cd(II) and Cr(II) (105). Studies were also carried out on the regeneration of peat by Sharma and Forster (106). Ho and Mckay (107) reported the kinetics of lead sorption on to peat. The batch sorption model, based on the assumption of a pseudo second order mechanism, has been developed to predict the rate constant of sorption. Kalmykova et al. (108) carried out adsorption of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) on Sphagnum peat. The kinetics of adsorption was analyzed using a second-order model and rate constants were calculated. The order of removal capacity was Pb(II) > Cu(II) > Ni(II) > Cd(II) > Zn(II) with optimization by pH and ionic strength.

Chitin and Chitosans

Chitin and chitosans are the most important materials examined for the removal of toxic metal ions due to their inexpensive and effective in natures. Chitin is found in the exoskeletons of crabs and other arthropods and also in the cell wall of some fungi (109,110). A large amount of chitin is produced from crab meat canning industry. More than 40,000 tons/annum of chitin is available from the fisheries of crustacean (111). Chitosan or glucosamine is a deacetylated derivative of chitin and can be chemically prepared from chitin. Chitosan is found in the cell wall of some fungi like *Mucorales* stains. About 2000 tons of chitosan could be produced at a cost of about $2.00 per kg (109). Deacetylation of chitin exposes free amino groups, enhancing its chelating capacity; hence, chitosan can chelate 5 to 6 times greater amount of metals than chitin itself.

Chitosan showed greater adsorption capacities than poly-(*p*-aminostyrene) which were constituents of expensive ion exchange resin. The fishery wastes including shrimp shell, lobster shell, crab shell and cattle bone were used to prepare chitosan by Tseng et al. (112). The removal of Cd(II), Cu(II) and Ni(II) was successfully carried out using this adsorbent. Chui et al. (113) studied the removal and recovery of Cu(II), Cr(III) and Ni(II) from solutions using crude shrimp chitin packed in small columns. Shrimp shell wastes from *Penaeus marginatus* were dematerialized by dilute HCl in small columns to yield shrimp chitin. 96% Calcium was efficiently removed by this method without removal of proteins. Wastewater of electroplating baths rinsing having Cu(II) gave encouraging results.

The shrimp chitin removed 92–96% Cu(II) from copper pyrophosphate and acid copper bath rinsing water. Kim et al. (114) studied the effect of deacetylation on sorption of chromium on chitin. Deacetylated chitins (10.7–67.2%) were prepared by alkaline hydrolysis on optimal degree of deacetylation, which could effectively removed chromium form textile effluent. Baran et al. (115) described adsorption of Cr(VI) ions onto various sorbents (chitin, chitosan, ion exchangers; Purolite CT-275 (Purolite I), Purolite MN-500 (Purolite II) and Amberlite XAD-7) in batch process. The optimized parameters were pH, agitation period and concentration of Cr(VI) ions. The optimum pH for Cr(VI) adsorption was found 3.0 for chitin and chitosan whereas it did not affect adsorption on ion-exchangers. The maximum chromium sorption occurred at 50, 40, 30 minutes, for chitin, Purolite II and Chitosan, Purolite I and Amberlite XAD-7, respectively. The authors described that adsorption could be increased by impregnating the reported adsorbents by EDTA. Over all, chitosan is a readily available, inexpensive adsorbent found suitable for maximum removing chromium from aqueous solution.

Jayakumar et al. (116) used alginate/phosphorylated chitin (p-chitin) blend films; prepared by mixing of 2% of alginate and p-chitin in water and then cross-linked with 4% $CaCl_2$ solution; for removal of Ni(II), Zn(II) and Cu(II) metal ions. These studies confirmed that alginate/p-chitin blend films were bioactive. The parameters optimized were pH, contact time and initial metal ion concentrations. The maximum adsorption capacities of alginate/p-chitin blend films for Ni(II), Zn(II) and Cu(II) at pH 5.0 were found to be 5.67, 2.85, and 11.7 mg/g, respectively. Briefly, abundance of these raw materials is quite high, i.e., available at large amount next to cellulose. Nevertheless, they could not achieve a good reputation of effective adsorbents in the removal of metal ions from wastewater. The serious drawback associated with these raw materials is their regeneration as the metal ions are strongly chelated with them. Costly chemicals are required for regeneration.

Live Sea Weed and Alginate

Seaweed is an abundant source for adsorbents to be used in adsorption experiment for the removal of various pollutants from water. Vijayaraghavan and Yun (117) reviewed adsorption of metal ions on various bio-adsorbents such as bacteria, fungi, algae, and industrial and agricultural wastes. The properties of the cell wall constituents, such as peptidoglycan, and the role of functional groups, such as carboxyl, amine and phosphonate, were discussed on the basis of their biosorption properties.

Some seaweed like brown algae has significant ion exchange properties associated with their polysaccharide contents. Brown marine algae, *Ascophyllum nodosum*, was used in sorption columns to remove Cd(II) with adsorption capacity to be approximately 67 mg g^{-1} (118). Certain unicellular green algae such as *Fucus serratus* and *Laminaria digitata* showed better uptake of Cd(II) and Hg(II) (119). The green seaweed *Ulva lactuca* was just slightly less effective than two brown seaweeds. Modifications of seaweeds by cross-linking increased the stability and mechanical properties. The cross-linking retarded the swelling so that the material would be amenable to column adsorption. *Ascophyllum nodosum* was found to adsorb Cd(II) (2.15 mg g^{-1}) while 149 mg g^{-1} was absorbed by formaldehyde cross-linked treated *A. nodosum*. It has demonstrated pronounced adsorption in comparison to other seaweeds experimented i.e. *Sargassum natans* (135 mg g^{-1}) and *Fucus vesiculosus* (Cd(II) = 73 mg g^{-1}).

Leusch et al. (120) studied adsorption capacities of *A. nodosum* and *Sargassum fluitans* after formaldehyde cross-linking, glutaraldehyde cross-linking and polyethylenimine embedding for the removal of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) metal ions. The brown seaweed was processed to obtain a high molecular weight polymer, algin. Alginate is a polysaccharide based biosorbent and it can be prepared from algin by replacing protons in the carboxylic groups with metal ions. During sorption process, heavy metal ions appear to exchange with calcium ions to form a metal alginate. The theoretical maximum binding capacity of sodium alginate is 138 mg g^{-1} for Cu(II), while a capacity of 107 mg g^{-1} was experimentally determined (121). Araujo and Teixeira (122) investigated the applicability of calcium alginate beads for the removal of Cr(III) from aqueous solutions.

The biomass of the marine alga *Sargassum baccularia* has been evaluated for its adsorption and desorption of Cd(II) ions (123). Desorption of Cd(II) was achieved by desorbing agents such as HCl and ethylenediaminetetraacetic acid (EDTA) using a batch reactor system. Both these desorbents were suitable to remove the adsorbed Cd(II) from the biomass. It was found that HCl at pH 2.0 could desorbs 80% of Cd(II) initially loaded on to the biomass.

Almost complete recovery of Cd(II) was achieved by a 3.24 mM EDTA solution. Malik et al. (124) used marine algal-based biosorbents for the removal of Pb(II) and Cu(II). The weakly acidic carboxyl groups of polysaccharides present within the algal matrix displayed high sorption capacity for both metals. Adsorption kinetics of Al(III), Zn(II), Hg(II), Pb(II), Cu(II), and Cd(II) onto living microalgae (*Scenedesmus subspicatus, Cyclotella cryptica* and *Phaeodactylum tricornutum*) has been studied (125). The highest values for the rate constants obtained for *Porphyridium purpureum* followed by *Phaeodactylum tricornutum*. High values for the maximum content were obtained for *Cyclotella cryptica* and *Scenedesmus subspicatus*. The maximum rate constant was 24 h^{-1} for the adsorption of Hg(II) on to *Porphyridium purpureum* whereas maximum metal content (0.243g g^{-1}) was obtained for Zn on *Cyclotella cryptica*.

Hall et al. (126) used two strains of *Pseudomonas syringae* (Blue and Brown) to remove copper from aqueous solutions and compared with the synthetic Linde LZ-52Y aluminosilicate zeolite. The two bacterial strains were tolerant to copper and were able to grow in media with Cu(II) concentrations up to 1000 ppm (1 g/L). As in case of chitin and chitosan the basic process of metal ion adsorption was through ion exchange mechanisms, which made the regeneration process complex and costly. That is why costly HCl and EDTA chemicals were used to recover metal ions from these adsorbents. Moreover, disintegration and swelling tendencies of these biomasses restricted their use at large scale; especially in columns.

Sari and Tuzen (127) described equilibrium, thermodynamic and kinetic studies of Al(III) bio-sorption on brown algae (Padina pavonica) biomass with optimum conditions of pH, biomass dosage, contact time and temperature. The bio-sorption capacity of *P. pavonica* biomass was found to be 77.3 mg/g. The metal ions were desorbed from *P. pavonica* using

1.0 M HCl. The high stability of *P. pavonica* permitted a slight decrease about 20% in the recovery of Al(III) ions after 10 times of adsorption-elution process. The adsorption mechanism described was chemical ion exchange with spontaneous and endothermic nature. Rathinam et al. (128) removed Cd(II) metal ions on red macro alga (Hypnea valentiae). The optimized variables were cadmium concentrations, pHs and temperatures; with maximum adsorption at pH 6.0 (250 mgL^{-1}). The authors described that the presence of neutral salts and other metal ions affected the cadmium uptake behavior of the biomass considerably.

Pahlavanzadeh et al. (129) reported the bio-sorption characteristics of Ni(II) ions using brown algae (*Cystoseria indica, Nizmuddinia zanardini, Sargassum glaucescens* and *Padina australis*) by varying pH, contact time, initial metal concentration and temperature as experimental parameters. Esmaeili et al. (130) reported the removal of Cu(II) metal ions aqueous solution and wastewater on marine brown alga *Sargassum* species as adsorbent. The effect of pH, bio-sorption time, adsorbent dose and metal ion concentration were studied. The optimum pH was 4.0 with maximum removal of 94.83% within 2 h. The uptake of heavy metals by these adsorbents was reversible and the mechanisms of uptake were not well known and, hence, the research on this issue is not completely developed. Briefly, in spite of quite good abundance, these materials could not be used at large scale for the removal of metal ions. Therefore, the need of further extensive studies in terms of cost, performance, preparation methodologies, energy, efficiency, kinetics, regeneration and management is evident.

Dead Biomass

The dead biomass of bacterial cell can be used as the suitable adsorbents for the removal of metal ions from wastewater. The effectiveness of dead biomass lies in the fact that the dead cells have greater accumulation capacity for heavy metals than living cells. The bacterial cell contains anionic surface, due to the presence of ionized groups in the cell wall, compelling the cell to attract metal cations. Large quantities of waste microbial biomass are produced in industries such as citric acid biosynthesis and penicillin production. About 790,000 tons of microbial waste are produced each year by fermentation industries, with 41,000 tons resulting from citric acid production by *Aspergillus niger* (109). The use of dead rather than live biomass eliminates the problems of waste toxicity and nutrient requirements. Many workers have used such biomass for the removal of Cd(II), (131) Pb(II), (132), etc. The optimum pH range for biosorption of Pb(II) ion, on *Penicillium chrysogenum*, was 4 to 5. The saturated sorption of Pb(II) was 116 mg g^{-1} by dry biomass, which was higher than that of activated charcoal, and some other microorganisms (133). At pH 4.5 *P. chyrsogenum* biomass exhibited a significant selectivity for Pb(II) compared to other metal ions such as Cd(II), Cu(II), Zn(II) and As(III). Sorption preference for metals decreased in the order of Pb(II) < Cd(II) < Cu(II) < Zn(II) < As(III).

Yetis et al. (134) studied the removal of Pb(II) by live, resting and dead cells of a lignolytic white rot fungus, *Phanerochaete chrysosporium*. Kinetic studies revealed the fact that adsorption was two stage process, i.e., very rapid surface adsorption within the first hour and a slow intracellular diffusion after 2 hrs of metal exposure. The results showed that the resting cells were able to uptake up to 80 mg g^{-1} Pb(II). The biomass originated from different growth phases exhibited different adsorption capacities for Pb(II). It appeared that the young resting cells held higher Pb(II) adsorption capacities than the older ones. Bai and Abraham (135) studied the bio-sorption of Cr(VI) by chemically modified biomass of *Rhizopus nigricans* and the possible mechanisms of Cr(III) complexation to the adsorbent.

Biomass modification experiments were conducted using cetyl trimethyl ammonium bromide (CTAB), polyethylenimine (PEI) and amino propyl trimethoxy silane (APTS) to improve the bio-sorption efficiency up to exceptionally high levels. In spite of anionic surface on the dead bacterial cells, they were used for metal ions removal only at laboratory scale. The restricted use of this material at pilot scale was due to the selective nature of these cells with fair adsorption capacities. The intracellular diffusion process in the dead bacterial cell was the main drawback associated with regeneration process. Sometimes, living bacterial cells may present along with dead cell, which contaminant wastewater with bacteria and this may be hazardous to health. In a nut shell, the dead bacterial biomass could not be used for the treatment of wastewater at large scale.

Petroleum Wastes

A number of researchers have been attracted by the large quantities of carbonaceous waste residues generated in the petroleum refineries. These wastes have been utilized as pre-cursors for activated carbon. The pitch beads (a mixture of petroleum pitch and polyaromatics) have been prepared by activation at 800°C to obtain the adsorbent of the optimum quality (136). Fasoli and Genon (137) used a refinery waste for the preparation of a granular carbon. The waste was carbonized in a rotary furnace and then activated under steam atmosphere. Ali and Saleem (138) tried heavy vacuum bottoms obtained from an Iraqi crude oil for the production of a carbonaceous adsorbent. Due to better uses of these wastes, they could not be investigated thoroughly for the preparation of activated carbons.

Fertilizer Industries Wastes

The waste slurry generated during the liquid fuel combustion in fertilizer plants can be converted into an inexpensive carbonaceous adsorbent material

(139). Generally, these wastes are treated with hydrogen peroxide and then heated to 200^0 C till the evolution of black soot stopped. The heated product is cooled and then activated in presence of air at 450° C for 1 hour yielding an adsorbent of 630 m^2 g^{-1} surface area. The developed adsorbent has good adsorption capacities for the removal of Cr(VI), Hg(II), Pb(II), Cu(II) and Mo(II) metal ions from metallurgical and electroplating wastewaters. The compositions of these adsorbents have been determined with carbon, alumina and iron oxide 92, 0.4 and 0.6%, respectively (140). The amorphous nature of the activated carbon was ascertained by X-ray diffraction analysis. A scanning electron microscope (SEM) was used to observe the surface structure of the activated product. SEM pictures of the material indicated texture and large porosity of the sample activated in air. The developed activated carbon was found to be quite stable in water, salt solutions, acids and bases. Despite of good future of this waste in the production of low-cost adsorbent, much work has not been carried out and the research work is under progress.

Fly-Ash

Thermal power plants, sugar industries, brick kilns and some other industries are discharging an aggressive waste product called fly-ash. Several workers tried fly-ash as the suitable adsorbent for the removal of metal ions from water. The estimated global production of fly ash is 290 metric tons per annum (141) and currently there is no set methodology to use it and a large amount is dumped as land filler. Fly-ash is an inorganic residue and its chemical constituents comprise 40–50% (w/w) silica (SiO_2), 20–35% (w/w) alumina (Al_2O_3) and 5–12% (w/w) iron oxide (Fe_2O_3). Fly-ash also contains 12–30% (w/w) carbon and unburnt residue (142). Many metal ions such as Cr(VI), Cu(II), Ni(II), Zn(II), Hg(II) etc. were removed from wastewaters (143–148). Grover and Narayanaswamy (143) observed that fly-ash can be used for the removal of Cr(VI). The adsorption capacity for Cr(VI) was pH depending and a maximum adsorption (4.25 mg g^{-1}) was achieved at pH 2.0 (143).

The adsorption capacity for copper, determined at pH 6.5, was 73–95% (w/w) (144). Uptake was explained in terms of a chemisorptive surface complex between the negatively charged silica surface and the hydroxylated copper species in solution. These investigations revealed that fly-ash wollastonite blend was most effective and reported 40–60 times cheaper than the activated carbon. Kapoor and Viraraghavan (145) described that the properties of fly ash were extremely variable and the adsorption capacity varied with the lime content. Furthermore, the same workers (146) studied the effectiveness of fly-ash in adsorbing mercury from wastewater. They found that a contact time of 2 h was necessary for the adsorption to reach equilibrium at pH between 5.0 and 5.5. Viraraghavan and Dronamraju (147) evaluated the effectiveness of fly-ash in adsorbing copper, nickel and zinc by conducting batch kinetic and isotherm studies. Daniels et al. (148) evaluated the feasibility of utilizing alkaline fly-ash to control acid mine drainage. The results revealed that this technique had potential for industrial-scale use.

The chemical composition of bagasse fly-ash obtained from sugar industries comprises silica 60.5%, alumina 15.4%, calcium oxide 2.9%, iron oxide 4.9% and magnesium oxide 0.81%. The density, porosity and surface area of this material were 1.01 g cm^{-3} , 0.36 fractions and 450 m^2 g^{-1} respectively. X-ray spectra of biogases fly-ash showed the presence of different minerals such as kaolinite, mullite, geothite, α-quartz, γ-alumina and haematite. Scanning electron microscope (SEM) studies indicated flocks and porous nature of the material. An adsorbent dose of 10 gL^{-1} was found satisfactory for 100% removal of lead (at $4.8 \times 10^{-4} - 4.83 \times 10^{-3}$ M concentrations of lead) indicating high efficiency of bagasse fly-ash (149). Experiments with actual wastewater from metal finishing plant bearing 17 mg L^{-1} Pb(II) provided some successful results. It was found that almost complete removal of Pb(II) from 50 mL of wastewater at pH 3.2 was possible with 4.0 g L^{-1} of the adsorbent.

Papandreou et al. (150) used coal fly ash for the removal of Cu(II) and Cd(II) from wastewaters. The data followed Langmuir model with maximum removal after 72 hrs. Ríos and co-workers (151) used coal fly ash, natural clinker and synthetic zeolites to remove Fe(II), As(III), Pb(II), Zn(II), Cu(II), Ni and Cr(III) metal ions from acid mine drainage of mining industry. According to the authors maximum removals were obtained at pH 7.70–9.43. The order of removal found was Fe(II) > As(III) > Pb(II) > Zn(II) > Cu(II) > Ni(II) >Cr(III). Mohan and Gandhimathi (152) used coal fly ash for the removal of Zn(II), Pb(II), Cd(II), Mn(II) and Cu(II) metal ions from municipal solid waste leachate. The fly ash concentration to achieve maximum removal was found to be 2.0 g/L with the removal efficiencies of 39, 28, 74, 42 and 71% for Cu(II), Mn(II), Pb(II), Zn(II) and Cd(II), respectively. Mishra and Tiwari (153) reported the removal of Cu(II), Co(II) and Ni(II) on sodium hydroxide-treated fly ash. The data followed Langmuir equation with the order of removal Cu(II) > Co(II) > Ni(II).

Elouear et al. (154) used a sewage sludge with a chemical composition similar to that of fly ash to remove Ni(II) and Cd(II) from wastewater. Jha et al. (155) prepared composite materials of activated carbon and zeolite from coal fly ash and used them for the removal of Ni(II), Cu(II), Cd(II) and Pb(II). The relative selectivity of metal ions were in the order of Pb(II) > Cu(II) > Cd(II) > Ni(II), with equilibrium uptake capacities of 2.65, 1.72, 1.44 and 1.20 mM/g, respectively. As per authors, Langmuir isotherm fitted well, and sorption was thought to be by ion exchange with Na^+.

The process was found to be pseudo–second-order with rate constants of 0.14, 0.17, 0.21 and 0.20 L g/mM for the uptake of Pb(II), Cu(II), Cd(II) and Ni(II). The cost of the prepared adsorbent was estimated to be about US$ 12 ton^{-1} 20 times lower than the cheapest commercially available carbon costs ~US$ 285 ton^{-1} . Bagasse fly-ash had been regenerated successfully using acid solutions, but this was not an economically worthwhile method. Fly-ash obtained from sugar industries is more economic, having higher adsorption capacities than the fly ash obtained from thermal power plants. Briefly, sugar industry fly-ash has a good potential in the adsorption of metal ions in wastewater. However, the capabilities of this fly-ash have not been fully explored till today and need further extensive research.

Miscellaneous Waste

Many other materials have been tested as suitable adsorbents for the removal of metal ions from water. These include flower stalks, sugar beet pulp, charcoal, and resins (156–160). The efficacy of sunflower stalks as an adsorbent for the adsorption of metal ions such as copper, cadmium, zinc and chromium ions from aqueous solutions was found to be satisfactory. The maximum adsorption for Cu(II), Zn(II), Cd(II) and Cr(II) metals were 29.3, 30.73, 42.18 and 25.07 mg g^{-1} , respectively (156). Sugar beet pulp was used for the removal of Cr(III) from aqueous solutions (157). The surface area of the charcoal was about 400 m^2 g^{-1} at a carbonization temperature of 700^{o} C. Namasivayam and Yamuna (158) utilized biogas residual slurry under different conditions of shaking time (5–180 min), metal ion concentration (10–40 mg L^{-1}) adsorbent dose (1.0–8.0 g L^{-1}) and pH (1.5–5.0) for the removal of Cr(III) from solutions. Maximum adsorption of 85% was observed using 4.0 g L^{-1} adsorbent at 3.0 or greater pH for a 10 mg L^{-1} Cr(III) concentration.

Removal of Cr(III) from tannery wastewater by biogas slurries was also successfully achieved. Certain resins having cross and complex structures have good adsorption capacities for some metal ions. Therefore, the resins have been used as the alternatives for activated carbon. The adsorption characteristics of trace organic substances have been reported and compared with the synthetic resins and granular activated carbon (GAC) by Chen (159). In batch experiments, the effect of dosage and pH showed that the resin is much better than GAC, and a lower temperature favors an increased capacity of resin and GAC.

PREPARATION OF ADSORBENTS FROM INORGANIC PRECURSORS

Some inorganic materials have also been used as low-cost alternatives of adsorbents due to their good adsorption capacities, free availability and wide range of applications. The selection criteria are similar as discussed for organic precursors. In this category metal oxides and hydroxides, clays, red mud, zeolites, blast furnace slag, sediment and soil, ore minerals and various other substances are important. Attempts have been made to describe their cost, performance, adsorption capacities and adsorption kinetics for the removal of toxic metal ions.

Metal Oxides and Hydroxides

The oxides and hydroxides of certain metal ions have free valences and can be used as appropriate adsorbents for the removal of toxic metal ions from water. Titanium oxide was tested for the removal of Cr(VI) (160). On the other hand, electrolytic manganese dioxide (MnO_2) was found suitable for the adsorption of Th(I), Pb(II), Cu(II), Bi(III) and Cr(III) at pH 2–5 (161). The amount of metal ion adsorbed increased with pH for lead and copper ions. There was a significant drop in adsorption of thallium and chromium between pH 3 and 4. Silica and alumina have also been investigated for the adsorption behavior of cadmium and zinc at 25°C at pH 6–6.5 (162). A mixture of dry waste Fe(III)/Cr(III) hydroxide obtained from Southern Petrochemical Industries Corporation Limited (SPIC), Tuticorin, Tamilnadu, India was used as an adsorbent, to investigate the effect of complexing organic ligands such as citrate, acetate and etylenediaminetetraacetic acid (EDTA) on the adsorption of Pb(II), Ni(II) and Cd(II) onto the adsorbent (163).

Similarly, in another study by Namasivayam and Senthilkumar (164) the waste of Fe(III)/Cr(III) hydroxide was tried as an adsorbent for the removal of As(III), Hg(III), Cr(III) metal ions. The same authors (165) used the same industrial waste (Fe(III)/Cr(III) hydroxide) as an adsorbent for the removal of toxic ions and dyes from wastewater. They also studied it for the adsorption of Ni(II) (166). The process was affected by temperature, pH and initial concentration. The desorption studies were also performed and 70% of Ni(II) could be removed from the adsorbent at a pH of 4.0. Srivastava et al. (167) optimized various conditions for the removal of Hg(II) from aqueous solution using the same waste of Fe(III)/Cr(III) hydroxide. The desorption of Hg(II) indicated that it was solubilized in 2% KI to the extent of 65%.

The adsorption of two metal ions, i.e., Pb(II) and Cd(II) on hydrous aluminum oxide and hydrous iron oxide had been reported. The removal of lead and cadmium was found to be greater on hydrous ferric oxide [Pb = 230 and Cd = 72 mg g^{-1} of oxide at pH 4.0] than on hydrous aluminum oxide (Pb = 33 mg and Cd(II) = 31 mg g^{-1} of oxide). Floroiu et al. (168) studied the adsorption of Cd(II) on aluminum oxide in the presence of polyacrylic acid. The metal oxides and hydroxides are proper adsorbents in a batch process but could not be used as column materials due to the high cost of production. Moreover, the management of the adsorbent used is a problem, which requires costly and specific operations. Briefly, these synthetic wastes cannot be an alternative to commercial activated carbon.

Clays

Fuller's earth has long been used industrially for its decolorizing properties all over the world, and it is a cheap and readily available mineral. The adsorption capabilities of clay are due to negative charge on the surface of fine grain silicate minerals. This negative charge is neutralized by the adsorption of positively charged cations such as heavy metals. Besides this, clays possess large surface areas up to 800 m^2 g^{-1} , which explains its high adsorption capacity (169). There are many types of clays but montmorillonite clays are known to have the highest sorptive capacities in comparison to others.

Many clays have been tested for adsorption process, i.e., uptake of Hg(II) by montmorillonite was 5 times greater than by kaolinite, (170) wollastonite for nickel, (171) fly-ash and wollastonite (1:1 mixture) for Cr(VI) (172). Beveridge and Pickering (173) observed the effect of a range of commercially available water soluble surfactants on the uptake of Cu(II), Zn(II), Cd(II) and Pb(II) ions by 3 types of clays, *viz.* kaolinite, illite and a montmorillonite. Their study revealed that the charged surfactants influenced the phase distribution process when present at low concentration (<0.005% w/v), but much higher levels of non-ionic species (>0.1 % w/v) were required to produce observable effects. Srivastava et al. (174) studied the adsorption of lead and cadmium on clay samples (montmorillonite and kaolinite). The sorption of metal ions was greater on montmorillonite and the sorption capacity increased with increasing pH. The wastewater from a metal finishing plant was treated on clay (montmorillonite) and all the metal ions except Ni(II) were removed with hundred percent efficiency.

China clay was utilized for the removal of As(III) (175) and Zn(II) (176) from aqueous solutions. Hawash and co-workers (177) studied the adsorption of nickel onto natural clay. Viraraghavan and Kapoor (178) reported the abundance and low-cost of bentonite and, thus, strongly recommended it as an adsorbent for the removal of heavy metals from wastewaters. Singh et al. (179) reported the ability of hematite to remove Cr(VI) from aqueous solutions, while Khan and co-workers (180) investigated sorption of Cr(III), Cr(VI) and Ag(I) from the aqueous solutions using bentonite. The results of zinc adsorption onto natural bentonite showed that the adsorption was physical in nature.

The operational parameters, i.e., agitation speed, solid liquid ratio, temperature, particle size, and initial zinc concentration influenced the rate of adsorption (181). Clay could be modified to enhance its efficiency for the removal of pollutants from wastewaters. In an attempt, Cadena et al. (169) modified bentonite by replacing the natural exchangeable cations present in the clay by the organophilic cations, tetramethyl ammonium ion (TMA^+). The prepared adsorbent was examined to adsorb Pb(II) and Cr(VI) from aqueous solutions. Adsorption capacities for the removal of Pb(II) and

Cr(VI) by natural bentonite were found to be 6.0 and 5.5 mg g^{-1} while that obtained using tailored bentonite was approximately 58 and 57 mg g^{-1} for lead and chromium, respectively.

The results of the heat and acid treatments on natural bentonite revealed that the adsorption capacity had improved by heat treatment while the acid treatment decreased the same (182). Tavani and Volzone (183) studied the adsorption of Cr(III) from a tanning wastewater on a kaolinite. The adsorption of Cr(III) rose steeply at low equilibrium concentrations and showed negligible changes at high equilibrium concentrations. Cd(II) metal ion was adsorbed on kaolinite through ion exchange at permanently charged sites on the silanol faces and complexation to aluminol and silanol groups at the crystal edges (184).

2-Mercaptobenzimidazole-loaded natural clay can be used for the removal of Hg(II) (185). The adsorption of Hg(II) increased with increasing pH and reached a plateau in pH range 4.0–8.0. The removal of Hg(II) was found to be >99% at an initial concentration of 50 mg L^{-1} . Lin and Puls (186) studied the adsorption/desorption and oxidation/reduction of arsenic at clay surfaces. In this investigation, three types of clay mineral were studied, i.e., 1:1 layer clays [halloysite (IN), sedimentary M-kaolinite, and weathered EPK-kaolinite]; 2:1 layer clays [illite (MT) and illite/montmorillonite (MT)]; 2 >1 layer clay [chlorite (CA)]. The halloysite and the chlorite had much greater As(V) adsorption (25–35-folds) than the other clay minerals.

Carvalho et al. (187) studied the removal of Ni(II) industrial effluents on silylated clays by optimizing pH and the desorption process. Aşçi et al. (188) compared the adsorption and desorption of Cd(II) on soils and clay. As per the authors, soil pH, initial metal concentration and clay mineralogy affected the sorption process. Soils with higher clay content; characterized with smectite as a dominant component; had the greatest sorption capacities and intensities as estimated by Freundlich model. Cd(II) recovery from the soils was investigated as a function of pH, amount of Cd(II) and rhamnolipid concentration. Chaari and co-workers (189) used Tunisian smectitic clay for the removal of Pb(II) metal ions. As per the authors the adsorption of lead increased with an increase in solution pH from 1.0 to 4.5 and then decreased, slightly between pH 4.5 and 6, and rapidly at pH 6.5 due to the precipitation of Pb(II) ions. The maximum adsorption (25 to 25.44 mg/g) was within 20 min. from 25 to 40°C.

Jiang et al. (190) used a kaolinite clay modified with 25% (w/w) aluminum sulfate and unmodified kaolin for adsorption of Pb(II) from aqueous solution. As per the authors the amount of Pb(II) adsorbed onto modified kaolin (20 mg/g) was more than 4.5 times than that adsorbed onto unmodified kaolin (4.2 mg/g) under the optimized condition. Guerra et al. (191) treated a natural montmorillonite and a synthetic kanemite with 1,4-bis (3-aminopropyl)piperazine reacted with methylacrylate and used them for the removal of Th(IV), Ur(VI) and Eu(III) from aqueous solution. The pH and metal concentration were optimized. The data followed non-linear adsorption isotherm model.

Vieira et al. (192) used calcined Bofe bentonite clay for removal of Ni(II) metal ions. The clay removed nickel with maximum adsorption capacity of 1.91 mg metal/g of clay (20°C; pH 5.3). Anirudhan et al. (193) removed U(VI) from aqueous solution using humic acid-immobilized zirconium-pillared clay. A maximum removal of 97.6% and 94.7% was observed for initial concentrations of 50 and 100 mg L^{-1} , respectively, at pH 6.0, adsorbent dose of 2.0 g L^{-1} and 180 min equilibrium time. The authors achieved complete removal of U(VI) from 1.0 L of a simulated nuclear industry effluent sample containing 10 mg U(VI) ions using only 1.5 g of adsorbent. From this discussion it was found that clays have not been used on large scale due to their limited adsorption capacities. Moreover, it is difficult to prepare clay in granular form that is required in column fillings.

Red Mud

Red mud is a waste material formed during the production of alumina when the bauxite ore is subjected to caustic leaching. A typical Bayer process plant generates a large quantity of red mud (1–2 tons red mud per ton of alumina produced) and the toxicity and colloidal nature of red mud particles create a serious pollution hazard. There have been many proposals for red mud utilization such as in the manufacture of red mud bricks, as filler in asphalt road construction, as iron ore, and as a source of various minerals. The physical, chemical and mineralogical properties of a red mud have been fully described with the composition of iron oxide (38.80%), titanium oxide (18.80%), silica (9.64%), alumina (17.28%) and sodium oxide (6.86%) (194). The density, porosity and surface area were 2.0 g cm^{-3}, 0.45% fraction, and 108 m^2 g^{-1}, respectively. The ‘d’ spacing values from X-ray diffraction suggested the presence of hematite, cancrinite, geothite, rutile, anataze and quartz. The scanning electron micrographs of activated red mud revealed the surface texture and porosity of the material with a texture like aluminum silicates distributed with heavy constituents such as iron (194).

Lopes et al. (195) assessed the feasibility of red mud for wastewater treatment. Red mud was obtained from Alumina-Aluminio of San Ciprian (Lugo, Spain). A salt-free preparation of red mud had specific surface area of 58 m^2 g^{-1} . Batch and continuous adsorption experiments were carried out for the adsorption of heavy metals *viz.* Ni(II), Cu(II), Cd(II) and Zn(II) using red mud aggregates. These experiments indicated that, after pretreatment red mud is apt for the treatment of wastewaters. Apak and coworkers (196) studied the removal of toxic metals, i.e., copper(II), lead(II) and cadmium(II) from water by using red mud. The sorption sequence of metals under consideration was Cu > Pb > Cd.

Altundoan et al. (197) used heat treatment and acid treatment methods for red mud to increase its arsenic adsorption capability. This treatment caused sodalite compounds to leach out. As(III) and As(V) adsorption characteristics of activated red mud were similar with raw red mud. Batch adsorption studies had shown that activated red mud in dosages ranging from 20 to 100 g L^{-1} could be used effectively to remove arsenic from aqueous solutions. In spite of quite good adsorption capacities of red mud, only few reports are available on the water purification by using red mud due to its recent introduction as a low-cost alternative to activated carbon.

Zeolites

Zeolites are naturally occurring silicate minerals, which can also be synthesized at commercial level. Clinoptilolite is probably the most abundant of more than 40 natural zeolite species (198). This mineral occurs in abundance throughout the western United States, making it readily available and inexpensive. The adsorption properties of zeolites depend upon their ion exchange capabilities. The three-dimensional structure of zeolite possesses large channels containing negatively charged sites. Sodium, calcium, potassium and other positively charged exchangeable ions occupy the channels within the structure, and can be replaced by heavy metals. Leppert (199) reported that zeolites particularly clinoptilolite exhibits strong affinity for Pb(II) and other heavy metals. The authors found that the overall adsorption capacities for zeolites varies for different species, but tends to be around 1.5 meq g^{-1} (155.4 mg Pb g^{-1} zeolite). In a preliminary report by Desborough (200) clinoptilolite rich rocks have preferential affinity for Pb(II) over other metal ions. However, zeolites ineffectiveness for Cr(VI) removal has been reported (201).

The different parameters namely zeolite particle size, pH, initial metal ion concentrations, slurry concentration and solution temperature were studied for the sorption of lead and nickel ions from aqueous solution (202). This study showed that zeolite (phillipsite) tuff is considerably efficient for removing both lead and nickel under all conditions tested. The removal capabilities are higher for lead than for nickel. Natural Bulgarian zeolite was tested for its ability to remove Cu(II) from model wastewater (203).

It was found that the optimum wastewater to zeolite ratio is 100:1 and the optimum pH value of water to be treated is 5.5 to 7.5. Zeolite modification by treating with NaCl, CH_3COONa and NaOH increased its uptake ability. Copper ions are strongly immobilized by modified zeolite. The secondary pollution of water caused by its contact with preloaded zeolite is very low [(1.5–2.5% of Cu(II)]. Uptake of Cu(II) by zeolite from wastewater has proved to be as effective as Cu(II) by precipitation in its hydroxide form. This fact, together with the correlation found between Cu(II) uptake and the amount of sodium, potassium and calcium released into solution by zeolite showed that the ion exchange sorption played a basic role in Cu(II) uptake by natural zeolite. Langmuir equilibrium constant shows moderate affinity of zeolite for Cu(II). Values of ΔG° and ΔH° showed the spontaneous and endothermic nature of Cu(II) uptake process by natural zeolite. Kim et al. (204) removed iron from aqueous solutions by batch ion exchange with a solid Na-Y zeolite.

In the case of Fe(II)/Na-Y exchange system, the pH of the iron solutions was low enough to prevent the oxidation of Fe(II) and subsequent hydroxide deposition. An increase in the initial Fe(II) concentration, in the range 0.005–0.05 M, lowered the removal efficiency, but the external Fe(II) was preferred to the indigenous sodium over the entire concentration range. A maximum Fe(II) recovery of 84% from the maximally exchanged zeolite was achieved using 2.0 M solutions of NaCl while the regenerated Na-Y delivered 68% of the original Fe(II) exchange capacity. Fe(II) recovery was lower from samples exchanged under reflux conditions, while drying the loaded zeolite at 110°C also suppressed the degree of recovery.

The treatment of Fe(III) solutions with Na-Y was not feasible due to the acidity associated with the zeolite/salt slurries, which promotes excessive hydroxide deposition and structural disintegration of the zeolite. Bostick et al. (205) utilized the natural chabazite zeolite for the removal of the fission products, ^{90}Sr and ^{137}Cs from wastewater and groundwater. The sorbent Ionsiv™ IE-911, a crystalline silicotitanate, is commercially developed and manufactured by Universal Oil Products (UOP, Des Plaines, Illinois, USA). It was recently tested for fission product removal and found to compare extremely well against the baseline material.

Baker et al. (206) removed Cd(II), Cu(II), Pb(II) and Zn(II) metal ions on Jordanian zeolites from drinking and wastewater samples by optimizing zeolite particle size, ionic strength and initial metal ion concentrations, respectively. Jha et al. (155) prepared composite materials of activated carbon and zeolite by activating coal fly ash for removal of Ni(II), Cu(II), Cd(II) and Pb(II) metal ions. The relative selectivity of adsorbent was Pb(II) > Cu(II) > Cd(II) > Ni(II), with equilibrium uptake capacities of 2.65, 1.72, 1.44 and 1.20 mM/g, respectively. The overall reaction was pseudo–second-order with rate constants of 0.14, 0.17, 0.21 and 0.20 L g/mM for removal of Pb(II), Cu(II), Cd(II) and Ni(II) metal ions, respectively. Zeolite may be good alternatives for activated carbon but these are in equilibrium with metal ions in the nature and, hence, needs pre-treatments, which may be costly. Moreover, the adsorption occurs through ion exchangeable channels. Therefore, the regeneration is possible by specific chemicals, which may be expensive. Clays are not good adsorbents for column operations as they may clog them due to their small particle size.

Blast Furnace Slag

Steel plants produce a large volume of granular blast furnace slag as a waste product, which causes a disposal problem. It is being used as filler or in the production of slag cement. Recently, it has been converted into an effective and economical adsorbent for the removal of some toxic pollutants from wastewater. The developed adsorbent found good adsorption capacities for Cu(II), Ni(II) and Zn(II) ions. Nehrenheim et al. (207) reported the removal of Cu(II), Ni(II), Zn(II), Pb(II) and Cr(III) metal ions using blast furnace slag as adsorbent. Among various variables studied contact time was found most crucial in controlling adsorption. The data followed a pseudo–second-order kinetic model. In spite of good future of blast furnace slag, it could not be used much for removal of metal ions. Most probably it is because of its costly pre-treatment and poor availability.

Sediment and Soil

Sand, sediment, and soil also have high free valences, which are responsible for their good adsorption properties for different pollutants. Therefore, many workers tried to use these adsorbents for the removal of metal ions from aqueous solutions. In this direction, Bailey et al. used iron oxide coated sand for the removal of Cr(VI). The authors optimized different parameters for the adsorption process. Khaodhiar and coworkers (208) studied the adsorption of copper, chromate and arsenate onto iron-oxide-coated sand (IOCS) in single-metal and mixed-metal systems. Copper and arsenate were strongly adsorbed or formed inner sphere surface complexes with the IOCS surface, while chromate was weakly adsorbed or formed an outer sphere surface complex with the IOCS surface. The triple-layer model (TLM) was applied and the model indicated that each metal used a different number of adsorption sites. For Cu(II), Cr(VI) and As(IV) metals IOCS systems, the equilibrium constants determined from single solute systems were not able to predict adsorption from multi-solute systems.

The TLM had not currently accounted for the heterogeneity of oxide surface sites and the formation of ternary complexes and/or solid phases that did not exist in single solute systems. The mechanism of sediment motion that affected cadmium adsorption on sediment particles was studied in a turbulence tank in the presence and absence of bed mud by Huang (209). The experimental results were verified by a mathematical model for heavy metal transport developed for the turbulence tank. The model confirmed the transport-transformation of heavy metal pollutants in surface waters following the law of convective diffusive of common tracers and the characteristics of fate and transport of sediment motion. Variations of dissolved Cd(II) concentrations and suspended particulate Cd(II) concentrations with time and in the water column were measured and computed.

Both the experimental measurements and computed results showed that it took about 6 h to reach equilibrium condition for cadmium adsorption by sediment particles.

Dali-Youcef et al. (210) used sediment of Tafna River in northwest of Algeria for the removal of Zn(II). The effect of various operating variables, viz. initial concentration, sediment dose and contact time has been optimized. The extent of adsorption increased with increase of concentration and decrease of adsorbent dose within 30 min contact time. It was also observed that the content of carbonate in sediment increased adsorption indicating the active support material towards zinc ions. The data followed pseudo–second-order mechanism. The thermodynamics of adsorption indicated spontaneous, endothermic and randomness nature of adsorption. Murakami et al. (211) used sediments collected from heavy traffic areas and a residential area with an infiltration-type sewage system in Tokyo, Japan for removal of Cu(II), Cd(II) and Zn(II) metal ions from groundwater in Japan. Soils have been used to remove the environmental pollutants by adsorption.

Flogeac et al. (212) reported the removal of Fe(II), Mn(II) and Cr(III) onto a soil as a function of the reaction time, pH, and metal concentration. The order of removal was Fe(II) > Cr(III) > Mn(II). Wang et al. (213) used two soils as adsorbents for the removal of Zn(II). Asci et al. (188) used three soils for removal of Cd(II) metal ions by enhancing their adsorption capacities by rhamnolipids as biosurfactants. The freely availability, good efficiency and performance of these materials made them potential adsorbents. The major drawbacks with these materials are that, sometimes, they require costly pre-treatment, i.e., removal of adherent impurities or coating by some chemicals.

Ore Minerals

Ore minerals were found suitable for the removal of inorganic pollutants by adsorption. Ferruginous manganese ore is the most important for removal of metal ions due to the presence of pyrolusite and goethite. It is also an inexpensive adsorbent, which had been studied for the removal of arsenic from groundwater (214). The presence of bivalent cations, *viz.* Ni(II), Co(II) and Mg(II) enhanced the adsorption capability of this ferruginous ore. It has been successfully used for the removal of arsenic from six real groundwater samples containing arsenic in the range of 0.04–0.18 ppm. Arsenic removal was 100% in all cases.

Prikryl et al. (215) studied the adsorption of U^{VI} on quartz and clinoptilolite, important mineral phases at the proposed U.S. nuclear waste repository at Yucca Mountain, NV, USA. The experiments were conducted at an initial U^{VI} aqueous concentration of ~2.0×10^{-7} M (0.1 M $NaNO_3$ matrix) and over the pH range ~2.5 to ~9.5. U^{VI} solutions were reacted with either quartz or clinoptilolite only, or with mixtures of the two minerals removing more than 90% of U^{VI}. Leyva et al. (216) studied the adsorption of Sb(III) from water on hydroxyapatite $[Ca_5(PO_4)(3–x)(CO_3)x(OH)(1 + x)\ (x = 0.3)]$. It was observed that more than 95% of the Sb(III) in solution adsorbed to the solid-phase by hydroxyapatite in less than 30 min. The equilibrium distribution of Sb(III) (solid *vs* liquid phase) was characterized by a Langmuir model with $\gamma_{max} = 6.7 \pm -0.1 \times 10^{-8}$ M $(1.4 \pm -0.2 \times 10^{-4}$ M and $K_{ads} = 1.5 \pm 0.2 \times 10^3\ dm^3\ L^{-1}$. The granite was used for the removal of lead, which displayed a typical cation sorption behavior with fractional uptake increasing with increasing pH (217). In addition, lead sorption was essentially ionic strength independent, suggesting strong binding and substantial retardation under these conditions. Only few reports are available on the adsorption of metal ions from water by ore minerals. The utility of these adsorbents is not quite good to be used at commercial level.

Miscellaneous Adsorbents

Many papers are found in the literature describing metal ion adsorption on a huge variety of different and original adsorbents. A non-exhaustive list of such applications and examples developed very recently was prepared following reviewers' requests and is given here as Table 1. The database is made of 222 recent articles (235–455). The tabulated results were sorted alphabetically by main extracted cation from silver (Ag) to zinc (Zn) (Table 1).

ADSORPTION VERSUS SPECIATION

Some heavy metal ions exist in more than two oxidation states and may possess different physicochemical and biological properties, which may be responsible for their different toxicities (218, 219). The phenomenon of the separation and identification of the different oxidation as well as chemical states of a particular metal ion is called *speciation* (220–224). Thus, in order to obtain the exact and correct information on the toxicities and bio-transformation of such types of metal ion species, their different adsorption capacities are very important source of information for the scientists and clinicians. Therefore, the speciation concept is very important and must be compared to the adsorption point of view. Some attempts have been made to study the adsorption extents of different species of the same metal. The metal ion species studied on different adsorbents are arsenic, chromium, iron and selenium.

Some adsorbents have been tried to find out the adsorption extents of above cited metal ion species. Adsorption of As(III) and As(V) was carried out on three types of clay minerals, i.e., 1:1 layer clays [halloysite, sedimentary M-kaolinite, and weathered EPK-kaolinite]; 2:1 layer clays [illite and

TABLE 1 Recent (2004–2010) Applications of Inexpensive Adsorbents for the Removal of Toxic Metal Ions from Water

No.	Metal ions	Adsorbents	Types of water	Remediation capacities	Contact time (min.)	pH	Refs.
1.	Ag(II), Cu(II) and Hg(II)	Expanded perlite	Lab. synthesized water sample	Ag: 8.46 mg/g Cu: 1.95 mg/g Hg: 0.35 mg/g	–	6.5	235
2.	As(III)	Activated carbon supported nano zero-valent iron.	Drinking water	–	–	6.5	236
3.	As(V)	Cu(II), Ni(II), Co(II)-doped goethite samples	–	19.55 mg/g	30–60.0	–	237
4.	As(III)	*Ulothrix cylindricum*	Lab. synthesized water sample	67.2 mg/g	–	–	238
5.	As(III) and As(V)	Macrofungus (*Inonotus hispidus*)	Lab. synthesized water sample	As(III): 51.9 mg/g As(V): 59.6 mg/g	30	As(III):6 As(V): 2	239
6.	As(III), As(V) & Fe(II)	Tea fungal	Ground water samples	–	30–90	–	240
7.	As(V) & As(III)	Pretreated spent grains	Effluent of metallurgical industry	As(V): 13.39 mg/g As(III):4.86 mg/g	–	–	241
8.	Au(I), Pd(II) & Pt(II)	Dimethylamine modified waste paper gel	–	0.9–4.6 mg/g	–	–	242
9.	Au(I), Ag(II) & Pd(II)	Nanometer-size titanium dioxide	–	11.82–22.63 mg/g	–	–	243
10.	Au(III), Pt(II) & Pd(II)	Glycine-modified chitosan	–	120.39–169.98 mg/g	–	2.0	244
11.	Au (I & III)	Polyurethane foams	Aqueous cyanide media	Au(I):11.21 mg/g	–	–	245
12.	Cd(II)	*Ceramium virgatum*	Lab. synthesized water sample	39.7 mg/g	–	–	246
13.	Cd(II)	*Lentinus edodes*	Wastewater	5.58 mM/g	–	–	247
14.	Cd(II)	Sugarcane bagasse, Maize corncob & Jatropha oil cake	Lab. synthesized water sample	99.5%,	60	6.0	248
15.	Cd(II)	Hydroxyapatite	Lab. synthesized water sample	63–83%	–	–	249
16.	Cd(II)	*Calotropis procera*	Groundwater and industrial effluents	90%	5.0	5.0 & 8.0	250
17.	Cd(II)	Modified pine bark	Lab. synthesized water sample	97%	90	7.0	251

18.	Cd(II)	Various types of dried sludge	Lab synthesized water sample	0.38 mM/g	–	–	252
19.	Cd(II)	Rhodotorula sp. Y11	–	19.38 mg/g	–	–	253
20.	Cd(II)	Manganese nodule residue	Lab. synthesized water sample	19.8 mg/g	–	2.0–6.0	254
21.	Cd(II)	Protonated macroalga *Sargassum muticum*	Lab. synthesized water sample	-	–	4.5	255
22.	Cd(II) & Pb(II)	Sugar beet pulp	Lab. synthesized water sample	70–75%	70	5.3-5.0	256
24.	Cd(II) & Pb(II)	Ethanol treated waste baker's yeast biomass	Lab. synthesized water sample	Cd: 31.75 mg/g Pb: 60.24 mg/g	–	–	257
25.	Cd(II) & Zn(II)	Aquatic moss *Fontinalis antipyretica*	–	Cd: 28.0 mg/g Zn: 14.7 mg/g	–	5.0	258
26.	Cd(II) & Pb(II)	Sawdust of *Pinus sylvestris*	Lab. synthesized water sample	Cd: 96% Pb: 98%	–	5.5	259
27.	Cd(II) & Cr(III)	Alumina or chitosan	Wastewater	Cd: 99.2% Cr: 83%	–	–	260
28.	Cd(II), Cu(II) & Zn(II)	Cassava waste	Lab. synthesized water sample	60–80%	20–30	–	261
29.	Cd(II), Cu(II) & Zn(II)	Petiolar felt-sheath of palm	Contaminated water	–	30	–	262
30.	Cd(II), Cu(II), Ni(II), Pb(II) & Zn(II)	Spruce sawdust	Lab. synthesized water sample	65%	–	–	263
31.	Cd(II), Cu, Mn, Pb, & Zn	Moroccan stevensite	Lab. synthesized water sample	–	–	1.5–7.0	264
32.	Cd(II), Cu(II) & Ni(II)	Lemna minor L.	Lab. synthesized water sample	59-Cd: 83 mg/g	40-60	–	265
33.	Cd(II), Pb(II), & U(III)	Powder of poplar leaves and branches	Lab. synthesized water sample	Cd: 2.3 mg/g Pb: 1.7 mg/g U: 2.1 mg/g	–	–	266
34.	Cd(II) & Pb(II)	*Pleurotus platypus, Agaricus bisporus & Calocybe indica*	Lab. synthesized water sample	–	–	6.0, 5.0	267
35.	Cd(II) & Pb(II)	Activated alumina	Lab. synthesized water sample	–	–	5.0	268
36.	Cd(II)	Ion-imprinted polymer	Lab. synthesized water sample	59.2%	50	–	269
37.	Cd(II)	Plant leaves	Lab. synthesized water sample	77%–85%	-	4.1	270
38.	Cd(II)	Bone char	Effluents	0.57 mM/g	–	–	271

(*Continued*)

TABLE 1 (Continued)

No.	Metal ions	Adsorbents	Types of water	Remediation capacities	Contact time (min.)	pH	Refs.
39.	Cd(II) & Cu(II)	Carbonate hydroxylapatite (eggshell waste)	Lab. synthesized water sample	Cd: 94% Cu: 93.17%	–	–	272
40.	Cd(II) & Pb(II)	Grape bagasse	–	Cd: 0.774 mM/g Pb: 0.428 mM/g	–	Cd: 7.0 Pb: 3.0	273
41.	Cd(II), Cu(II), Pb(II), Ni(II), & Zn(II)	Immobilized phytic acid	Lab. synthesized water sample	6.6–7.7 mg/g	–	–	274
42.	Cd(II), Ni(II), Zn(II), Cu(II), Cr(III) & Pb(II)	*Eichhornia crassipes, Valisneria spiralis & Pistia stratiotes*	Lab. synthesized water sample	98%	–	6.0	275
43.	Cd(II), Cr(II), Cu(II), Fe(III), Ni(II), Pb(II) & Zn(II)	Adsorbent extracted from a cactus	Lab. synthesized water sample	~83%	–	–	276
44.	Cd(II), Cu(II), Ni(II) & Zn(II)	Biomass of brown algae	Lab. synthesized water sample	3.0 gL^{-1}	–	4.3-6.5	277
45.	Cd(II), Hg(II), Cr(II) & Pb(II)	Dithizone-anchored poly microbeads	–	4.3–16.4 mg/g	–	5.0	278
46.	Cd(II) & Pb(II)	Pine cone with Fenton reagent	–	Cd: 91% Pb: 89%	Cd: 90 Pb: 105	7	279
47.	Cd(II) & Pb(II)	*Lobophora variegata*	–	Cd: 1.71 mM/g Pb 1.79 mM/g	90	5.0	280
48.	Cd(II) & Ga(II)	Metallothionein fusion protein	–	26.6–12.1	–	Cd:5.2 Ga:6.5	281
49.	Cd(II), Zn(II) & Pb(II)	Brown marine macro algae	Lab. synthesized water sample	75%	10		282
50.	Cd(II), Cu(II), Fe(II), Se(II), Pb(II), Cr(III) & VI), Ni(II), Zn(II), Co(II), As(III)	Gum kondagogu (*Cochlospermum gossypium*),	Lab. synthesized water sample	–	–	5.0	283
51.	Cr(III)	Tannin-immobilized mesoporous silica bead	Lab. synthesized water sample	–	–	5.5	284
52.	Cr(VI)	Banana peel	Industrial wastewater	–	–	2.0	285

53.	Cr(VI)	*Helianthus annuus* (sunflower waste)	Lab. synthesized water sample	76.5%	–	2.0	286
54.	Cr(VI)	Grape waste	Lab. synthesized water sample	1.91 mol/kg	–	4.0	287
55.	Cr (VI)	*Agaricus bisporus*	Lab synthesized water sample	–	–	1.0	288
56.	Cr(VI)	Carbonaceous	Lab. synthesized water sample	56.49 mg/g	–	–	289
57.	Cr(III)	Agro-waste biosorbents	–	12.97 mg/g	–	4.0	290
58.	Cr(VI)	*Nostoc muscorum*	–	22.92 mg/g	–	3.0	291
59.	Cr(VI)	Red pine sawdust	Lab. synthesized water sample	87.7%	–	3.0	292
60.	Cr (VI)	*Trichoderma viride* biomass	–	–	90	2.0	293
61.	Cr(VI)	*Rhizopus arrhizus*	Saline solutions	78.0 mg/g	72h	2.0	294
62.	Cr(III)	*Spirogyra sp.*	Lab. synthesized water sample	81.02%	15–180	5.0	295
63.	Cr(VI)	Maghemite nanoparticles	Wastewater	–	15	2.5	296
64.	Cr(III)	Eggshells	–	160 mg/g	60	5.0	297
65.	Cr(VI)	Rice husk carbon and Activated alumina	Electroplating wastewater	75.3%	60	2-4	298
66.	Cr(VI)	Mucilaginous seeds of *Ocimum basilicum*	–	205 mg/g	–	1.5	299
67.	Cr (VI)	*Rhizopus nigricans*	Lab. synthesized water sample	99.2%	8 h	2.0	300
68.	Cr(VI) & Cu(II)	Ethylenediamine modified rice hull	Lab. synthesized water sample	Cr: 0.45 mM/g Cu: 0.06 mM/g		Cr: 2.0 Cu: 5.5	301
69.	Cr (VI)	Biomass of two marine strains of *Yarrowia lipolytica*	Lab. synthesized water sample	–	–	1.0	302
70.	Cr (VI) & Fe(II)	Cajanus cajan	–	~96.05 mg/g	–	2.0 & 2.5	303
71.	Cr(III), Fe(II), Cu(II), Cd(II) & Pb(II)	Hybrid inorganic/ organic alumina adsorbents-	Groundwater	–	–	1.0–7.0	304
72.	Cr(VI), Cd(II) & Co(II)	*Chryseomonas luteola* TEM 05	Lab. synthesized water sample	–	–	6.0	305

(*Continued*)

TABLE 1 (Continued)

No.	Metal ions	Adsorbents	Types of water	Remediation capacities	Contact time (min.)	pH	Refs.
73.	Cr(III) & Cr(VI)	White, yellow and red sands from the United Arab Emirates	Lab. synthesized sample	–	–	2.0–5.0	306
74.	Cr(III), Ni(II) & Cu(II)	Poly(gamma-glutamic acid) (gamma-PGA) derived from *Bacillus subtilis* NX-2	Electroplating effluent	Cr(III): 95.11% Ni: 89.32%	–	3.0–5.0	307
75.	Cr(VI), Cu(II) & Cd(II)	4-vinyl pyridine/2-hydroxyethylmethacrylate monomer mixture grafted poly(ethylene terephthalate) fiber	Lab. synthesized sample	Cr(VI): 99%.	–	3.0	308
76.	Cr(III), Cu(II), Mn(II) & Zn(II)	*Pseudomonas aeruginosa* AT18	Lab. synthesized sample	–	–	5.46–7.72	309
77.	Cr(VI), Pb(II), Hg(II) & Cu(II)	Sawdust (Acacia arabica)	Lab. synthesized sample	Cr: 111.61 mg/g Pb: 52.38 mg/g Hg: 20.62 mg/g Cu: 5.64 mg/g	–	6.0	310
78.	Cr(III), Mn(II), Fe(II), Ni(II), Cu(II), Zn(II), Hg(II), Pb(II), Pd(II), Pt(II), Ag(II) & Au(III)	Silica gel matrix inorganic-organic composite material	Lab. synthesized sample	1.700 mM/g	–	–	311
70.	Co(II), Cu(II), & Zn(II)	Cyanobacterium *Spirulina platensis*	–	63–77%	1–2	6.0	312
80.	Co(II) & Zn(II)	Various low-cost adsorbents	Lab. synthesized water sample	>94%	–	1.5–9	313
81.	Co(II)	Carboxylate-functionalized polyacrylamide grafted lignocellulosics	–	99%	–	6.5–9.0	314
82.	Co(II)	Clay Minerals (hectorite)	Lab. synthesized water sample	–	48 h	–	315
83.	Co(II)	*Oscillatoria anguistissima*	Lab. synthesized water sample	76%	15	–	316

84.	Cs(III)	Chemically modified biomass of marine algae	–	–	30	4.0	317
85.	Cs(III) & Cu(II)	Aluminum-pillared-layered montmorillonites (PILMs)	Lab. synthesized water sample	–	–	3.0–8.0	318
86.	Cu(II)	Triethylenetetramine and tetraethylenepentamine	Polyamine-functionalized Adsorbent	63.44 mg/g	–	–	319
87.	Cu(II)	Chemically modified chitosan	Lab. synthesized water sample	43.47 mg/g	–	5.0	320
88.	Cu(II)	Marine algae *Gelidium* and algal composite material	Lab. synthesized water sample	13 mg/g	–	5.3	321
89.	Cu(II)	Palm shell activated carbon with polyethyleneimine	Lab. synthesized water sample	75.86%	–	5.0	322
90.	Cu(II)	*Rhizopus oligosporus*	Lab. synthesized water sample	79.37 mg/g	1–48 h	2.0–6.0	323
91.	Cu(II)	Soybean straw	Lab. synthesized water sample	0.64 mM/g	–	6.0	324
92.	Cu(II)	Sewage sludge and pomace ashes	Lab. synthesized water sample	6.98 mg/g	–	–	325
93.	Cu(II)	*Rhizopus oryzae*	Lab. synthesized water sample	–	–	4.0–6.0	326
94.	Cu(II)	Marrubium globosum subspleaves	–	45.90%	–	5.5	327
95.	Cu(II)	Green alga *Cladophora fascicularis*	Wastewater	–	30	–	328
96.	Cu(II)	*Spirulina platensis*	Lab. synthesized water sample	67.93 mg/g	–	–	329
97.	Cu(II) & Co(II)	*Penicillium brevicompactum*	–	–	60	5.0	330
98.	Cu(II) & Pb(II)	Calcined starfish (SF) and iron-coated SF (ICSF)	Wastewater	8600 mg/kg	150	–	331
99.	Cu(II)	*Tectona grandis L.f.* leaves powder	Lab. synthesized water sample	15.43 mg/g	–	–	332
100.	Cu(II)	Poly-gamma-glutamic acid	Wastewater	77.9 mg/g	–	4.0	333

(*Continued*)

TABLE 1 (Continued)

No.	Metal ions	Adsorbents	Types of water	Remediation capacities	Contact time (min.)	pH	Refs.
101.	Cu(II)	*Cladonia rangiformis* hoffm	Lab. synthesized water sample	7.6923 mg/g	–	5.0	334
102.	Cu(II)	Cotton boll	–	11.40 mg/g	2–24 h	5.0	335
103.	Cu(II)	*Capsicum annuum* (red pepper) seeds	–	4.47×10^{-4} mol/g	60	–	336
104.	Cu(II)	Dried activated sludge	Lab. synthesized water sample	294 mg/g	–	4.0	337
105.	Cu(II)	Smectitic clay	–	94.6 to 96.0%	30	–	338
106.	Cu(II) & Cd(II)	Activated carbon derived from *Ceiba pentandra* hulls	Lab. synthesized water sample	Cu: 20.8 mg/g Cd: 19.5 mg/g	–	6.0	339
107.	Cu(II) & Pb(II)	Chaff	Lab. synthesized water sample	Cu: 1.98 mg /g Pb: 6.72 mg /g	–	–	340
108.	Cu(II)	Marine algae *Padina sp*	Lab. synthesized water sample	0.80 mM/g	30	5.0	341
109.	Cu(II) & Pb(II)	Iron-coated sand	Lab. synthesized water sample	Cu: 0.259 mg/g Pb: 1.211 mg/g	–	–	342
110.	Cu(II) & Fe(II)	Sawdust of beech, linden and poplar trees	Lab. synthesized water sample	7–8 mg/g	~ 20	Cu: 3.5 Fe: 5.0	343
111.	Cu(II) & Pb(II)	Manganese oxide coated sand II	Lab. synthesized water sample	Cu: 7.56 mM/g Pb: 9.22 mM/g	–	–	344
112.	Cu(II) & Pb(II)	Tartaric acid modified rice husk	Lab. synthesized water sample	Cu: 29 mg/g Pb: 108 mg/g	–	–	345
113.	Cu(II), Pb(II) & Zn(II)	Mulch (cypress bark, hardwood bark, and pine bark nugget)	Urban runoff	–	–	5.0 & 6.0	346
114.	Cu(II), Zn(II), Cd(II) & Pb(II)	Waste tea and coffee adsorbents	Lab. synthesized water sample	–	–	4.0–10.0	347
115.	Cu(II)	Microwave stabilized heavy metal sludge	Lab. synthesized water sample	18 to 28 mg/g	–	9.2–9.5	348
116.	Cu(II), Cd(II) & Pb(II)	Pyrite and synthetic iron sulfide	Lab. synthesized water sample	–	–	3.0–6.0	349

117.	Cu(II), Cd(II) & Pb(II)	Calcium alginate beads from *Laminaria digitata*	Acidic solutions	–	–	4.5	350
118.	Cu(II), Pb(II) & Cd(II)	Cross-linked carboxymethyl konjac glucomannan	Lab. synthesized water sample	~41.7 mg/g	20	5.0–6.0	351
119.	Cu(II), Ni(II), & Cr(VI)	Sawdust (*Quercus coccifera*)	Lab. synthesized water sample	Cu: 93% Ni: 82% Cr(VI): 84%	–	Cu: 4.0 Ni: 8.0 Cr: 3.0	352
120.	Cu(II), Cd(II), Zn(II), Ni(II) & Pb(II)	Activated sludge	Lab. synthesized water sample	–	–	4.0–5.0	353
121.	Cu(II), Cd(II), & Pb(II)	Slag	Lab. synthesized water sample	Cu: 0.101 mM/g Cd: 0.058 mM/g Pb: 0.120 mM/g	–	–	354
122.	Cu(II) & Zn(II)	Humic acid (HA)	Lab. synthesized water sample	–	–	6.0	355
123.	Cu(II), Zn(II) & Cr(III)	Schwertmannite	–	Cu: 99.3%, Zn: 99.4% Cr: 87.6%,	–	6.0–7.0	356
124.	Cu(II)	*Cladosporium sp.*	Lab. synthesized water sample	28.31 mg/g	–	5.0	357
125.	Cu(II) & Pb(II)	Waste beer yeast	Wastewater	Cu: 0.0228 mM/g Pb: 0.0277 mM/g	–	–	358
126.	Cu(II)	Gum arabic modified magnetic nano-adsorbent	Lab. synthesized water sample	–	2	-	359
127.	Cu(II), Pb(II), Zn(II) & Cd(II)	Tourmaline	Lab. synthesized water sample	Cu: 78.86 mg/g Pb: 154.08 mg/g Zn: 67.25 mg/g Cd: 66.67 mg/g	–	–	360
128.	Cu(II) & Pb(II)	Expanded perlite	Lab. synthesized water sample	Cu: 8.62 mg/g Pb: 13.39 mg/g	–	–	361
129.	Cu(II), Zn(II), Pb(II), Ni(II), Cd(II) & Ce(III)	Natural seaweed waste	Lab. synthesized water sample	0.78–0.71 mM/g	–	5.5	362
130.	Cu(II), Hg(II) & Pb(II)	1-Acylthiosemicarba-zide activated carbon	Lab. synthesized water sample	48.56–78.20 Mgg^{-1}	–	3.0	363
131.	Cu(II) & Pb(II)	Dolomite powder	Lab. synthesized water sample	Cu(II) 8.26 mg Pb(II) 21.74 mg	–	–	364

(*Continued*)

TABLE 1 (Continued)

No.	Metal ions	Adsorbents	Types of water	Remediation capacities	Contact time (min.)	pH	Refs.
132.	Cu(II)	Azolla rongpong ions	Lab. synthesized water sample	–	–	3.5	365
133.	Cu(II), Zn(II), Pb(II) & Mn(II)	Sargassum biomass	Urban storm water	20.2–214 mg/g	50	6.0	366
134.	Cu(II), Ni & Mn	Marine algae (*Ulva lactuca*)	–	Cu: 92% Ni: 80% Mn: 75%	–	2.0–8.0	367
135.	Cu(II) & Cr(VI)	Nano-adsorbent	Lab. synthesized water sample	Cu: 12.43 mg/g Cr: 11.24 mg/g	–	–	368
136.	Cu(II), Cr(III), Ni(II) & Pb(II)	Meranti sawdust	Lab. synthesized water sample	–	–	6.0	369
137.	Cu(II) & Cd(II)	*Trichosporon cutaneum* strain R57	Lab. synthesized water sample	65%	–	24 h	370
138.	Cu(II), Co(II) &Ni(II)	Chitosan/clinoptilolite composite	Lab. synthesized water sample	4.209–11.32 Mm/g	–	–	371
139.	Fe(III) & Fe(II)	Trimesic acid-coated alumina	–	Fe(III): 26.6 mg/g Fe(II): 8.4 mg/g	–	1.5	372
140.	Fe(II), Zn(II), & Cu(II)	Rice husk and *Desulfotomaculum nigrificans*	Acid mine drainage	Fe(III): 99% Fe(II): 98% Zn & Cu: 95%	–	–	373
141.	Fe(II), Fe(III), & Mn(II), Zn(II)	Lignite	Lab. synthesized water sample	11.90–34.22	–	–	374
142.	Hg(II)	Nonviable *Bacillus sp.*	Lab. synthesized water sample	–	20	4.5 & 6.0	375
143.	Hg(II)	Aminated chitosan bead	–	90%	100	–	376
144.	Hg(II)	*Pseudomonas fluorescens* BM07	–	82.25 mg/g	–	7.0.	377
145.	Hg(II)	*Aspergillus versicolor*	Lab. synthesized water sample	75.6 mgg^{-1}		5.0–6.0.	378
146.	Hg(II), Cd(II) & Pb(II)	Microalgae *Chlamydomonas reinhardtii*	–	Hg(II) 72.2 mg/g Cd(II) 42.6 mg/g Pb(II) 96.3 mg/g	60	Hg: 6.0 Cd, Pb: 5.0	379

147.	Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Pd(II), Cu(II), Ag(II) & Au(III)	Novel silica gel matrix composite adsorbent	Lab. synthesized water sample	Cu: 0.472 mM/g Ag: 0.822 mM/g Au: 0.810 mM/g	–	–	380
148.	Ni(II)	Baker's yeast	–	9.8 mg/g	–	6.75	381
149.	Ni(II)	Dried vegetative cell and spore-crystal mixture of *Bacillus thuringiensis var. thuringiensis*	Lab. synthesized water sample	15.7%	–	–	382
150.	Ni(II)	*Azadirachta indica* leaf powder	Lab. synthesized water sample	92.6%	–	5.0	383
151.	Ni(II)	*Thuja orientalis*	Lab. synthesized water sample	90%	3 .0	–	384
152.	Ni(II)	Activated alumina	Plating Ind. effluents	–	–	9.0	385
153.	Ni(II)	Pine tree materials	-	80%–97%	–	8.0	386
154.	Ni(II)	Genetically engineered *Escherichia coli* JM109	Industrial wastewater	95%	10	4.0-10.0	387
155.	Ni(II)	Sawdust	Lab. synthesized water sample	–	1.0 h	2.0 – 5.0	388
156.	Ni(II) & Co(II)	Octadecyl silica gel	Lab. synthesized water sample	96%	–	–	389
157.	Ni(II) & Zn(II)	Activated carbon from *Hevea brasiliensis*	Lab. synthesized water sample	22.03 mg/g	–	–	390
158.	Ni(II) & Cu(II)	*Pseudevernia furfuracea* (L.) Zopf	Lab. synthesized water sample	Ni : 49.87 and Cu: 60.83 mg/g	–	Ni: 4.0 Cu: 5.0–6.0	391
159.	Ni(II), Cd(II) & Cr(VI)	Metal tolerant *Aspergillus niger* and *Penicillium sp.*	Industrial effluents	Cr: 19.3 mg/g Cd: 19.4 mg/g Ni: 25.05 mg/g	18 h	–	392
160.	Ni(II) & Cu(II)	Iron oxide-coated sand	Lab. synthesized water sample	–	–	2.0–9.0	393
161.	Ni(II) & Cu(II)	*Undaria pinnatifida*	Lab. synthesized water sample	Ni: 24.71 mg/g Cu: 38.82 mg/g	–	3.0–7.0	394
162.	Ni(II) & Cr(III & VI)	*Cochlospermum gossypium*	Lab. synthesized water sample	–	–	Ni: 5.0 Cr: 2.0	395
163.	Ni(II)	Lewatit cation-exchange resin	Lab. synthesized water sample	171 mg/g	30–180	2.0–8.0	396

(*Continued*)

TABLE 1 (Continued)

No.	Metal ions	Adsorbents	Types of water	Remediation capacities	Contact time (min.)	pH	Refs.
164.	Ni(II), Co(II), Cd(II), Cu(II), Pb(II), Cr(III) & VI)	Activated carbon prepared from apricot stone	Lab. synthesized water sample	–	–	1.0–6.0	397
165.	Pb(II)	Chitosan, Chitosan-GLA and Chitosan-alginate beads	Lab. synthesized water sample	34.98, 14.24 & 60.27 mg/g	–	–	398
166.	Pb(II)	Seed powder of *Prosopis juliflora DC*	Lab. synthesized water sample	40.322 mg/g	–	6.0	399
167.	Pb(II)	Macroreticular poly(vinyl alcohol) (MR-PVA) beads	Lab. synthesized water sample	213.98 mg /g	–	–	400
168.	Pb(II)	Seed husk of *Calophyllum inophyllum*	Lab. synthesized water sample	–	–	4.0	401
169.	Pb(II)	Raw and activated charcoals of *Melocanna baccifera* Roxburgh (bamboo)	Lab. synthesized water sample	–	15–360	2.0–6.0	402
170.	Pb(II)	Tea wastes	Lab. synthesized water sample	–	–	5.0	403
171.	Pb(II)	Shells of hazelnut and almond	Lab. synthesized water sample	–	10-240	2-9	404
172.	Pb(II)	Dried waste beer yeast	–	94%	90	–	405
173.	Pb(II)	Seaweed *Sargassum horneri*	Lab. synthesized water sample	696 mM/g	30	–	406
174.	Pb(II)	Quebracho tannin resin	–	86.207 mg/g	–	5.0	407
175.	Pd(II)	*Aspergillus niger*	Lab. synthesized water sample	96.21%.	–	2.8–7.2	408
176.	Pb(II)	Waste biomass of aerial roots of *Rhizophora mangle* (red mangrove)	Lab. synthesized water sample	–	–	5.0	409
177.	Pb(II)	Chemically modified carbon adsorbents	Lab. synthesized water sample	79.43–98.89%	–	–	410
178.	Pb(II)	Hydroxyapatites	Lab. synthesized water sample	330–450 mg/g	–	–	411

179.	Pb(II)	Wheat bran	Lab. synthesized water sample	69.0–87.0 mg/g	–	–	412
180.	Pb(II)	Crop milling waste	Metal solutions	19.56–49.97 mg/g	30	–	413
181.	Pb(II) & Cd(II)	Waste Chinese herb Pang Da Hai	Tap water and river water	Pb: 27.1 mg/g Cd: 17.5 mg/g	–	–	414
182.	Pb(II) & Cr(III)	Lichen (*Parmelina tiliaceae*)	Lab. synthesized water sample	Pb: 75.8 mg/g Cr: 52.1mg/g	–	–	415
183.	Pb(II) & Cd(II)	Micro-particles of dry plants.	Aqueous solution	90%.	–	–	416
184.	Pb(II) & Cu(II)	*Penicillium simplicissimum* immobilized with loofa sponge	-	152.6 & 112.3 mg/g	60	5.0	417
185.	Pb(II) & Cd(II)	Grape stalk waste	Aqueous solutions	Pb(II) 0.241 mM/g Cd(II)0.248 mM/g	–	5.5	418
186.	Pb(II), Cu(II) & Cd(II)	*Phomopsis sp.*	Wastewater	0.110–0.870 mM/g	24 h	4–6	419
187.	Pb(II), Cd(II) & Ni(II)	Sawdust of walnut	Lab. synthesized water sample	–	60	–	420
188.	Pb(II), Cu(II) & Zn(II)	Polysaccharide produced from *Bacillus firmus*	Lab. synthesized water sample	Pb: 98.3% Cu: 74.9% Zn: 61.8%,	10	–	421
189.	Pb(II), Ni(II), Cd(II) & Zn(II)	Fungus *Mucor rouxii*	Lab. synthesized water sample	20.49–53.75 mg/g	–	6.0	422
190.	Pb(II), Cu(II) & Cd(II)	*Enterobacter sp.*	Industry & wastewater	32.5–50 mg/g	–	3.0	423
191.	Pb(II), Cd(II), Ni(II) & Zn(II)	*Azolla filiculoides*	Lab. synthesized water sample	–	–	10.5	424
192.	Pb(II), Cd(II) & Cu(II)	*Ulmus carpinifolia* and *Fraxinus excelsior*	Lab. synthesized water sample	69.5–201 mg/g	–	2.0–5.0	425
193.	Pb(II), Cd(II), Cu(II) & Ni(II)	Anaerobic granular biomass	Lab. synthesized water sample	60–255 mg/g	30	–	426
194.	Pb(II), Cu(II), Cd(II), Zn(II) & Ni(II)	Tobacco dust	Lab. synthesized water sample	24.5–39.6 mg/g	–	<2.0	427
195.	Pb(II), Ag(II), Cs(III) & Sr(II)	Brewery's waste biomass	Lab. synthesized water sample	0.076–0.413 mM/g	–	–	428
196.	Pb(II), Cd(II), & Cu(II),	Chitosan	Lab. synthesized water sample	0.010–0.036 mM/g		4.0	429
197.	Pb(II), Zn(II), Cu(II) & Cd(II)	Activated carbon of *Phaseolus aureus* hulls	Lab. synthesized water sample	15.7–6.021.8 mg/g	–	7.0–8.0	430

(*Continued*)

TABLE 1 (Continued)

No.	Metal ions	Adsorbents	Types of water	Remediation capacities	Contact time (min.)	pH	Refs.
198.	Pb(II) & Cd(II)	Rhizobacteria, *Azotobacter chroococcum* & *Bacillus megaterium*	Lab. synthesized water sample	Pb: 59.8% Cd: 75.6%	–	–	431
199.	Pb(II) & Cu(II)	Exopolysaccharide	–	Pb: 243.3 mg/g Cu: 36.7 mg/g	–	4.5–6.0	432
200.	Pb(II) & Cu(II)	EDTAD-modified baker's yeast	–	Pb: 192.3 mg/g Cu: 65.0 mg/g	–	2.7 to 6.0	433
201.	Pb(II), Hg(II), & Cd(II)	Loofa sponge	Lab. synthesized water sample	3.8–247.2 mg/g	–	–	434
202.	Pb(II), Cd(II), Zn(II) & Cu(II)	Rice husk activated	Lab. synthesized water sample	–	–	1.0–10.0	435
203.	Pb(II), Cd(II), Fe(II), La(III) & Ce(III)	Laminaria japonica with epichlorohydrin	–	0.87–1.35 M/ kg	–	–	436
204.	Pt(II) & Pd(II)	Thiourea-modified Chitosan microspheres	Lab. synthesized water sample	129.9 mg/g	–	2.0	437
205.	Pt(II), Pd(II) & Au(II)	L-lysine modified crosslinked chitosan resin	Lab. synthesized water sample	70.34–129.26 mg/g	–	1.0–2.0	438
206.	Sn(II)	Solid-phase Quercetin	Lab. synthesized water sample	–	–	1.8–2.2.	439
207.	Sr(II)	Bone char	Lab. synthesized water sample	0.271 mM/g	–	4.0–10.0	440
208.	U(III)	*Citrobacter freudii.*	Wastewater	–	30	–	441
209.	U(III)	*Cystoseria indica* algae	–	233 mg/g	–	4.0	432
210.	V((II), Re((II), Mo(III), Ge(II), As(V), Cd(II), Hg(II), Al(III), Pb(II), Fe(II) & Cu(II)	Modified *Pinus radiata* bark and tannins	Copper mine acidic residual waters	7.0–83%	–	3.0	443
211.	Zn(II) & Cd(II)	Young brown coals YBC (lignite), humic acids (HAs) and commercial humic acid	Lab. synthesized water sample	–	–	5.0–5.7	444

212.	Zn(II), Pb(II) & Co(II)	Natural Jordanian sorbent	Lab. synthesized water sample	0.320–2.860 mM/g	–	4.5–7.0	445
213.	Zn(II) & Cu(II)	Dead bio-sludges	Industrial wastewater	Zn: 92.61% Cu: 83.77%	–	–	446
214.	Zn(II) & Cu(II)	Sugar beet pulp and fly ash	Lab. synthesized water sample	60–97%	60	4.0–6.0	447
215.	Zn(II)	Natural zeolites	Industrial wastes	–	–	4.0–6.0	448
216.	Zn(II)	*Botrytis cinerea*	–	12.98 mg/g	–	5.0–6.0	449
217.	Zn(II)	*Saccharomyces cerevisiae*	–	74.8–654.8 mM/g	0–38h	5.65	450
218.	Zn(II)	Synthesized hydroxyapatites	Lab. synthesized water sample	98%	20	6.0–8.0	451
219.	Zn(II)	*Azadirachta indica* bark	Lab. synthesized water sample	33.49 mg/g	–	6.0	452
220.	Zn(II), Cu(II) & Co(II)	*Oscillatoria angustissima*	Lab. synthesized water sample	0.12–33 mM/g	–	4.0–5.0	453
221.	Zn(II)	Wood sawdust and sugarcane bagasse modified with EDTA dianhydride	Electroplating wastewater	105 mg/g	–	–	454
222.	Zn(II)	PVA/EDTA resin	Polluted water	125 mg/g	30	6.0	455

illite/montmorillonite] and 2:>:1 layer clay [chlorite]. The clay minerals had lower As(III) adsorption than As(V) adsorption, and the adsorption was affected by pH. The quantities of extractable As(III) and As(V) decreased with increasing aging time.

The results demonstrated that oxidation of As(III) to As(V) occurred on the clay surfaces, whereas reduction of As(V) to As(III) was never found in any of the clay minerals studied. The oxidation of As(III) was affected by the types of clay and aging time. Red mud was used for As(III) and As(V) adsorption and the process of arsenic adsorption followed first order rate expression. It was found that the adsorption of As(III) and As(V) was exothermic and endothermic, respectively. The heat and acid treatments were given to the red mud to increase the adsorption for As(III) and As(V) species (225). The process was pH dependent and the optimum range being 5.8–7.5 for As(III) and 1.8–3.5 for As(V). The maximum removals were 96.52% for As(V) and 87.54% for As(III) for solutions with a final pH of 7.25 and 3.50, respectively, for the initial arsenic concentration of 133.5 μM L^{-1} (10 mg L^{-1}), activated red mud dosage of 20 g L^{-1} , contact time of 60 min and temperature of 25°C.

Ore minerals have been tested for the adsorption of both As(III) and As(V) without any pre-treatment, adsorption of As(III) being stronger than of As(V) in pH range of 2–8 (226). The kinetics of arsenate [As (V) and arsenite (As (III)] removal by zerovalent iron was studied in aqueous solution. Pseudo–first-order rate equations were found to describe satisfactorily both As(V) and As(III) removal kinetics in the presence of various competing anions. The anions competing affected were also studied of zerovalent iron for field applications to remediate As(V) and As(III). Titanium dioxide loaded Amberlite XAD-7 resin had also been used for the removal of arsenic species [As(III) and As(V)] using different experimental conditions. The resin was prepared by impregnation of Ti $(OC_2H_5)_4$ followed by hydrolysis with ammonium hydroxide. The resin showed a strong adsorption for As(V) from pH 1.0 to 5.0 and for As(III) from pH 5.0 to 10.0. The adsorption isotherm data for As(V) at pH 4.0 fitted well to a Langmuir equation with a binding constant of 59 dm^3 M^{-1} and a capacity constant of 0.063 mM g^{-1} . The data for As(III) at pH 7.0 also fitted well to a Langmuir equation with binding constant of 5.4 dm^3 M^{-1} and a capacity constant of 0.13 mMg^{-1} (226).

Column adsorption experiments also showed that the adsorption of As(III) was more favorable in comparison to As(V), due to both faster adsorption and larger capacity for As(III) than As(V) (225). A comparison of arsenic species [As (III) and As(V)] uptake was investigated onto amorphous iron oxide, goethite, and magnetite at varying solution compositions. Sorption of As (V) onto amorphous iron oxide and goethite was more favorable than As(III) below pH 5–6, while above pH 7–8, As(III) had higher affinity for the solids.

The pH at which As(V) and As(III) were equally sorbed depended on the solid-to-solution ratio and type and specific surface area of the minerals and shifted to lower pH values in the presence of phosphate, which competed for sorption sites. As(V) and As(III) sorption isotherms indicated similar surface site densities on the three oxides. Intrinsic surface complexation constants for As(V) were higher for goethite than amorphous iron oxide, whereas As(III) binding was similar for both of these oxides and also for magnetite (226).

The hazelnut shell had selective adsorption capacities for chromium species [Cr(III) and Cr(VI)] in the 2.5 to 3.5 pH range. At these pHs the reduction of Cr(VI) and the adsorption of Cr(III) took place (227). The uptake of chromium species was studied on column packed with pyrolusite (β-MnO_2)-coated sand. β-MnO_2 effectively oxidized Cr(III) to Cr(VI) and the extent of oxidation was sensitive to pH, effluent velocity and concentrations of Cr(III). The breakthrough data on chromium transport could be matched closely by calculations of a simple model that accounts for (1) advective-dispersive transport of Cr(III), Cr(VI), and dissolved oxygen, (2) first-order kinetics adsorption of the reduced and oxidized chromium species, and (3) nonlinear rate-limited oxidation of Cr(III) to Cr(VI) (228).

The removal of Cr(III) and Cr(VI) from aqueous solutions using sugar beet pulp as biosorbent substrate was presented. The kinetics of both species removal was studied under various experimental conditions. Cr(III) ions were adsorbed onto the biosorbent by ion-exchange mechanism with calcium cations. The influence of the solution pH was found to greatly affect the adsorption efficiency of Cr(VI). The Cr(VI) removal was largely involved in a reduction mechanism with the appearance of Cr(III) ions in the solution (229).

Aluminum oxide-coated sand was used for the selective adsorption of selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) anions from water. The adsorption of these species increased with pH increase but the selenite (SeO_3^{2-}) adsorption was significantly higher than the selenate (SeO_4^{2-}) one. In this system, the adsorption of selenite was inhibited by selanate only at pH ranging from 3.0 to 8.0 (230). Ten coal mine soils were studied for the selective adsorption of selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}), and the results indicated that the percent sorption varied from 48 to 99% for SeO_3^{2-} and 44 to 95% for SeO_4^{2-} (231). Generally, the differences in adsorption of metal ion species are greatly depending on the bulk pH values. However, the advection (transport of the pollutants by natural meteorological motion of water or air), dispersion, oxidation-reduction are also very important to be considered in this respect. Briefly, the adsorption study of metal ion species is a new concept and definitely it must get great attention in the near future.

COLUMN STUDIES

As discussed above, the adsorption of metal ions from polluted water has been carried out by different workers using various adsorbents in batch procedures, which provide the basic and initial knowledge and data of the adsorption. The information of batch designs needs to be used to fabricate the column operations, which are required for water purification at large scale. The transfer of batch experimental conditions to the column requires special attention and skill. Despite of the high importance of column operations in water purification very little work has been carried out in this direction. A column design is shown in Figure 3. The developed column was found suitable for the removal of many toxic metal ions using a variety of low-cost adsorbents.

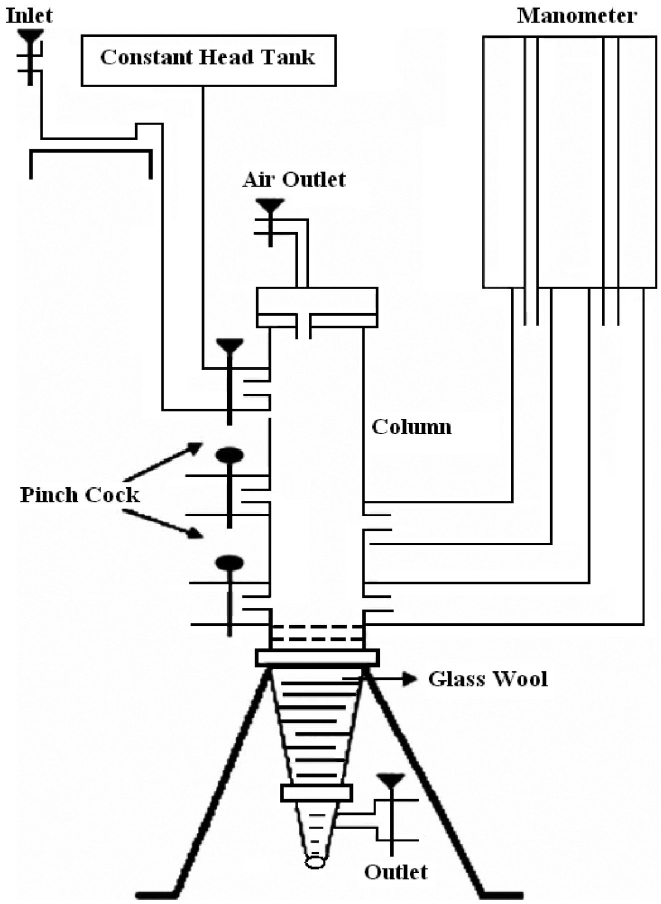

FIGURE 3 Schematic diagram of a column used for water treatment by adsorption technology.

Many workers tried column experiments for the removal of metal ions from aqueous solutions. Adsorption capacities of 34 conifer species leaves have been evaluated by column experiments (59). The maximum adsorption capacity of *G. biloba* leaves was 27.5 mg g^{-1} for Cr(III) by column experiments. Rice husk carbon was used for uptake of Cr(VI) from industrial wastewater (71). The column capacities for Cr(VI) uptake were compared with commercial carbon and found to be 8.9 mg g^{-1} and 6.3 mg g^{-1} of rice husk carbon and commercial carbon, respectively. The column packed adsorbent was successfully used for the treatment of an actual waste from a real plating shop bearing Cr(VI) up to 300 mg L^{-1} .

Crude shrimp chitin was packed in small columns and used for the removal of Cu(II), Cr(III) and Ni(II) metal ions from solutions (114). Shrimp shell wastes from *Penaeus marginatus* were demineralised by dilute HCl in small columns to yield shrimp chitin. 96% of calcium was efficiently removed by this column without removal of proteins. An actual wastewater of electroplating baths rinsing waters rich in Cu(II) gave encouraging results. The shrimp chitin removed 92–96% Cu(II) from copper pyrophosphate and acid copper bath rinsing water.

Leusch et al. (120) used the brown marine algae, *Ascophyllum nodosum*, for the removal of Cd(II) by column. The maximum adsorption capacity for Cd(II) was shown to be approximately 67 mg g^{-1} . Guha et al. (228) examined the processes of advection, dispersion, oxidation and reduction and adsorption to affect the transport of chromium through columns packed with pyrolusite (MnO_2) coated sand. It was reported that MnO_2 effectively oxidized Cr(III) to Cr(VI) and that the extent of oxidation was sensitive to changes in pH, pore water velocity, and influent concentrations of Cr(III). Cr(III) oxidation rates, although initially high, declined well before the supply of MnO_2 depleted, which suggested that a reaction product inhibited the conversion of Cr(III) to Cr(VI). The rate-limiting reactions governed the weak adsorption of each chromium species. The breakthrough data on chromium transport matched closely by calculation of a simple model that accounts for advective dispersive transport of Cr(III), Cr(VI) and dissolved oxygen. It accounted for first-order adsorption kinetics of the reduced and oxidized chromium species and finally considers the nonlinear rate limited oxidation of Cr(III) to Cr(VI).

Baker et al. (206) used columns containing Jordanian zeolites for removal of Cd(II), Cu(II), Pb(II) and Zn(II) metal ions from drinking and wastewater samples. The concentrations ranged from 5 to 20 mg L^{-1} with average particle size of zeolite between 90 and 350 μm, and ionic strength from 0.01 to 0.05 M. The removal mechanism was ion exchange at pH 6.0 whereas, no clear affect of low ionic strength values is noticed on the removal process. Han et al. (232) removed Cu(II) and Pb(II) metal ions by column using manganese oxide coated zeolite as adsorbent. The experiments were optimized by particle size, bed length, influent flow rate and influent metal concentration on breakthrough time during the removal of copper and lead ions from aqueous solutions. Logically, the breakthrough time increased with increase of bed length and decreases of influent metal concentration. The Thomas model was applied to adsorption at bed length, particle size, different flow rates and different initial concentrations to predict the breakthrough curves and to determine the characteristic parameters of column useful for process design.

The removal of metal ion decreased when other additional heavy metal ions were added, but the total saturation capacity of the column was not significantly changed. This competitive adsorption showed that adsorption of lead ions was not modified when copper ions was added to the influent, whereas a dramatic decrease was observed on the adsorption of copper ions by the presence of lead ions. The removal of copper and lead ion by the zeolite column followed the descending order, i.e., Pb(II) > Cu(II). The adsorbed copper and lead ions were easily desorbed from adsorbent with 0.5 ML^{-1} HNO_3 solution.

Li and Champagne (233) used Sphagnum peat moss as a low-cost natural and inexpensive adsorbent for the removal of Cd(II) and Ni(II) metal ions from binary aqueous solutions. The authors studied removal efficiencies and adsorption capacities for column operations for maximum removal. Furthermore, the authors reported a flow rate of 1.5 mL min^{-1} (surface loading of 27.5 cm^3)/cm^2 day) and bed depth of 15 cm for good removal capacities (47.9% and 42.7% cadmium and nickel, respectively).

Recently, Sousa et al. (234) used green coconut shells for the removal of Cu(II) > Pb(II) > Cd(II) > Zn(II) > Ni(II) using a column process. As per the author flow rate of 2.0 mL/min and a bed height of 10 cm, the column process was most feasible. The breakthrough curves for cation removal were in the order of adsorption capacity [Cu(II) > Pb(II) > Cd(II) > Zn(II) > Ni(II)]. The developed method was successfully applied for the removal these metal ions from electroplating industry effluent samples.

CONCLUSION

It is not possible today to point out a particular adsorbent that will be able to replace the ubiquitous active carbon adsorbent. The critical evaluation and comparison of all the possible replacement adsorbents have been discussed in the individual sections. Briefly, adsorption has been used extensively for the uptake of toxic metal ions from ground, surface and wastewaters using batch experiments. Many workers tried to develop inexpensive alternatives to activated carbon. After the analytical observation and comparison of the adsorbents; based on the performance, adsorption capabilities and cost; it was found that the most important and economically feasible adsorbents are fly-ashes, red mud and sand because of their free availability and good adsorption capacities. The cost of these adsorbents only involves the transportation and simple pre-treatment. Moreover, the management of the exhausted adsorbents is the serious and challenging problem for the scientists and it is very interesting to note that heavy metal loaded fly-ashes, red mud and sand can still be used as building materials, which make these adsorbents ideals. The adsorption of metal ion species is very crucial for the toxicologists and, hence, such types of inexpensive adsorbents should be developed more. Moreover, the application range of the adsorbent should be wide with a large selectivity so that a single adsorbent could be used for greater number of toxic metal ions.

Most often, the removal capacities of these potential replacement adsorbents have been explored by using batch operations and, hence, there is a great need to transfer batch conditions to column operations so that the desired columns can be used for water purification and recycling purposes at large scale. To make the adsorption technique more popular and applicable, for the removal of toxic metal ions, the development of more useful columns and their applications are required. Basically, column operations are the demand of today and, hence, these should be carried out first at a pilot-scale plant, followed by large community level. In addition, more inexpensive adsorbents should be developed and utilized in packing the columns for the removal of a wide range of toxic metal ions. All the column experiments should be designed by keeping in mind the cost, performance, energy, kinetics and regeneration aspects.

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