Chapter 2
Adsorption Technology for Removal of Toxic Pollutants

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Abstract Metals present in natural waters are nondegradable, unlike organic compounds. These metals lead to somatic cell mutation that causes increased cancers amongst children throughout the world. The existing remediation methodologies for removal of such toxic metals are oxidation, coagulation and flocculation, precipitation, ion exchange, membrane filtration, ozone oxidation and bioremediation. Most of the methods involve production of high metal-contaminated sludge and high maintenance cost or the use of a relatively expensive mineral matrix that offset the performance and efficiency advantages. Adsorption has largely emerged as significant technology for removal of toxic metals. The review of over 240 published studies (1982–2016) shows an exhaustive list of adsorbents in the literature, including chitosan, fly ash, used tyre rubber, wood char, rice husk, aluminosilicates, etc. This review shows that the modification of most of the adsorbents offers outstanding performances to solve heavy metal related pollution issues. The removal of toxic metals using natural adsorbents is economical and environment friendly. Treated clay shows increased removal of metal ions under the same conditions compared to the untreated clay minerals due to increased surface area. One of the best adsorption capacities reported for As is 95% from 1 mg/L using hybrid adsorbents, 98% of Sb from 0.05 mg/L using hydroxyapatite and 97% of Cd from 10 mg/L using *A. rubescens* biomass.

Keywords Adsorption • Antimony • Arsenic • Cadmium • Efficiency • Lead • Modified adsorbents • Mercury • Phenolic compounds • Zinc

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2.1 Introduction

The development of science and technology has led to intensified environmental pollution as well as deterioration of many ecosystems with accumulation of pollutants such as heavy metals and synthetic compounds. According to the United Nations World Water Development Report in 2003, almost two million tons of waste is disposed off within receiving waters per day including industrial, human and agricultural wastes. Many water bodies are contaminated with heavy metals that are toxic and carcinogenic such as arsenic, antimony, cadmium, chromium, lead, mercury, nickel and zinc. Thus, the removal of such metals from water has been documented as a priority issue by the World Health Organization that accounts to their urgent remediation.

Several remediation methodologies have been developed for removal of heavy metals from water; the most common are oxidation and sedimentation, coagulation and filtration, sorptive media filtration and membrane filtration. The detailed analysis of the mentioned methodologies does not potentially satisfy the essential critical requirements such as efficient removal of metal, low cost and easy maintenance, long life expectancy and high rate of metal removal, mechanical strength and large surface area. Moreover, they are incapable to disintegrate in water flow and overcome the changes in pH, hardness or microbiology that affect the water quality. However, most of the common methodologies adopted for the removal of heavy metals from water are expensive that increase the economic pressure on rural communities with high levels of toxicant in food and drinking water. Thus, amongst the approaches proposed, adsorption is one of the mostly adopted methods for remediation as it is found to be very effective, economical and versatile.

2.1.1 Background

The introduction of contaminants such as synthetic chemicals, non-biodegradable plastics and heavy metals into the natural environment that cause adverse changes is called pollution. Pollution can be toxic with varied toxicity defined as the degree to which a substance, i.e. a toxin or poison, can harm humans or animals. It is often described as *point source* (that enters the water body from a specific site) or *diffuse* or *non-point pollution* (arise where substances are widely used and dispersed over an area). Commonly encountered heavy metals are arsenic, antimony, chromium, cobalt, mercury, selenium, cadmium, zinc and lead. Valko et al. (2006) state that heavy metals are a heterogeneous group of highly reactive substances that may act as essential cofactor for physiologic processes and/or as toxic elements. Some metals exhibit toxicity by inducing oxidative stress directly such as iron redox cycling between Fe^{3+} and Fe^{2+} that create superoxide (O_2^-) in the process. Some metals undergo redox-cycling reactions under physiological conditions such as iron (Fe), copper (Cu), chromium (Cr), vanadium (V) and cobalt (Co). There are other metals such as mercury (Hg), cadmium (Cd), nickel (Ni) and arsenic (As) that increase oxidative stress indirectly by depleting glutathione and bonding to sulfhydryl groups of proteins. Such metals are considered as toxic pollutants as they are not essential for biological functions (Ahsan et al. 2006).

Heavy metals are introduced into the environment through products of mining, smelting and refining of fossil fuels, production and use of metallic commercial products and vehicular exhaust products, domestic sewage, industrial effluents and thermal power plants, agricultural and animal wastes, coal ashes and fertilizers. Arslanoglu et. al. (2009) described the heavy metal binding properties of esterified lemon Babel et al. (2003), Wan et al. (2008) and Bhattacharyya et al. (2008) show studies on the removal of heavy metals that have been investigated using chemical precipitation and physical treatment such as ion exchange, solvent extraction, osmosis and adsorption. The process of coagulation used for removal of heavy metal generates toxic sludge that adds supplemental toxic substances back to the environment. The treatment of water by membrane filtration involves synthetic membrane filters with appropriate pore size, and thus it becomes an expensive technique membrane.

2.1.2 Issues and Problems

A multitude of scientific publications and popular articles appeared during the last three decades on metal pollution and their respective toxicity. The increased concentrations of heavy metals in water have triggered a worldwide campaign for innovative water management practices.

In 2001, a TNN report says that out of 20,000 metal-contaminated sites in England, 38% of the sites have been found to be located in groundwater areas. Another recent survey in the United States reports 79% of 727 samples of surface water are contaminated with arsenic. The metal concentration may be present up to

500 mg/kg of soil, either as dissolved in the soil solution, exchangeable in structural components of the lattices of soil minerals or as insoluble precipitates with other soil components. Aydinalp and Marinova (2003) reported that the heavy metals that are in dissolved and exchangeable forms are available to plants, whereas the metals that compose the structural components of lattices of soil minerals or exist as insoluble precipitates with other soil components are potentially available in the longer term. This leads to contamination of groundwater supply of nearby human-inhabited areas in many countries where most of the water supplies originate from rivers and streams.

A research by Stollenwerk (1994) at mine sites reports 20,000–50,000 sites in the United States where heavy metals are introduced to groundwater. The plume of acidic water (pH = 2–3) contains very high concentrations of aluminium, cobalt, copper, iron, manganese, zinc and nickel (>2000 mg/L). The plume from copper mining migrates through the water bodies; the oxidation of reduced iron occurs by manganese oxides in the sediment. The acidic water reacts with carbonate minerals in soil, and sorption of hydrogen ions on precipitated iron increases the pH to 5–6. This affects the sorption reactions of aqueous copper, cobalt, nickel and zinc that depend on the increase in pH. Hence, aluminium precipitates out and is slowly introduced to the aquifer solids. Certain industrial processes release toxic heavy metals in the environment as listed in Table 2.1. A study at the Department of Environment (1995) reports that oil refineries are likely to be the largest source of vanadium to the environment.

The United States share the maximum percentage of refinery capacity per day, together with China as shown in Table 2.2. China has been the largest producer of lead (3000 metric tons) in 2013. According to a joint report published by the FAO, the United Nations Environment Programme (UNEP) and the World Health Organization (WHO) in 2013, the maximum consumption of insecticides (22,549 tons) is reported to be in Japan, whereas France shows the maximum consumption of herbicides (26,808 tons) in 2007. A study by the Blacksmith Institute Assessment

Table 2.1 Industrial activities that release heavy metals to the environment

Industry/process	Major countries affected	Contaminating metals/ metal compounds
Oil refineries spent catalyst	The United States, China, Russia, Japan, India, South Korea, Italy, Saudi Arabia, Germany, Canada	Vanadium
Lead works	China, Australia, the United States, Peru, Mexico, India, Bolivia, Russia, Sweden, Poland, South Africa, Ireland, Canada	Lead, arsenic, cadmium, sulphides, sulphates, chlorides
Pesticide manufacturing works	The United States, Africa, Brazil, France, Calamari, Naeve	Arsenic, copper, sulphate, thallium
Dye works, waste batteries, zinc smelting, e-waste	The United States, Mexico, China, India	Aluminium, cadmium, mercury

Source: Department of Environment (1995)

Process (2010) in low- and middle-income countries suggests that 56 million people in Europe are at risk of cadmium, arsenic, lead and mercury poisoning. The total emission of 575 tons of arsenic in the environment in Europe was reported in 1990. A study by Jarup (2003) shows that more than 100 million people have been affected by arsenic contamination in several member countries of the European Union in the 1980s.

Besides the industrial sources listed in Table 2.1, lead is also introduced through gasoline additives, can solder, ceramic glass, cosmetics and the battery/plastic recycling industry. According to a study by Krishnaswamy and Kumar (1998), many cosmetics like talcum powder, lipsticks, shampoos "kajal" and hair colour contain heavy metals. This has resulted in a growing number of cases of different kinds of cancer, tumours and some genetic disorders with high pace.

The ubiquitous presence of heavy metals in the environment and their widespread toxicity has led to numerous approaches for its remediation. Out of the removal methodologies, adsorption shows the possibility of regeneration and reuse of adsorbents along with low capital cost. Hence, adsorption has acquired global importance for minimization of the contamination of the environment. It has become a significant addition to green chemistry endeavours.

2.1.3 State of Metal Pollution

Metals are ubiquitous in the environment primarily trapped in some stable form in rocks, soils and sediments. The metals are introduced into the environment through geological and anthropogenic sources. Vahter (2008) reports that arsenic is released into the environment through volcanic activity, erosion of rocks and forest fires. Soil erosion and leaching contribute to 612×10^8 g/year and 2380×10^8 g/year of arsenic, respectively. A report by Khan (1996) states that elevated concentration, of arsenic in Bangladesh and West Bengal (India) in groundwater is the consequence of the ignorance of standard water testing procedures that did not include tests for any toxic metal. The geological and hydrological survey discovered a 450 km long layer of arsenic-rich silt clay, between 21 m and 61 m below the surface of the delta.

Table 2.2 Refinery capacity of the countries with oil refineries

Countries	Percentage of refinery capacity per day
United States	18.8
China	12.5
Russia	6.2
Japan	4.6
India	4.4
South Korea	3.1
Saudi Arabia	13
Canada	2.2

A study by Thornton (1992) shows that 9.5% of Japanese rice paddies have been rendered as incapable of producing consumable products.

Lead is largely introduced into water from atmospheric pollution, e.g. lead arsenate [$Pb_3(AsO_4)_2$], an insecticide. A research by Tong et al. (2000) indicates that 70% of lead in water and over 50% of many of the other trace metals in the Great Lakes are derived from atmospheric transfer. *Arsenic* ranks 20th in natural abundance comprising about 0.00005% of the Earth's crust as stated by Bromssen et al. (2007). It is introduced through various potential sources in waterways such as industrial mining and smelting operations including dissolution of pyrites, minerals and ores, effluents of coal, iron and other metal mining industries, burning of fossil fuels, heat-resistant alloys, antifouling paints, textile printing pigments, pulp and paper production, as depicted in Fig. 2.1.

Antimony is present in various oxidation states. A source study by Deorkar and Tavlarides (1997) states that the total consumption of antimony in various industrial products is 100,000 tons per year worldwide. Smichowski (2008) reports the elevated concentration of antimony in water as well as soils around mining and smelter areas at shooting ranges and along roadsides (dust from brake pads and tyres). Gebel (1997) describes the chemico-toxicological similarity of antimony with arsenic-clastogenic, but not mutagenic, carcinogenic potential. *Aluminium* pollution is associated with bauxite mining with steady increase in demand for aluminium in India. India ranks sixth in bauxite mining and eighth in aluminium production. Orissa in India is the worst aluminium affected state. The *cadmium* total input rate as reported by Hooda and Alloway (1998), Candinas et al. (1999), Eckel (2005), Lijzen and Ekelenkamp (1995) and Wilcke and Dohler (1995) in Germany is

Fig. 2.1 Champagne Pool Waiotapu near Rotorua (North Island of New Zealand). Silica sinter (*white*) with encrustations of arsenic-rich mineral material (*orange*) deposited from cooling water. Arsenic is a common pollutant in streams draining thermal areas (Source: http://en.wikipedia.org/wiki/Champagne_Pool)

500 g/km^2 followed by the Netherlands (450 g/km^2). According to Aylett (1979), cadmium was used in the 1940s in many industries, and it is only during the last three decades that serious consideration has been given to cadmium as an environmental contaminant. It is a recognized renal toxicant (WHO 1992). The maximum contaminant level (MCL) of cadmium assigned by the US Environmental Protection Agency (EPA) and Canada is 5 ppb, but this value was decreased to 3 ppb by the World Health Organization (WHO) in 1993. Chromium (pentavalent) is 100-fold more toxic than the trivalent form as reported by Petrilli and De Flora (1978). The chromium is introduced to the environment from textile industry (Barnhart, 1997). Mercury occurs in the Earths' crust at a concentration of 0.08 mg/kg (Mason and Morre 1982). It is used as slimicides and fungicides for many organisms. Atmospheric mercury is usually produced during mining and refining and incineration of garbage containing electrical equipment. Venezuelan crude oil has the highest vanadium content of 1400 mg/kg (Robert 2000). In Member States of the European Community, the different concentration ranges are remote areas 0.001–3 ng/m^3, urban areas 7–200 ng/m^3 and industrial areas 10–70 ng/m^3, respectively (Lahmann et al. 1986). Concentrations up to 2 μg/m^3 of vanadium have been reported in several cities in the Northeastern United States.

2.2 Existing Methodologies for the Removal of Toxic Metals

2.2.1 Oxidation

Most of the methodologies adopted for the removal of toxic metals perform better with anionic species than uncharged species at circum-neutral pH values. Therefore, a pre-oxidation step is required as the first treatment step before applying the main removal process to obtain toxic metal-free drinking water. Chlorine, ozone, potassium permanganate, manganese oxides and hydrogen peroxide have been used to accelerate oxidation of metals, including arsenic and antimony. A high oxidation efficiency is obtained using chlorine, but at the same time, the elevated concentrations of unwanted disinfection by-products with organic matter and the release of taste and odour compounds from algal cells should be considered. Potassium permanganate produces no harmful by-products but may give colour to water and cause filtration problems later in the treatment plant. Thus, oxidation alone cannot serve as a sufficient technology for the removal of metals though it may well be employed as a pretreatment step to increase the efficiency of the removal method. Copper, arsenic and lead may be removed separated by oxidation (Ahluwalia and Goyal 2007).

2.2.2 Coagulation-Filtration

Chemical precipitation through coagulation and filtration includes alum coagulation, iron coagulation and lime softening. Coagulants are substances capable of removing colloidal impurities from water, and coagulation is the process by which such removal is brought about. Co-precipitation occurs when an inorganic contaminant (e.g. arsenic) forms an insoluble complex (e.g. metal hydroxide flocs) with the coagulant. This may occur via adsorption inclusion or occlusion (Edwards 1994). Aluminium or ferric chlorides/sulphates can be added as coagulants, and following their addition, the relevant amorphous aluminium hydroxide [$Al(OH)_{3(am)}$] or ferric hydroxide [$Fe(OH)_{3(am)}$] is precipitated. Copper and zinc can be removed using coagulation (Adhoum et al. 2004).

The addition of aluminium or iron coagulants facilitates the conversion of soluble inorganic species of arsenic into insoluble products by precipitation, co-precipitation or adsorption. The formation of insoluble products facilitates the subsequent removal of metals from water by sedimentation and filtration processes. At high coagulant dosages, the adsorption of inorganic arsenic to precipitated metal hydroxide solids takes place, but entrapment of adsorbed contaminants in the interior of the growing particle and solid solution formation may also take place especially at low coagulant dosages.

Lime treatment is similar to coagulation with trivalent metal salts, but instead of metal hydroxides, hydrated lime ($Ca(OH)_2$) or $Mg(OH)_2$ is formed. The toxic metal removal mechanisms involve calcite precipitation (less effective) and sorption to $Mg(OH)_2$ solids (more effective). The process, however, does not serve as a major toxic metal removal mechanism due to low removal efficiencies and unfavourable operating conditions (very high pH and chemical dose rates are required).

Arsenate and antimonate removal is more effectively removed than As(III) and antimonite when using coagulation. Thus, a pre-oxidation step to oxidize As(III) to arsenate is beneficial as shown in Fig. 2.2.

The costs associated with this method include coagulation chemicals, pH adjustment before and after treatment, and sludge residue management. The methodology is advantageous as the monitoring of a breakthrough point is not required, whereas it requires low-cost chemicals.

The disadvantages of the methodology are that the procedure is effective only over a narrow pH range and coagulant dosage and the disposal of arsenic-contaminated coagulant (toxic) sludge poses problems. The presence of competing ions needs to be considered. As(III) needs to be oxidized to arsenate for effective removal. Hence, secondary treatment is necessary to meet the arsenic standard in lime treatment.

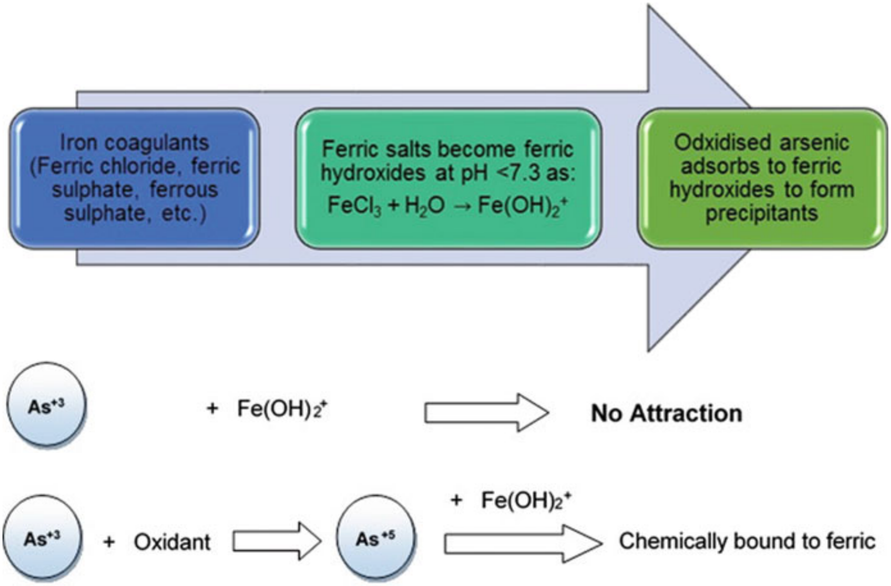

Fig. 2.2 Schematic of coagulation for removal of arsenic

2.2.3 *Ion Exchange*

Ion-exchange resins usually consist of a solid phase saturated with an anion that is exchangeable for metals in water as shown in Fig. 2.3. The media are regenerated with a solution of the exchangeable anion or replaced. An effective medium has a longer cycle between regenerations and thus capable of treating more bed volumes of water. It has high regeneration properties due to loss of media capacity. The resin has a preference for anions because of close charge spacing distance, functional group mobility and flexibility as well as the presence of hydrophilic groups (e.g. hydroxyl groups). Inglezakis and Grigoropoulou (2003) investigated the removal of lead from water by ion exchange.

The main disadvantage of ion exchange is that regeneration of resin and monitoring of breakthrough or filter use are required. It may be due to expensive technology depending on the resin/ion exchanger and is difficult to handle for some small systems. Oxidants may harm the ion exchanger if pre-oxidation is required. The removal of bicarbonate reduces the pH that increases the corrosiveness of treated wastewater. If the ion exchange is used beyond the point of sulphate exhaustion, the removed metal ion as arsenic may be released back into the treated water.

Fig. 2.3 Removal of As^{+3} from water using anion-exchange resin

2.2.4 Membrane Processes

Membrane processes include microfiltration, ultrafiltration, nanofiltration, reverse osmosis and electrodialysis. In these processes, the dissolved species are passed or retained by membranes based on the size, shape or charge of the compound.

Microfiltration and ultrafiltration exclude water constituents based on size which is 10–0.1 μm for microfiltration and 0.1–0.01 μm for ultrafiltration. Nanofiltration has a smaller pore size than microfiltration or ultrafiltration and can, therefore, exclude significant portions of dissolved metal as shown in Fig. 2.4. Potgieter et al. (2005) reported the removal of iron and manganese using nanofiltration membranes. However, it is more susceptible to fouling than microfiltration or ultrafiltration in reverse osmosis. The range of particles retained by reverse osmosis membranes lays between 0.005 and 0.5 μm including ions. In electrodialysis selective cation or anion membranes are used in integration with direct current electric field. Electrodialysis reversal simply means the polarity of the electric field is reversed to flush scale from the membrane. Electrodialysis and electrodialysis reversal have a similar particle size retention range to reverse osmosis.

The use of membrane processes for removal of metals may be desirable where microfiltration can be used to modify a process like coagulation, and multiple treatment objectives are necessary. Although the reverse osmosis unit is effective for a shorter time, it helps to improve the overall water quality by removing other constituents. It is disadvantageous due to the low ratio of treated product water to required inflow that is undesirable in areas with water shortages. The water pH does not affect removal in the range studied (4.0–8.0), although in the case of cellulose acetate membrane materials, it is pH selective (5.5–6.5) for arsenic. Advancements of membrane technology as electro-ultrafiltration possess good potential in removing arsenic from water (Weng et al. 2005).

The associated disadvantages of membrane processes are high operating and investment costs. The method usually requires a power source and controlled pressure, flow rate and pH. The guideline values are not met for high initial arsenic concentrations, whereas in water-scarce regions, the loss of influent water (20–25%) may be a concern. Pretreatment of the water may be necessary, e.g. for removing salts along with the readjustment of water quality after the treatment. Highly concentrated wastewater is produced at the reactor side and the membrane may not withstand the oxidant. Fouling must be considered for long-term use of membranes.

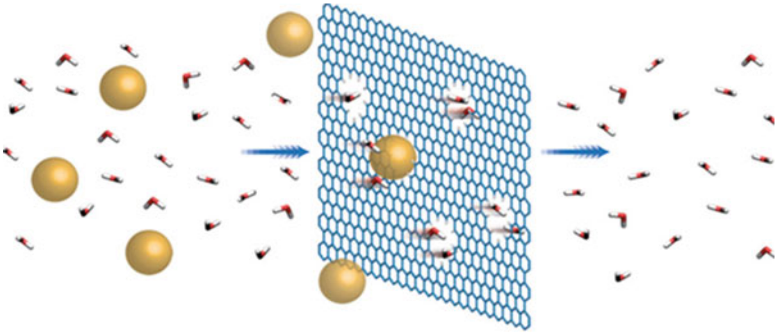

Fig. 2.4 Graphene membrane as a reverse osmosis membrane. Water molecules are driven to the *right* (*red* and *white*) and bigger molecules (*spheres*) are *left* behind (Wang and Karnik 2012)

2.2.5 Alternative Processes

Besides the methodologies discussed above, a few other alternative water treatment processes have been investigated for the removal of metals. Some alternatives involve variation of the implementation of existing treatments such as blending raw husk with contaminated water. This method is useful if a trace amount of pollutant like fluoride is desired in the effluent. Zero-valent iron is considered as a good adsorbent due to its high reactivity in water via spontaneous corrosion. When Fe(0) corrodes, FeOOH is produced on the surface, which has a good ability to adsorb metal(oid)s such as arsenic and antimony. Although Fe(0) is cheap and non-toxic, the necessary corrosion rate may be difficult to control for quantitative treatment of drinking water. Moving bed active filtration is a combination of co-precipitation and adsorption processes that utilize iron affinity for toxic metals like arsenic. The process includes a pre-reactor for introducing iron into the influent water and a moving bed sand filter. The sand filter is converted to an active filter by introduction of iron. Iron oxide-coated sand is continually formed abraded and regenerated within the filter.

Powdered alumina is also used followed by microfiltration wherein the influent water is mixed in a slurry with alumina particles below 200 μm diameter and then fed to a membrane unit for microfiltration. Alumina particles with bound metal ions are rejected by the filter and returned to the slurry reactor.

Another alternative process for the removal of toxic metals includes the biological treatment of water. Microbial mats immobilized on glass wool have been used to remove various metals and metalloids including arsenic from water. The studies suggest that arsenic may be removed from surface waters by phytoplankton with subsequent burial in lacustrine sediments. Phytoplankton either removes the metals by biological uptake and the organisms eventually settle or can act simply as particulate organic matter that adsorbs metals such as arsenic.

2.2.6 Adsorption

Adsorption is a mass transfer process in which a substance is transferred from a liquid phase to the surface of a solid and becomes bound by physical and/or chemical interactions. Adsorption is recognized as an effective and economic method for heavy metal waste water treatment. The process offers flexibility in design and operation and in many cases produces high-quality effluent. In addition, since adsorption is sometimes reversible, adsorbents can thus be regenerated by suitable desorption processes as mentioned by Fu and Wang (2011). Adsorption involves the passage of contaminated water through a bed of specially developed media where the contaminant (heavy metal) is adsorbed and removed from water. This generates two general types of residuals from media adsorption:

- Spent media
- Regeneration solutions

There are many performance measures of the ability of an adsorbent removal technology. The bed adsorption media is the number of bed volumes of water passed through a filter before the heavy metal concentration of effluent water is higher than a predetermined maximum contamination level. The metal removal capacity is a comparison of the amount of metal ion removed by weight or volume of media usually measured in “mg/litre” of wet media or “µg/grams” of dry media. The empty bed contact time is used to quantify the time required for the liquid in an adsorption bed to pass through the column assuming that there is proper dispersion and no preferential flow in the column. Adsorption has various advantageous features as:

- Low capital cost
- Ease of operation
- Effectivity and versatility
- Suitability for batch processes
- Generates less sludge
- Possibility of regeneration and reuse of adsorbent
- Potential to be applicable at very low concentrations

The adsorbent can be considered as cheap or low cost if it is abundant in nature and requires little processing or is a by-product of any industrial process. The reported literature of the last two decades has been compiled in this chapter that highlights the methodology of adsorption adopted for removal of heavy metal. A review of work re-counted for removal of heavy metals by adopting the methodology of adsorption has been premeditated with the details of research work performed by various authors using different adsorbents. The development of technologies for arsenic removal from industrial wastewater and contaminated drinking water has been the subject of several studies in the last decades.

2.3 Adsorbent Materials for Metal Removal

The adsorbents can be broadly classified as naturally occurring adsorbents; it includes the adsorbents that are obtained from natural resources as in Fig. 2.5. These can be used as treated or nontreated adsorbents, e.g. clay minerals and biosorbents. The chemically synthesized/modified adsorbents include chemical compounds or chemically synthesized adsorbents for adsorption, e.g. metal oxides and carbon nanotubes. Cationic hydrogels for arsenate removal from aqueous solution were studied by Barakat and Sahiner (2008).

Although the techniques mentioned earlier have been observed to be practical and cost-effective with concentrated wastewater, they are ineffective at low concentration wastewater that contains heavy metal ions less than 100 ppm. Many natural and/or synthetic adsorbents can effectively remove dissolved heavy metals, but most of them show some disadvantages such as poor adsorption capacity, low efficiency/cost ratio and ineffectiveness at high metal concentration. Thus selective adsorption utilizing various adsorbents including biological materials, mineral

Fig. 2.5 Adsorbents used for removal of metal from water: (**a**) activated alumina, (**b**) activated carbon, (**c**) rice hull, and (**d**) corncob

oxides, clay minerals, zeolite, fly ash, activated carbon or polymer resins has generated increasing interest.

The most common and effective method for removal of heavy metals from water is activated carbon, but it does not prove to be attractive due to high regeneration costs. This made biosorption to be investigated by researchers that use biomass as either living or dead microorganisms for removal of heavy metal ions from industrial wastewater. Several kinds of microorganisms (fungi, bacteria and algae) and bio-sludge of activated sludge systems have been reported to adsorb both organic and inorganic matter from wastewater. Dead biosorbents are more favourable as they are cheap, easily operated and not affected by the heavy metals. Moreover they can be regenerated and reused and are easily maintained.

Depending on the cell metabolism, the mechanisms of biosorption can be divided as metabolism dependent and non-metabolism dependent. On the basis of the ways for the metal to be captured by the cell, biosorption may be further classified according to the location of the metal ion removed from the solution as extracellular accumulation/precipitation or cell surface sorption/precipitation and intracellular accumulation.

Biochar by-products from fast wood/bark pyrolysis have been investigated as adsorbents for removal of As(III), Cd(II) and Pb(II) from water by Wang et al. (2015). Oak bark, pine bark, oak wood and pine wood char are obtained from fast pyrolysis at 400 °C and 450 °C in an auger-fed reactor. Maximum adsorption occurs over a pH range of 3–4 for arsenic and 4–5 for lead and cadmium. This study shows that the by-product char from bio-oil production can be used as plentiful inexpensive adsorbents for water treatment at a value above their pure fuel value. Igwe et al. (2005) reported the use of agricultural by-products for bioremediation of heavy metal ions that has proven to be an active field of interest. The methodology utilizes inactive (nonliving) microbial biomass that binds with heavy metals from waste streams by chelation and adsorption.

2.3.1 Adsorbents Used for Removal of Arsenic

Conventional and nonconventional treatment technologies for arsenic remediation have been compared in this section. The removal of arsenic from water involves specific adsorption by chemical attraction leading to bonds on specific sites of sorbents (Fig. 2.6).

Currently about 100 million people are consuming water with arsenic concentrations up to 100 times the concentration assigned by the guideline of the World Health Organization (10 μg/L) as cited by Kinniburgh and Smedley (2001). An article in Science by Ahmed et al. (2006) focuses on the problems of drinking water in Bangladesh. It demonstrates that two different approaches have had maximum impact, i.e. testing tube wells followed by switching away from contaminated wells to alternate uncontaminated water sources and the installation of deep wells that supply water from older aquifers that do not contain elevated arsenic levels.

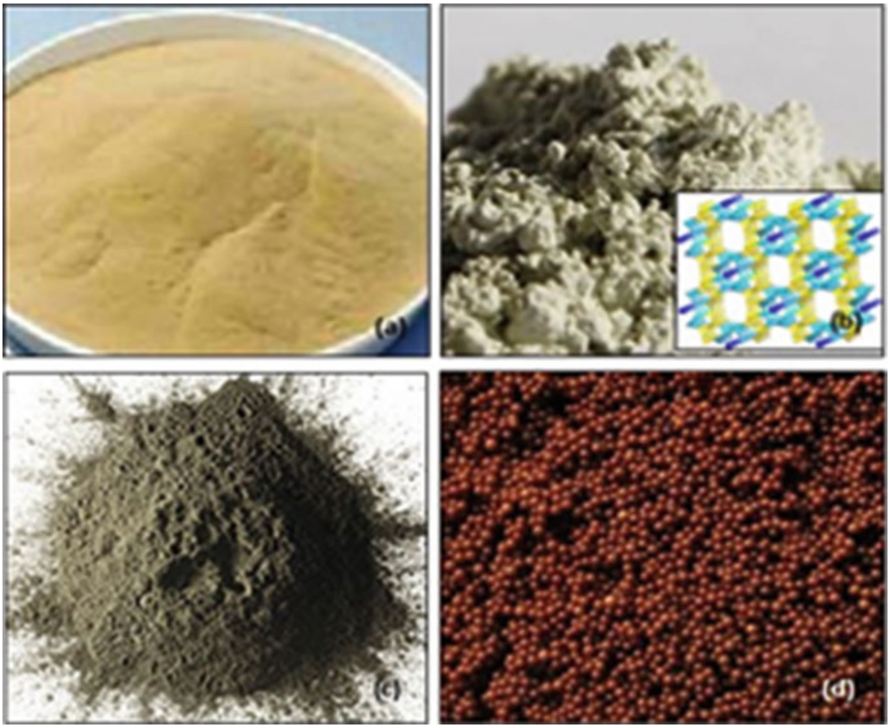

Fig. 2.6 (**a**) Palygorskite, (**b**) zeolite with structure as inset, (**c**) fly ash, and (**d**) polymer resin as adsorbents

Furthermore three major recommendations were made: (a) stimulate the periodic monitoring of water quality no matter what mitigation option exists, (b) encourage the wise use of deep aquifers low in arsenic, and (c) publicize widely the known effects of arsenic on the mental development of children. This illustrates that a variety of low-cost approaches must be employed in many developing locations throughout the world. When these approaches are exhausted, then adsorption is likely to contribute to further mitigation efforts.

Most of the technologies discussed in the literature are known to remove arsenic more effectively from water containing high initial arsenic concentrations (usually >100 mg/L), but residual arsenic concentrations exceed the 0.01 mg/L water quality standard used in most countries. Selective adsorption utilizing various adsorbents, including biological materials, mineral oxides, clay minerals, zeolites, fly ash, activated carbons or polymer resins has generated increasing interest (Fig. 2.6). It is observed that in villages of India and Bangladesh, a highly successful technology may not succeed in rural areas unless it fits into rural circumstances and is well accepted by the people. Technology development is only possible when a partnership exists involving proper village level participation. Hence, arsenic removal technologies all suffer from one or more drawbacks or limitations.

The effect of pH on the adsorption capacity depends on the surface charge or zeta potential of the sorbent at different pH and presence of different electrolytes. The number of available binding sites depends on the amount of sorbent taken. However, increasing the adsorbent dose can result in the formation of aggregates of the adsorbent. This leads to electrostatic interferences that diminish attractions between the adsorbing solute and the surface of the adsorbent. New resources such as hazelnut shell, rice husk, pecan shells, jackfruit, maize cob or husk have also been used as an adsorbent after chemical modification or conversion by heating into activated carbon for arsenic adsorption.

The theoretical calculations combined with instrumental analyses for removal of arsenic indicate inner-sphere complexation as a feasible mechanism for adsorption of arsenic on gibbsite as well as other adsorbents in the pH range from 5 to 9. The extended X-ray absorption fine structure EXAFS results indicate the formation of inner-sphere complexes of $As^{3+}$with gibbsite. Arsenic is coordinated to three oxygen atoms in the first shell at a distance of 1.77 Å and to aluminium in the second shell at a distance of approximately 3.20 Å in a bidentate-binuclear configuration for all evaluated pH values (5, 7 and 9). In addition, an $As\text{-}Al_2$ interaction is ascribed to a monodentate-binuclear complex due to its interatomic distance of 3.47 Å. This interaction of As^{3+} has also been observed with other adsorbents as well, such as montmorillonite and modified montmorillonite. The observed adsorption capacities for various sorbents are summarized in Tables 2.3 and 2.4, respectively.

The comparison of conventional and nonconventional treatment technologies for aqueous arsenic remediation by Ngo et al. (2002) shows that the first adsorbent that gained importance for successful removal of arsenic from water was granular-activated alumina. However, activated carbon has been used extensively for the removal of arsenic from water. Three types of activated carbons with different ash contents were studied by Lorenzen et al. (1995) for arsenic adsorption: coconut shell carbon with 3% ash, peat-based extruded carbon with 5% ash and a coal-based carbon with 5–6% ash. The removal of As(V) was observed to be higher using carbon with a high ash content, and its removal capacity increased after its pretreatment with Cu(II) as arsenic forms an insoluble metal arsenate with the impregnated copper. The optimum pH for arsenic adsorption by Cu-pretreated carbon was observed to be around 6.

Many adsorbents have been proposed and investigated during last two decades. Low-cost adsorbents that can be afforded in rural areas have been investigated as well. Agricultural products and their by-products have been used as low-cost adsorbents for the removal of arsenic from water. The adsorption efficiency using 0.1 g of rice husk was investigated by Nasir et al. (1997) from initial concentrations of 6.0×10^{-3} M arsenic. The adsorption follows the Freundlich isotherm over the concentration range from 8.7×10^{-5} M to 1.7×10^{-3} M arsenic ($K = 4.43$ mmol/g). An increase in temperature causes an increase in the removal of arsenic. Complete removal of arsenic [As(III) as well as As (V)] was achieved using 6 g

Table 2.3 Adsorptive removal of arsenic using naturally occurring adsorbents

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Magnetic biochar	60 mg/L	0.27 mg/g	SEM-EDS TGA	Wang et al. (2015)
Modified peat	45 mg/L	90%	FT-IR	Ansone et al. (2013)
Zr-loaded orange waste gel	20 mg/L	4.2 mg/g	BET-SA ICP/AES	Biswas et al. (2008)
Maize cob wastes	500 μg/L	0.01 mg/g	AAS UV/VIS CHN	María and González (2008)
Maize leaves	50 mg/L	84.9%	FT-IR SEM	Kamsonlian et al. (2011)
Staphylococcus xylosus	100 mg/L	54.3 mg/g	FT-IR Titration	Aryal et al.(2010)
Rhodococcus sp.	100 mg/L	77.3 mg/g	FT-IR AAS	Prased et al. (2011)
Iron-impregnated potato peels	1 mg/g	0.11 mg/g	SEM WD/XRFS XRD	Dhoble et al. (2011)
Zeolite	150 mg/L	4.4 mg/g	AAS	Gülbas et al. (2011)
Aspergillus niger	0.10 mg/L	0.1 mg/g	AAS SEM TEM	Pokhrel and Viraraghavan (2008)
Human hair	0.360 mg/L	0.013 mg/g	TEM FT-IR HG/AF	Wasiuddin et al. (2002)
Chicken feathers	1.34 mM	27×10^5 M/g	XANES EXAFS	Teixeira and Ciminelli (2005)
Volcanic stone	0.2 mg/L	86%	ICP/AES	Elizalde-González et al. (2001)
Clinoptiloite-rich zeolitic tuff	0.360 mg/L	0.02 mg/g	XRD FT-IR UV/VIS	María and González (2008)
Kaolinite	2 mM	0.004 mol/Kg	ICP/AES HPLC	Kundu et al.(2004)
Sand	1.00 mg/L	17 mg/g	FT-IR SEM SEM	Gupta et al. (2012)
Iron oxide-coated sands	0.300 mg/L	0.009 mg/g	EDX ICP-OES	Hsu et al. (2008); Jessen et al. (2005)
Activated carbon	0.5 mg/L	0.03 mg/g	SEM BET	Ouma et al. (2011)
Mesoporous carbon	0.05 mg/L	8.1 mg/g	XRD HPLC HG/AFS	Gu et al. (2007)
Iron-modified activated carbon	22 mg/L	30 mg/g	AAS-HV ICP/MS	Chen et al. (2007)
Iron-impregnated mesoporous carbon	16 mg/L	8.0 mg/g	TEM FT-IR HG/AFS	Masih et al.(2009)
Powder activated carbon	5 g/L	8.4 mg/g	ICP-OES BET-N_2	Tien et al. (2004)
Limestone	520 mg/L	0.007 mg/g	AAS SEM	Hossain and Islam (2008)

(continued)

Table 2.3 (continued)

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Biogenic manganese oxides	5 mg/L	0.1 mg/g	BET-SSA GF-AAS	Masue et al. (2007)
Oxides and clay minerals	0.020 mM	0.3 µmol/g	GF/AAS	Sabine Goldberg (2002)
Synthetic siderite	0.010 mg/mL	10.0 mg/g	SEM EDAX FT-IR	Guo et al. (2011)
Treated laterite	500 mg/L	8.4 mg/g	XRD SEM FT-IR TEM	Maiti et al. (2010)
Goethite	0.10 mM	0.0014 mmol/m^2	TGA DSC BET-N_2	Luxton et al. (2006)
Tropical soil	1 mg/L	97.6%	ICP-OES BET	
Natural laterite	0.20 mM	58%	ICP/MS GF/AAS	Goh and Lim (2004)
Red soil	100 mg/L	10%	TEM SEM BET -SSA	Singh et al. (2007)
Crushed crab shell chitosan	10 mg/L	6.2 mg/g	AAS	Rana et al. (2009)
Chitosan-coated ceramic alumina	1000 mg/L	56.5 mg/g	ICP/MS FT-IR XPS	Boddu et al. (2008)
Molybdate-impregnated chitosan beads	0.1 mg/L	95%	SSA ICP/AES	Jin Su et al. (2011)
Surfactant-modified MMT	100 mg/L	90%	XRD FT-IR SEM	Anjum et al. (2011)
MMT modified chitosan beads	10 mg/L	91%	XRD FT-IR-ATR SEM	Anjum et al. (2013)
Chitosan	400 mg/L	58 mg/g	XRD FT-IR	Chen and Chung (2006)
Tea fungal biomass	1.3 mg/L	1.1 mg/g	XRD SEM FT-IR TEM	Murugesan et al. (2006)
Shirasu zeolite	1.3 mM	66.0 mg/g	XRD SEM FT-IR TEM	Yan-hua Xu et al. (2002)
Penicillium purpurogenum	10–750 mg/L	35.6 mg/g	AAS SEM	Ridvan Say et al. (2003)
Olivier soil	5–100 mg/L	0.4 mg/g	EDX ICP-OES	Hua et al. (2006)
Sharkey soil	5–100 mg/L	0.74 mg/g	XRD ICP-OES	Hua et al. (2006)
Coconut coir pith anion exchanger	5–100 mg/L	13.6 mg/g	EDAX FT-IR	Anirudhan and Unnithan (2007)

(continued)

Table 2.3 (continued)

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Pine wood char	10–100 mg/L	0.0012 mg/g	SEM FT-IR TEM	Mohan et al. (2007)
L. nigrescens	50–600 mg/L	45.2 mg/g	AAS SEM	Hansen et al. (2006)
Immobilized biomass	50–2500 mg/L	704.1 mg/g	AAS	Kamala et al. (2005)

Note: *AAS* atomic absorption spectroscopy; *FT-IR* Fourier Transform-InfraRed, *SEM* scanning electron microscopy, *EDAX* energy dispersive X-ray analysis, *XRD* X-ray diffraction, *ICP-OES* inductively coupled plasma-optical emission spectrometry, *TEM* transmission electron microscopy; *BET-SSA* Brunauer-Emmett-Teller-specific surface area, *GF/AAS* graphite furnace-atomic absorption spectroscopy, *HPLC* high-performance liquid chromatography, *DSC* differential scanning calorimetry, *XRFS* X-ray fluorescence

of untreated rice husk columns with an average particle size of 780 μm and 510 μm from an initial concentration of 100 μg/L at a flow rate of 6.7 and 1.7 mL/min at pH of 6.5 and 6, respectively.

Industrial by-products/wastes such as lignite, peat, chars and bone char have received increasing attention in wastewater treatment. Red mud is a low-cost waste material formed during the production of alumina when bauxite ore is subjected to caustic leaching. Brunori et al. (2005) utilized red mud for treatment of contaminated waters and soils. Treated mud exhibited a high metal trapping capacity that increased with an increase in adsorbent dose in contact with the solution. Only 35% of the arsenic was removed after 48 h of contact time with an adsorbent dose of 2 g/L, but the percentage significantly increased up to 70% with increased adsorbent dose to 10 g/L.

Industrial by-products thus act as good substitute for activated carbon due to their ease of availability and they are inexpensive (Couillard 1992, 1994; Viraragharan and Ayyaswami 1987). Sneddon et al. (2005) studied the removal of As (V) using a mixture of synthetic hydroxylapatite and barite or bone char in the concentration range of 4–100 mg/L. Bone char was found to be a very effective adsorbent for As(V) in the pH range of 2–5.

A large volume of granular blast furnace slag has been generated by steel plants that is used as filler or in the production of slag cement. Blast furnace slag has been reported as an effective and economical adsorbent for the removal of aqueous arsenic as reported by Zhang and Itoh (2005) and Ahn et al. (2003). An adsorbent was synthesized for aqueous arsenic removal by loading iron(III) oxide onto melted municipal solid waste incinerator slag. The loading of iron oxide on slag increased the surface area of Fe(III)oxide-loaded melted slag (IOLMS) by 68% compared to FeOOH due to the porous structure formed in IOLMS during the synthesis process.

The removal capacities of IOLMS for As(V) and As(III) were observed to be 2.5 and 3 times of those of amorphous hydrous ferric oxide, respectively. About 15 g of IOLMS can remove 200 mg As(V) from 1 L of aqueous solution that meets the

Table 2.4 Adsorptive removal of arsenic using synthesized/modified adsorbents

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Fe-Mn oxide-impregnated chitosan	0.233 mg/L	54 mg/g	AAS FT-IR	Qui et al. (2015)
Iron oxide-coated sand	0.200 mg/L	0.08 mg/g		Devi et al. (2014)
Synthetic siderite	10 mg/L	10.0 mg/g	SEM EDAX FT-IR	Guo et al.(2011)
Bauxite	1 mg/L	95%	TEM SEM BET	
α-Fe_2O_3 nanoparticles	120 mg/L	95 mg/g	FT-IR SEM	Tang et al.(2011)
Iron-zirconium binary oxide	20 mg/L	120 mg/g	XRD FT-IR	Ren et al.(2011)
α-Fe_2O_3-impregnated chitosan beads	50 mg/L	9.3 mg/g	XRD SEM BET	Liu et al. (2011)
Surfactant (OTMA BDMA DODMA)-modified bentonite	5 mg/L	0.102 mg/g	XRD FT-IR	Jin Su et al. (2011)
Magnetite nanoparticles	1000 mg/g	168 mg/g	SEM EDAX BET	
Phosphorylated orange waste	15 mg/L	0.9 mmol/g	AAS BET-SA	Ghimire et al. (2003)
Portland cement	0.2 mg/L	88.0%	UV/VIS	Kundu et al. (2004)
85% fly ash	100 mg/L	0.45 mg/g	XRD UV-VIS BET	Polowczyk et al. (2007)
Surfactant-modified zeolites	2 mM	0.002 mmol/g	ICP/AES HPLC	Li et al.(2007)
Ferrihydrite (FH)	0.325 mg/L	0.3 mg/g	P-XRD EDAX FT-IR	Jessen et al. (2005)
Iron-modified activated carbon	22 mg/L	30 mg/g	AAS-HV ICP/MS	Chen et al. (2007)
Iron-impregnated mesoporous carbon	0.2–16 mg/L	8.0 mg/g	TEM FT-IR HG/AFS	Masih et al. (2009)
Activated alumina	300 mg/L	80.0%	Titration	Manjare et al. (2005)
Powder activated carbon	5000 mg/L	8.4 mg/g	ICP-OES BET	Tien et al. (2004)
Titania-silica binary oxide-loaded polyacrylonitrile polymer	15 mg/L	0.4 mmol/g	XRD FT-IR TEM TGA	Nilchi et al. (2010)
Iron oxide-coated biomass	0.001 mg/L	0.1 mg/g	GF-AAS	Pokhrel et al. (2008)
Metal(III)-loaded amberlite resins	15 mg/L	484 mmol/kg	XRD BET SEM	Shao et al. (2008)

(continued)

Table 2.4 (continued)

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Ferric hydroxide microcapsule-loaded alginate beads	100 mg/L	4.8 mg/g	SEM CSV	Sarkar et al. (2010)
Fe-Mn binary oxide	0.133 mM	1.8 mmol/g	XRD XPS BET ICP-OES	Zhanga et al. (2007)
Modified calcined bauxite	1 mg/L	98.8%	XRD EDAX UV/VIS	Zhanga et al. (2007)
Modified calcined bauxite	10,000 mg/L	1.4 mg/g	XRD Zeta studies EDAX UV/VIS	Maji et al. (2007)
Limestone	520 mg/L	0.007 mg/g	AAS SEM	Hossain and Islam (2008)
Aluminium, iron hydroxides	1 mg/L	0.09 mol/mol	XRD XPS	
Mn-substituted iron oxyhydroxide	25 mg/L	4.6 mg/g	XRD BET-SSA FT-IR HG-AAS	Lakshmipathiraj et al. (2006)
Nanocrystalline titanium dioxide	0.300 mg/L	32.4 mg/g	AAS	Bang et al. (2005)
Granular titanium dioxide	0.0267 mM	0.1 mmol/g	GF-AAS	Bang et al. (2005)
Iron hydroxide-coated alumina	1 mM	0.1 mmol/g	BET-SSA GF-AAS	Hlavay and Polyak (2005)
Activated alumina and carbon	300 mg/L	80%	Titration	Manjare et al. (2005)
Biogenic manganese oxides	5 mg/L	0.1 mg/g	BET-SSA GF-AAS	Katsoyiannis et al. (2004)
Goethite	0.10 mM	1.4 μmol/mg	TGA DSC BET	Luxton et al. (2006)
Hybrid adsorbents	1 mg/L	95%	UV/VIS	Nemade et al. (2009a, b)
Basic yttrium carbonate	5–0.2 mmol/L	305.8 mg/g		Wasey et al. (1996)

Note: *AAS* atomic absorption spectroscopy, *FT-IR* Fourier Transform-InfraRed; *SEM* scanning electron microscopy, *EDAX* energy dispersive X-ray analysis, *XRD* X-ray diffraction, *ICP-OES* inductively coupled plasma-optical emission spectrometry, *TEM* transmission electron microscopy, *BET-SSA* Brunauer-Emmett-Teller-specific surface area, *GF/AAS* graphite furnace-atomic absorption spectroscopy, *HPLC* high-performance liquid chromatography, *DSC* differential scanning calorimetry, *XRFS* X-ray fluorescence, *UV-VIS* ultraviolet-visible spectroscopy metal ion concentrations allowed by regulations for industrial wastewater discharge. On the other hand, 65 g of IOLMS was necessary to remove As(III) from 1 L solution to meet the permissible limit. The interactions involved in the removal of arsenic using IOLMS are affinity adsorption that depends on the surface area of IOLMS, the reaction with iron oxides that depends on the existing forms of arsenic species and the reaction with calcium and other metallic elements initially contained in the slag.

The interaction between metal ions and the adsorbent depends on the pH of the solution since the dominant arsenic species {As(V)} in the pH range of 2–7 is H_2AsO_4. Hence the following reaction occurs for the removal of arsenic:

$$\mathrm{FeOOH} + 3H_2\mathrm{AsO_4}^- + 3\mathrm{H}^+ \leftrightarrow \mathrm{Fe}(H_2\mathrm{AsO_4})_3 + 2H_2O \qquad (2.1)$$

The coagulation of Ca^{2+} is involved in the removal of As(III) at pH 10 wherein the anionic $H_2AsO_3^-$ predominates. This leads to the possibility of formation of $Ca(H_2AsO_3)_2 \cdot nH_2O$ in the leachate. If the pH of solution increases, only small amounts of Ca^{2+} could be leached, while at $pH < 9$, H_3AsO_3 could not react with Ca^{2+}.

Efforts have been made to utilize fly ash as an adsorbent since the major chemical constituent of fly ash is aluminosilicate. Fly ash is produced as a by-product by combustion of coal in thermal power plants. The disposal of fly ash requires large disposal sites, while its applications have been limited to the production of cement brick and roadbeds. Gupta et al. (2005) report the use of bottom ash as an adsorbent. The kinetic and equilibrium studies performed by Rahman (2004) to evaluate the As(V) removal efficiency using lignite-based fly ash show the metal ion removal at pH 4 as significantly higher than that at pH 7 or 10. Maple wood ash without any chemical treatment was also utilized to remediate As(III) and As(V) from contaminated aqueous streams in low concentrations. Static tests removed almost 80% of arsenic, while the arsenic concentration was reduced from 500 to <5 ppb in dynamic column experiments.

Other aluminosilicates that can be used as adsorbent are clay minerals. These are hydrated aluminosilicates (sometimes with minor amounts of iron magnesium and other cations) and are widespread and abundant in aquatic and terrestrial environments. The structure of clays forms flat hexagonal sheet-like micas. Finely divided clay minerals and oxides exhibit large surface areas. Clay minerals and oxides can adsorb cationic, anionic and neutral metal species. Their sorption capacities, cation- and anion-exchange properties and binding energies vary widely. The investigations of Dousova et al. (2006) and Anjum et al. (2011) show adsorption of arsenic on clay minerals including natural metakaolin, natural clinoptilolite-rich mineral and montmorillonite in both untreated and Fe-treated forms. The studies of Anjum et al. (2011) show the adsorption capacity of cetylpyridinium chloride-modified montmorillonite to be 90% from an initial concentration of 100 mg/L. The lowest level of As(III) that could be extracted was found to be 0.4 mg/L, whereas another

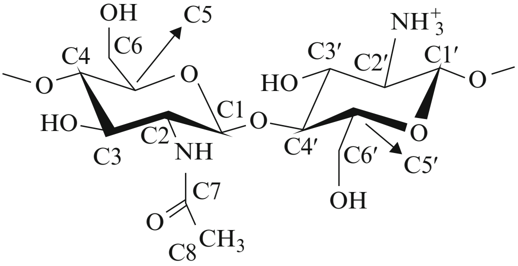

Fig. 2.7 Chemical structure of chitosan

research by Anjum et al. (2013) reports the lowest detection limit as 0.04 mg/L using chitosan-modified montmorillonite. This is due to a large positively charged organoclay surface which facilitates stronger interactions between the adsorbent and the adsorbate, thereby leading to a higher removal capacity of As(III). The sorption capacity of Fe-treated sorbents was 20 mg/g that increased significantly as compared to untreated material (from about 0.5 mg/g) that represented more than 95% of total arsenic removal.

Chitin is the most widely occurring natural carbohydrate polymer next to cellulose. It is a long unbranched polysaccharide derivative of cellulose where the C_2 hydroxyl group has been replaced by the acetyl-amino group – $NHCOCH_3$. Chitin is found in the exoskeleton of *Crustacea*, shellfish, shrimp, crabs and insects. 2-Deoxy-2(acetyl-amino) glucose is the primary unit in the polymer chain. These units are linked by β $(1 \rightarrow 4)$ glycosidic bonds forming long linear chains with degrees of polymerization from 2000 to 4000. Chitosan as shown in Fig. 2.7 is derived from chitin by deacetylation of chitin using concentrated alkali at high temperature. Chitin and chitosan are excellent natural adsorbents that possess high selectivities due to large numbers of hydroxyl and amino groups. These give chitosan a high hydrophilicity: the primary amino groups provide high reactivity or polymer chains of chitosan provide suitable configurations for efficient complexation with metal ions.

The adsorption of arsenic on chitosan, chitin and biomass from *Rhizopus oryzae* was studied by Mcafee et al. (2001). The immobilized biomass offered an outstanding capacity of 0.13 μ equivalents of arsenic per gram at pH 7.

The study by Anjum et al. (2013) shows sorptive removal of As(III) by chitosan-montmorillonite (MMT) composites (in the form of powder and beads). The maximum As(III) sorption capacity of 48.7 mg/g (achieved within 10 min of contact time) was obtained using chitosan-MMT beads in the pH range of drinking water (6–8) at 298 K. The biocomposites show a comparable high sorption capacity with detection and estimation of As(III) from 0.004 (4 ppb) to 100 μg/ml (100 ppm) of aqueous solution. The analyte was found to undergo instantaneous adsorption onto the surfaces as well as surface complexation that further enhanced the adsorption capacity of the analyte onto the sorbents as suggested by kinetic studies as depicted in Fig. 2.8.

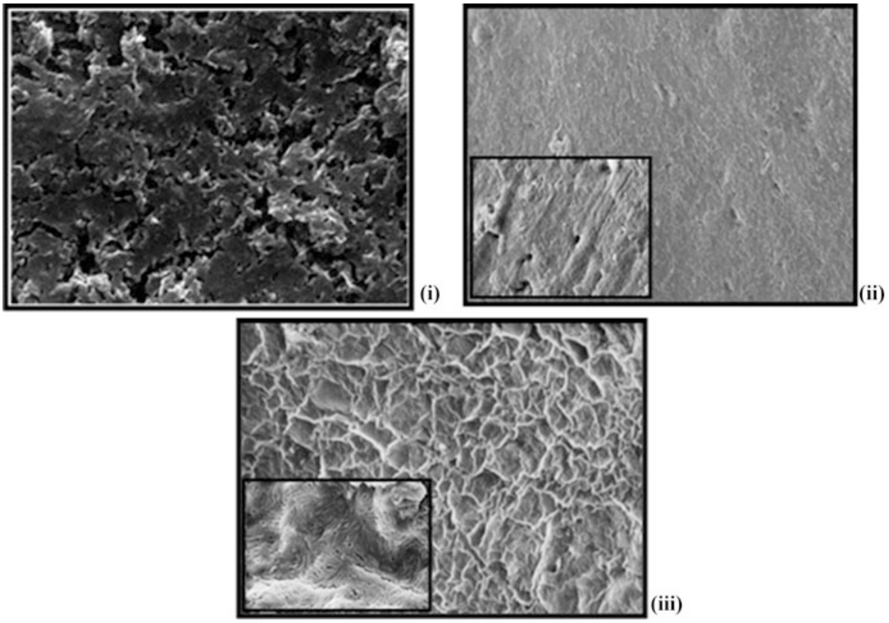

Fig. 2.8 Scanning electron microscopic analysis of (**a**) chitosan-montmorillonite bead (CHMB), (**b**) chitosan bead (CHB), and (**c**) chitosan-montmorillonite composites (CHI-MMT)

The FT-IR-ATR analysis of the adsorbents after As(III) adsorption also supported arsenic sorption and indicated surface complexation between –OH, −NH sites and As(III), respectively, rather than solid-phase precipitation that might generate a large amount of sludge.

2.3.2 *Adsorbents Used for Removal of Antimony*

Antimony has been used by human cultures since the Early Bronze Age. Nriagu (2005) reports that the excavations at Tello in Ancient Chaldea in the far south-eastern corner of Mesopotamia found fragments of an antimony base that dates back to 4000 B.C. Alchemists and quacks have used antimony compounds in medicine, veterinary and cosmetics. It was prescribed in the past as the universal remedy for syphilis, chest pains, the plague, melancholy and especially for fever.

Bowen (1979) reports the concentrations of antimony in groundwater and surface water normally range from 0.1 to 0.2 μg/L. But unfortunately only very few sorption studies of antimony using natural sorbents have been reported.

Sb(III) and Sb(V) bind strongly to hydroxides of Fe and Mn and only weakly to clay minerals (Blay 2000). Extended X-ray adsorption fine structure (EXAFS) measurements of soils from shooting ranges provide evidence for a strong preference of antimony binding to Fe hydroxides. However, the binding mechanism is still unclear.

The observed adsorption capacities for the removal of antimony using various sorbents are summarized in Tables 2.5 and 2.6, respectively.

The surface coverage and pH have a strong influence on the removal of Sb(III) and Sb(V) using iron hydroxides (Blay 2000; Enders and Jekel 1996; Ambe 1987;

Table 2.5 Adsorptive removal of antimony using natural adsorbents

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Brown algae	100 mg/L	5.4 mg/g	AAS, FT-IR	Ungureanu et al. (2015)
Hematite-modified nanoparticles	0.11 mg/L	95%	XRD, TEM	Shan et al. (2014)
Bentonite	1 mg/L	90%	HPLC H-GAAS BET	Xi et al. (2011)
Bayoxide	0.1 mg/L	95%		Ilavský et al. (2015)
Sodium montmorillonite	0.05 mol/L	0.0003 mol/g	BET GF-AAS ICP	Zhao et al. (2010)
Diatomite	10 mg/L	35.2 mg/g	BET GF-AAS	Ahmet Sarı et al. (2010)
Zero-valent iron	2 mg/L	1.6 µg/g	AAS	
Goethite	2–127 µM	180 µmol/g	HPLC ICP/AES	Leuz et al. (2006)
Brown forest soil	500 mg/L	0.6 mg/kg	XRD ICP/AES	Manaka (2006)
Manganite	0.13 mmol/L	56.5 mg/g	AAS ICP/AES	Filella et al. (2002)
Goethite	1.34 mM	270 mol/g	HPLC HG-AAS	Leuz et al. (2006)
Cerium zirconium hydrous oxides	100 mg/L	98%	AAS	Eva Mištová et al. (2009)
Magnetite	130 µM	56.5 mg/g	BET-SA GF-AAS	Filella et al. (2002)
Hydroxide-type adsorbents	20 mg/L	45 mg/g	AAS FT-IR	Fujita et al. (2006)
Weakly basic ion exchanger	8 µmol/L	0.008 mM	ICP/AE titration	Mercy and Wolfgang (2006)
Rice husks	1.92×10^{-5} M	91%	Radio trace	Khalid et al. (2000)
Zero-valent iron	2 mg/L	1.6 µg/g	AAS	
Alum and ferric salt	0.05 mg/L	90%	HG/AFS	Guo et al. (2009)

(continued)

Table 2.5 (continued)

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Hydroxyapatite	0.05 mg/L	98%	BET GF-AAS ICP	Leyva et al. (2001)
Olivine	0.100 mM	90%	ICP CHN	
Kaolinite	1 mg/L	27.1%	HG/AFS UV-VIS	Xi et al. (2010)
Silene vulgaris		51.7 mg/kg	HG-AAS	Baroni et al. (2000)

Note: *AAS* atomic absorption spectroscopy, *FT-IR* Fourier Transform-InfraRed, *SEM* scanning electron microscopy, *EDAX* energy dispersive X-ray analysis, *XRD* X-ray diffraction, *ICP-OES* inductively coupled plasma-optical emission spectrometry, *TEM* transmission electron microscopy, *BET-SSA* Brunauer-Emmett-Teller-specific surface area, *GF/AAS* graphite furnace-atomic absorption spectroscopy, *HPLC* high-performance liquid chromatography, *DSC* differential scanning calorimetry, *XRFS* X-ray fluorescence

Thanabalasingam and Pickering 1990). The maximum sorption of Sb(V) on Fe hydroxides was reported at low pH values and extended up to pH 7 at low surface coverage. The adsorption is pH dependant in the absence of organic ligands, namely, tartrate and acetate. This indicates that Sb(III) strongly adsorbs in the pH range 6–10 from an initial concentration of 41 μM.

The mineral surfaces in aqueous systems not only bind metal ions, but can also accelerate oxygenation of Fe(II), Mn(II) and Mn(V) (Wehrli and Stumm 1988). The metal ions bind to oxygen donor ligands of the surface, forming an inner-sphere coordination that has a similar effect as hydrolysis for homogeneous reactions. The adsorption capacity of Sb(V) using goethite was above 96% in the presence of ionic strengths of 0.01 M and 0.1 M between pH 3 and 6, respectively. The adsorption of Sb(V) decreased at pH values of 6.8 and 6.1 at an ionic strength of 0.01 M and 0.1 M, respectively. The EXAFS spectra of goethite after metal ion adsorption show that a Sb(V) octahedron [$Sb(OH)_6^-$] shares an edge with an $Fe(OH)_6$ octahedron and forms an edge-sharing inner-sphere sorption complex at the surface of goethite. The influence of ionic strength on the sorption of Sb(V) was strong above pH 6. This resulted in a lower adsorption of Sb(V) at higher ionic strength. On the other hand, the maximum adsorption capacity of diatomite reported by Sari et al. (2010) for Sb(III) was found to be 35.2 mg/g at pH 6. The adsorption of Sb(III) in the presence of 0.001 M $NaNO_3$ at pH 6 was 68%. If the ionic strength was changed to 0.01 and 0.1 M $NaNO_3$, then the adsorption efficiency decreased to 56% and 48%, respectively, at the same pH. The calculated mean free energy was found to be 7.32 kJ/mol indicating physical adsorption of Sb(III). The investigations for reusability of diatomite show the highest desorption efficiency of 94% using 0.5 M HCl, whereas a decrease of 10% in desorption yield and about 3% adsorption yield was observed after ten adsorption/desorption process cycles due to high stability of

Table 2.6 Adsorptive removal of antimony using synthesized/modified adsorbents

Adsorbent used	Initial concentration	Efficiency of adsorbent	Nature of investigation	References
ZSVI zeolite	100 mg/L	80%	XRD, XPS	Zhou et al. (2015)
$FeCl_3$-modified activated carbon	0.02 mol/L	96.4%	BET	Yu et al. (2014)
Surfactant-modified montmorillonite	100 mg/L	99%	XRD FT-IR	Anjum and Datta (2012)
Zero-valent iron	2 mg/L	0.0016 mg/g	AAS	Tomáš Klimko et al. (2011)
Soil and allophane from hexamethylenetetramine silicic acid	40 mg/L	0.8 mg/g	XRD XRF ICP/MS	Takahash et al. (2010)
Brown forest soil	500 mg/L	0.0006 mg/g	XRD ICP/AES	Manaka (2006)
Manganite	0.13 mmol/L	56.5 mg/g	AAS ICP/AES	Filella et al. (2002)
Bayoxide E33	0.06 mg/L	0.085 mg/g	AAS	Ilavsky (2008)
Goethite	1.34 mM	270 mol/g	HPLC HG-AAS	Leuz et al. (2006)
Cerium and zirconium hydrous oxides	5 mg/L	98%	AAS ICP/AES	Eva Mištová et al. (2009)
Zr(IV)-loaded SOW		114.4 mg/g	FT-IR AAS	Biswas et al. (2009)
Fe(III)-loaded SOW		136.4 mg/g	FT-IR AAS	Biswas et al. (2009)
Chemically bonded adsorbent			FT-IR AAS	Deorkar and Tavlarides (1997)
Amorphous iron and Mn oxyhydroxide	5–20 mg/L	70 mg/g	ACSV	Nelson Belzile et al. (2001)
Magnetite	0.13 mM	56.5 mg/g	BET GF-AAS	Filella et al. (2002)
Hydroxide-type adsorbents	20 mg/L	45 mg/g	AAS FT-IR	Toyohisa Fujita et al. (2006)
Hydrous oxide of Fe		12.1 mg/g	FT-IR AAS	Thanabalasingam and Pickering (1990)
Goethite (α-FeOOH)		61.2	FT-IR AAS	Watkins et al. (2006)
Hydrous oxide of Mn	0.027 mM	17.0 mg/g	ASV	Thanabalasingam and Pickering (1990)
Alum and ferric salt	0.05 mg/L	90%	HG/AFS	Guo et al. (2009)
Pyrrolidine dithiocarbamate	2.5 M	98%	Radiotracer	Sun and Yang (1999)
Diatomite	10 mg/L	35.2 mg/g	BET-SSA GF-AAS	Ahmet Sarı et al. (2010)

diatomite. The calculated thermodynamic parameters show adsorption of Sb(III) onto diatomite as feasible spontaneous and exothermic under the experimental conditions studied.

2.3.3 Adsorbents Used for Removal of Mercury

Chemical reduction by $SnCl_2$ is widely used in mercury analysis in which Hg(II) is reduced to gaseous mercury Hg(0), which is then detected and quantified by methods such as Cold Vapor Atomic Fluorescence Spectrometry (CVAFS). Using $SnCl_2$ to remove Hg(II) (especially trace amounts of mercury) from wastewater was first conceived by Southworth (1996). Field tests demonstrated that stannous tin (Sn^{2+}) was capable of converting dissolved Hg(II) to dissolved elemental mercury Hg(0) in one of the outfalls (Outfall 51) within the Y-12 complex. The study shows that (1) about four to five times more stoichiometrical Sn^{2+} than Hg(II) (Sn/Hg ratio ~ 5) was required to convert the available inorganic mercury to Hg(0), indicating favourable reduction of Hg(II) by $SnCl_2$, given the wastewater chemistry of Outfall 51, and (2) an air/liquid ratio of 20 was sufficient to strip all the resulting Hg(0). The study also indicated that the same chemical reduction might be applied to convert Hg(II) to Hg(0) in the storm drain discharge at Outfall 200 after removal of residual chlorine (Southworth 1997).

The reported adsorption capacities for the removal of mercury using various synthesized sorbents are summarized in Table 2.7. Research was conducted upon the substitution of various functional groups by organic acids, amine bases and sulphur compounds onto the chitosan for Hg(II) adsorption. Recent researches by Peniche et al. (1992) report the effectiveness of chitosan, chitin and crab shell for the chelation of heavy metal ions as shown in Fig. 2.9.

The polyaminated highly porous chitosan beads (PEI-CS) prepared by cross-linking of chitosan beads followed by reaction with EPI and polyethylenimine and the use of N-(2-pyridylmethyl) chitosan (PMC), N-(2-thienylmethyl)chitosan (TMC) and N-[3-(methylthio) propyl]chitosan (MTPC), TMC and MTPC containing sulphur presented higher selectivity to Hg(II) ions than PMC attributable to the fact that Hg(II) is a soft acid that prefers to associate with soft ligand atoms on the basis of the hard and soft (Lewis) acids and bases concept. MTPC shows a higher Hg(II) adsorption capacity (421.3 mg/g) due to the higher coordination ability of the thioether group than the thienyl group and to the existence of a propyl chain spacer unit which would allow for better flexibility of the main ligating atom (the sulphur atom). The adsorption of metal ion on polyaminated highly porous chitosan chelating resin was reported by Kawamura.

Dias et al. (2007) show Hg(II) can be sorbed by some of the reported low-cost adsorbents such as inorganic materials (including zeolites, clay minerals, puzzolanes, iron oxides); industrial wastes generated as by-products (such as lignin, iron (III)hydroxide and red mud); low-rank coal lignite, fly ash and coal; agricultural wastes – natural/chemically modified (such as rice bran, rice husk, wheat bran,

Table 2.7 Adsorptive removal of mercury using synthesized adsorbents

Adsorbent used	Efficiency of the adsorbent	References
Aluminosilicate sieve from fly ash	20 mg/g	Liu et al. (2013)
Activated sludge treated with NaOH	19.3 mg/g	Geetha et al.(2013)
Egyptian mandarin peel	34.8 mg/g	Husein (2013)
Coal ash	90%	Abdelhadi et al. (2011)
Sewage sludge activated with $ZnCl_2$	137.2 mg/g	Otero et al. (2009)
Activated carbon	138 mg/g	McKay et al. (1985)
Polymerization of calix	74.2 mg/g	Tabacki and Yilmaz (2008)
Chitosan immobilized in polyvinyl alcohol	1895.7 mg/g	Son et al. (2004)
2-Mercaptobenzothiazole-treated clay	2.7 mg/g	Dias et al. (1995)
Mesoporous silica-coated magnetic particles	14 mg/g	Dong et al. (2008)
Dithiocarbamate-anchored polymer/ organosmectite composites	157 mg/g	Say et al. (2008)
Polymer/organosmectite composites	214 mg/g	Say et al. (2008)
Fe(III)/Cr(III) waste industrial product	37.3 mg/g	Namasivayam and Senthilkumar (1997)
Activated carbon from fertilizer slurry	560 mg/g	Srivastava et al. (1989)
Chitosan-coated magnetite	99%	Rahbar et al. (2014)
PPN-6 functionalized polymer	99%	Li et al. (2014)
Cation-exchange resin of carboxyl banana	90.8 mg/g	Anirudhan et al. (2002)
Chemically treated sawdust (*Acacia arabica*)	20.6 mg/g	Meena et al. (2008)
Polyacrylamide grafted on banana stalk	138 mg/g	Shibi and Anirudhan (2002)
Used tyre rubber	14.6 mg/g	Meng et al. (1998)
Bicarbonate-treated peanut hull carbon	109.8 mg/g	Namasivayam and Periasamy (1993)
Formaldehyde polymerized sawdust	38.8 mg/g	Raji and Anirudhan (1996)
Photofilm industrial waste sludge	11.7 mg/g	Selvaraj et al.(1998)
From furfural	174 mg/g	Yardim et al. (2003)

wheat husk, sawdust of various plants, bark of the trees, groundnut, hazelnut and coconut shells, cottonseed hulls, waste tea leaves, maize corncob, sugarcane bagasse, apple, banana and orange peels, soybean hulls, grape stalks, sunflower stalks and coffee beans); and activated carbon (AC) prepared from waste materials (agriculture and wood industry, industrial activities and municipal waste). AC is an efficient adsorbent to remove many pollutants from aqueous solutions, but its large-scale production is limited by high production costs. Anoop and Anirudhan (2002) states the removal of mercury (II) from aqueous solutions and chlor-alkali industry effluent by steam activated and sulphurised activated carbons prepared from bagasse pith. Chemically modified wastes enhance the adsorption of heavy metal ions, but at the same time, the cost of the chemicals used in the treatments may increase the cost of the low-cost adsorbents. The use of low-cost adsorbents for heavy metal removal from solution was reviewed by Babel and Kurniawan (2003a, b),

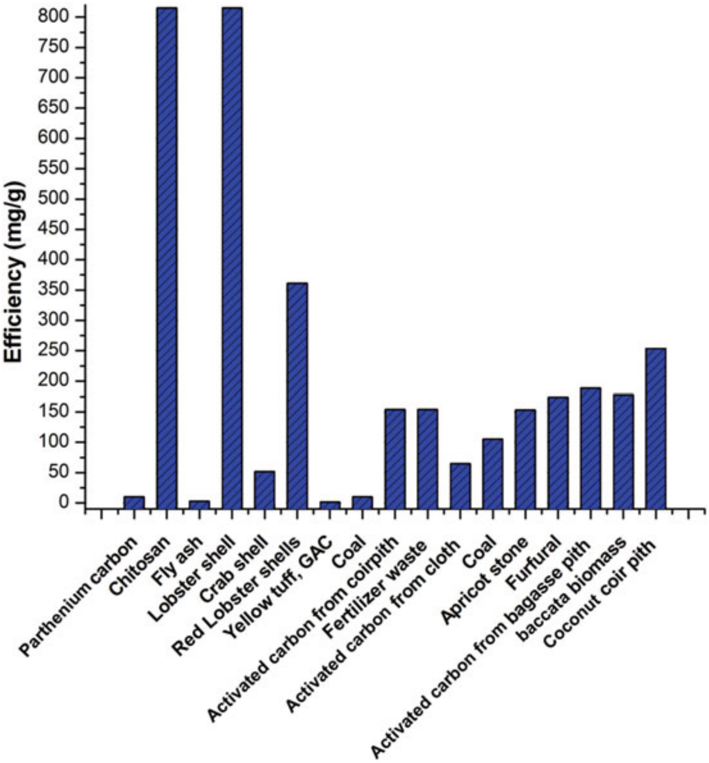

Fig. 2.9 Adsorptive removal of mercury that shows maximum removal efficiency by chitosan and lobster shell. [*Parthenium* carbon (Kadirvelu et al. 2001); chitosan (McKay et al. 1989); fly ash (Sen and Arnab 1987); Lobster shell (Nadeem et al. 2009); crab shell (Peniche Covas et al. 1992); red lobster shells (Taboada et al. 2001); char pozzolana yellow tuff GAC (Di Natale et al. 2006); coal (Karthikeyan and Chaudhuri 1986); activated carbon from coir pith (Namasivayam and Sangeetha 2006); activated carbon from fertilizer waste (Mohan et al. 2001); activated carbon from cloth (Babic et al. 2002); activated carbon from biomass and coal – coals apricot stones furfural (Ekinci et al. 2002); activated carbon from bagasse pith (Krishnan and Anirudhan 2002); marine macroalga *Cystoseira baccata* biomass (Herrero et al. 2005); polyacrylamide-grafted coconut coir pith (Anirudhan and Unnithan 2007; Anirudhan et al. 2008)]

the use of waste materials for activated carbon preparation by Dias et al. (2011), the use of chemically modified plant wastes as adsorbents by Wan Ngah and Hanafiah (2008) and the use of agricultural waste material by Sud et al. (2008).

2.3.4 Adsorbents Used for Removal of Cadmium

The conventional techniques for remediation of cadmium in water have some inherent limitations, such as low efficiency, sensitive operation conditions, production of secondary sludge and costly for their disposal. Thus, numerous adsorbents have been used for the removal of cadmium from water. Balkaya and Cesur (2008) and Ngah and Hanafiah (2008) have reported many low-cost adsorbents obtained from plants for the removal of cadmium. The chemical treatment of these adsorbents has been widely discussed. Chemically modified plant wastes were found to have higher adsorption capacities than unmodified forms possibly due to a higher number of active binding sites, better ion-exchange properties and formation of new functional groups. The modification of rice husk with sodium hydroxide results in an almost double of adsorption. Özer et al. (1999) found that wheat bran had a much higher surface area when treated with sulphuric acid. Hence, the adsorption capacity of wheat brans changed by increasing the conversion of macropores to micropores.

According to Ngah and Hanafiah (2008), the highest adsorption capacity for cadmium was observed to be 313 mg/g using triethylenediamine-treated sugarcane bagasse. The adsorbent consists of increased nucleophilic sites (amide groups) due to chemical modification by triethylenetetramine. The amide group is a result of the chemical reaction between the carboxylic acid group (which was originally the hydroxyl group in sugarcane and converted to carboxylic group by using succinic anhydride) and an amine group. Pretreating sugarcane bagasse with methanol instead of triethylenediamine did not show a good adsorption of cadmium, since methanol acts as an extracting agent for the phenolic groups found in the sugarcane bagasse which means less binding sites, although Ibrahim et al. (2006) considered methanol as a washing agent only.

Activated carbon prepared from various raw materials with high carbonaceous materials including wood, sawdust, coconut shell, coir pith, bone char, nut shells, almond shells, and peanut husks (Rao et al. 2009; Cheung et al. 2001; Ricordel et al. 2001; Ferro-Garcia et al. 1988), has been used for the removal of Cd(II). The activation of carbon can be achieved by thermal decomposition in a high-temperature oxidation or low-temperature chemical dehydration reaction. The adsorption capacity of activated carbon was improved by treating with sulphur (Gomez-serrano et al. 1998), sulphur dioxide (Macías-García et al. 2003), surfactant (Nadeem et al. 2009) or electrochemical oxidation (Rangel-Mendez et al. 2000). Activation was also carried out using $ZnCl_2$ (Kula et al. 2008). The studies revealed that the adsorption occurred through a film diffusion mechanism and the adsorption efficiency for cadmium is higher than that of zinc.

For adsorptive removal of cadmium, agricultural wastes, industrial wastes, low-grade ores, clays and low-cost synthetic oxides/hydroxides such as iron/manganese/aluminium have been used. Some of the low-cost adsorbents with high loading capacities of more than 90 mg/g that have been used for remediation of cadmium are mesoporous silica, mesoporous silicate, broad bean peel, fig leaves, kraft lignin, *Platanus orientalis,* rice husk, modified sugarcane bagasse, modified wheat bran and baker's yeast. Karnitz et al. (2006) show adsorption of metal ions from aqueous single metal solution by chemically modified sugarcane bagasse.

Hydrogels have the capacity to expand their volumes due to their high swelling in water. Hence, they are widely used in the purification of wastewater. Kesenci et al. (2002) prepared poly(ethyleneglycol dimethacrylate-coacrylamide) hydrogel beads with adsorption efficiencies of heavy metals in the order Pb(II) $>$ Cd(II) $>$ Hg(II).

The metal ion removal is governed by the water diffusion into the hydrogel carrying the heavy metals inside, especially in the absence of strong binding sites. The maximum binding capacity increases with an increase in pH to more than 6. The observed adsorption capacities for the adsorption of cadmium using various sorbents are summarized in Tables 2.8 and 2.9, respectively.

The adsorption behaviour of hazelnut shell and hazelnut shell ash as a function of equilibrium time depends on the amount of adsorbent, concentration, pH and

Table 2.8 Adsorptive removal of cadmium using natural adsorbents

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Luffa cylindrica	100 mg/L	6.7 mg/g		Shahidi et al. (2015)
Chromite mine overburden		22.4 mg/g		Mohapatra and Anand (2007a) and Mohapatra et al. (2009c)
Treated fly ash		14.3 mg/g	XRD EDAX	Chaiyasith et al. (2006)
Iron ore slime		34.7 mg/g		Mohapatra and Anand (2007b)
Manganese nodule residue	100 mg/L	47.6 mg/g		Agarwal and Sahu (2006)
Sugarcane bagasse modified with sodium bicarbonate		189 mg /g	AAS ICP/AES	Ngah and Hanafiah (2008)
Sugarcane bagasse modified with ethylenediamine		313 mg/g	Elemental Analysis FT-IR	Junior et al. (2006)
Sugarcane bagasse modified with methanol		6.7 mg/g	FT-IR	Ibrahim et al. (2006)
Triethylenetetramine m ethanol		7 mg/g	XRD ICP/AES	Ngah and Hanafiah (2008)
Lime-preconditioned phosphogypsum	50 mg/L	132 mg/g	AAS	Balkaya and Cesur (2008)
Aluminium oxide	30 mg/L	127 mg /g	AAS BET-SA	Minamisawa et al. (2005)
Nanoscale diboron/ titanium dioxide	0.1 mg/L	> 95%	ASV	Kalfa et al. (2009)
TiO_2-SiO_2	5 mg/L	≈100%	BET-SA GF-AAS	Ismail et al. (2008)
Amino functional mesoporous silica	100 mg/L	<80%	AAS FT-IR	Aguado et al. (2009)
Humic acid-coated Fe_3O_4 nanoparticles	≈1 mg/L	>91%	AAS	Liu et al. (2008)
ZrPS-001	45 mg/L	~87%	ICP/AE Titration	Zhang et al. (2008)

Table 2.9 Adsorptive removal of cadmium using synthesized/modified adsorbents

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Chitosan	1000 mg/L	153 mg/g	XRD, FT-IR	Seyedi et al. (2013)
Agricultural waste	125 mg/L	3.9 mg/g		Ali et al. (2013)
Aluminosilicates	*NA*	57.9 mg/g		Rangel et al. (2006)
Calcite	500 μg/L	18.5 mg/g	XRD FT-IR	Yavuz et al. (2000)
Chemically treated clay		12.6 mg/g	XRD FT-IR	Samir (2010)
Low-grade manganese ore	100 mg/L	59.1 mg/g	TEM FT-IR AAS	Mohapatra et al. (2010)
Nalco plant seed	100 mg/L	58.1 mg/g	AAS FT-IR	Mohapatra et al. (2009)
Nickel laterite (high iron)	100 mg/L	13.2 mg/g	AAS FT-IR	Mohapatra and Anand (2007b)
Palygorskite	150 mg/L	4.54 mg/g	AAS	Ayuso and Sanchez (2007)
Perlite		0.64 mg/g		Mathialagan and Viraraghavan (2002)
Red bauxite		38.7 mg/g		Rout et al. (2009)
Sugarcane bagasse		189 mg/g	AAS	Ngah and Hanafiah (2008)
Eucalyptus bark	100 mg/L	15 mg/g	AAS ICP/AES	Ghodbane et al. (2008)
Coffee beans	5 mg/L	>90%	XRD XRF ICP/MS	Minamisawa et al. (2005)
Hazelnut shell ash	30 mg/L	99.1%	AAS	Jamali et al. (2009)
A. rubescens biomass	10 mg/L	97%	HPLC HG-AAS	Sari and Tuzen (2008)
Montmorillonite, kaolin, tobermorite	1–100 mg/L	>80%	ASV	Katsumata et al. (2003)
Red mud	0.002 M	13.0 mg/g	XRD XRF	Gupta and Sharma (2002)
Silica mesoporous		111.3 mg/g	AAS	Ilhan et al. (2004)
Nitric acid-modified corncob		19.3 mg/g	XRD	Ramos et al. (2005)
Sodium hydroxide-modified rice husk		20.24 mg/g	AAS XRD XRF	Kumar and Bandyopadhyay (2006)
Modified cassava tuber bark waste		26.3 mg/g	XRD XRF	Horsfall Jr. et al. (2006)
Sawdust of *Pinus sylvestris*		19.0 mg/g		Costodes et al. (2003)

(continued)

Table 2.9 (continued)

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Sugar beet pulp		17.2 mg/g		Zacaria et al. (2002)
Teak leaf powder	100 mg/L	86.7%	FT-IR SEM	Rao et al. (2010)

Note: *AAS* atomic absorption spectroscopy, *FT-IR* Fourier Transform-InfraRed, *SEM* scanning electron microscopy, *EDAX* energy dispersive X-ray analysis, *XRD* X-ray diffraction, *ICP-OES* inductively coupled plasma-optical emission spectrometry, *TEM* transmission electron microscopy, *BET-SSA* Brunauer-Emmett-Teller-specific surface area, *GF/AAS* graphite furnace-atomic absorption spectroscopy, *HPLC* high-performance liquid chromatography, *DSC* differential scanning calorimetry, *XRFS* X-ray fluorescence

sorbent particle size using batch system (Jamali et al. 2009). An increase in adsorption efficiency was observed with the increase in pH of the solution. But beyond pH 6, the adsorption efficiency decreased. The maximum adsorption efficiency of 98.2% for hazelnut shell and 99.1% for hazelnut shell ash was attained at pH 6 within a contact time of 3 hours and from an initial concentration of 30 mg/L.

The sorption characteristics of cadmium onto palygorskite as a function of contact time of 0.5–48 h, initial cadmium concentration (5–150 mg/L or 0.044–1.34 mmol/L), ionic strength ([Ca(II)]: 0–0.1 mol/L), pH 3–7 and adsorbent dose of 1–20 g/L were investigated by Ayuso et al. (2007). The equilibrium was attained within 30 min of interaction of adsorbent with cadmium. This process is described by the Langmuir model and gave a maximum Cd sorption of 4.54 mg/g. The sorption decreased with a decrease in solution pH especially at proton concentrations similar to those of cadmium at which competition for the silanol groups on the palygorskite surface appeared to be important. High competing electrolyte concentrations also decreased significantly (close to 60%) the amount of sorbed Cd, suggesting a great contribution of the replacement of exchange cations in this metal removal by palygorskite. The efficiency of the adsorbent was increased to 85–45% using an adsorbent dose of 20 g/L.

Katsumata et al. (2003) investigated removal of Cd(II), Cr(VI), Cu(II) and Pb (II) (initial concentration 1.0 mg/L) from wastewater using montmorillonite, kaolin, tobermorite, magnetite, silica gel and alumina by the column method. The adsorption efficiency of cadmium increased with increase in solution pH. A high removal efficiency of more than 80% was obtained from an initial concentration range of 1–100 mg/L of metal ion. However, with increasing concentration of cadmium ions at more than 100 mg/L, the adsorption efficiency gradually decreased.

Sari and Tuzen (2008) studied the adsorption of cadmium and lead ions using *A. rubescens* biomass from aqueous solution. The sorption capacity for cadmium was observed to be 27.3 mg/g at pH 5 within a contact time of 30 min at 20 °C. With an increase in pH from 2 to 4, the sorption efficiency increased from 35 to 70% for cadmium ions. However, the maximum sorption was found to be 97% at pH 5. Thermodynamic calculations showed that the nature of the sorption of the metal ion was exothermic and spontaneous.

Aguado et al. (2008) used modified oxide sorbent (bound or coated) to remove cadmium ions. Mesoporous silica was functionalized with organic chains containing one, two or three amino groups. The results show that the adsorbent prepared by co-condensation had a negligible metal adsorption capacity, whereas amine-grafted materials adsorb significant amounts ranging from 30 to around 75% of Cd(II) from an initial aqueous solution of 100 mg/L, depending on the amino functional groups present on the sorbent.

2.3.5 Adsorbents Used for Removal of Lead

Lead is introduced to the environment as a consequence of many human activities, such as lead paint production (Mielke 1993), mining (Cotter-Howels and Thornton 1991) and production of agricultural fertilizers, insecticides and pesticides (Ma et al. 1995). Studies have shown that there is a strong correlation between chronic lead exposure to children and impaired cognitive skills (Tong 1998), intellectual impairment, reduced IQ and mental retardation (Nevin 2009). Thus, removal of lead from water and soil will have positive and beneficial implications on the ecosystem, global economy, agriculture and health. Currently, many technologies such as phytoremediation (extraction, stabilization and volatilization) have emerged for the removal of lead from soil (Lone et al. 2008; Chane 1997). The observed adsorption capacities for the adsorption of lead using various sorbents are summarized in Table 2.10.

Annadurai et al. (2002) and Tarley and Arruda (2003) report that the use of some agricultural products, such as sugarcane bagasse, rice husks and coconut husks, has gained attention as biosorbents due to their economic viability and abundance availability from renewable sources.

Transmission electron micrographs of lyophilized *B. longum* 46 and *L. fermentum* ME3 before and after lead binding show the presence of lead on the surface of both strains after binding. Small deposits of lead were also visible inside the bacteria. These deposits were transferred from the bacterial surface during the sample preparation for electron microscopy. Transmission electron micrographs established that lead binding occurred at the surface of the bacterial cells.

Giraldo (2008) and Moreno-Pirajan et al. (2008) used activated carbon from sawdust (ACS) for the removal of lead. The adsorbent showed a sorption capacity of 17.5 mg/g at an initial concentration of 10–100 mg/L. The adsorption efficiency of industrial waste (sludge from blast furnace) investigated by Lopez et al. (1998) shows a sorption capacity of 79.8 mg/g. Vassileva et al. (1996) showed a maximum metal sorption capacity of 10 mg/g at a concentration range of 0.001 to 0.02 mg/L using ceria (CeO_2). Magnetic γ –Fe_2O_3 nanoparticles studied by White et al. (2009) show an adsorption capacity of 15 ± 3 mg/g from a dilute solution of 1 mg/L of metal ion. On the other hand, nanosized magnetite was studied by Yavuz et al. (2000). It shows an adsorption efficiency of more than 90% that forms a dilute solution of 0.1 mg/L. The active sites on adsorption media may show charge over

Table 2.10 Adsorptive removal of lead using natural adsorbents

Adsorbent used	Initial concentration	Efficiency of the adsorbent	References
Activated carbon	200 mg/L	584 mg/g	Yarkandi (2014)
Bentonite	200 mg/L	559 mg/g	Yarkandi (2014)
Instant coffee (IC-S)	211 mg/ L	83.5%	Agwaramgbo et al. (2013)
Coffee bean (CB-S)	225 mg/L	82.4%	Agwaramgbo et al. (2013)
Alginate-SBA-15	200 mg/L	222.2 mg/g	Cheraghali et al. (2013)
Alginate of calcium beads		58.0 mg/g	Zhang et al. (2013)
Tea (tea-S)	44 mg/L	97%	Agwaramgbo et al. (2013)
Fish bone (FB-S)	298 mg/L	77%	Agwaramgbo et al. (2013)
Caffeine (CAF-S)	1263 mg/L	1%	Agwaramgbo et al. (2013)
F. vesiculosus	1–100 mg/L	468.2 mg/g	KatsuMata (2003)
Peach and apricot stones	10 mg/L	93%	Rashed (2006)
Hazelnut shell	1 mM	28.1 mg/g	Pehlivan et al. (2009)
Almond shell	0.1 mM	8.0 mg/g	Pehlivan et al. (2009)
Modified sugarcane bagasse		52.6 mg/g	Dos Santos et al. (2010)
B. lactis Bb12	1.0 mg/L	111 mg/g	Teemu et al. (2008)
B. longum 2C	1.0 mg/L	47 mg/g	Teemu et al. (2008)
B. longum 46	0.10–1.0 mg/L	176 mg/g	Teemu et al. (2008)
L. casei shirota	0.10–1.0 mg/L	98 mg/g	Teemu et al. (2008)
L. fermentum ME3	0.10–1.0 mg/L	136 mg/g	Teemu et al. (2008)
L. rhamnosus GG	1.0 mg/L	107 mg/g	Teemu et al. (2008)
Granular-activated carbon		26.5 mg/g	Dwivedi et al. (2008)
Activated carbon from African palm pit (ACP)		15.2 mg/g	Giraldo and Moreno-Pirajan (2008)
Activated carbon from sugar-cane bagasse (ACB)		13.7 mg/g	Giraldo and Moreno-Pirajan (2008)
Olive stone		5.8 mg/g	Calero et al. (2009)
Activated carbon from coconut (CA)	100 mg/L	4.3 mg/g	Gueu et al. (2007)
Activated carbon from palm tree (GA)	100 mg/L	3.7 mg/g	Gueu et al. (2007)
Tunisian smectite-rich clay		41%	Chaari et al. (2008)
Activated-waste mud (a-WM)	235 ppm	82%	Ozdes et al. (2009)
Zeolite clinoptilolite		1.6 mg/g	Babel and Kurniawan (2003a, b)
Modified zeolite MMZ		123 mg/g	Nah et al. (2006)

(continued)

Table 2.10 (continued)

Adsorbent used	Initial concentration	Efficiency of the adsorbent	References
Clay/poly(methoxyethyl) acrylamide		81 mg/g	Sölenera et al. (2008)
Clay/poly(methoxyethyl) acrylamide		85.6 mg/g	Aklil et al. (2004)
Maize cope and husk		456 mg/g	Igwe et al. (2005)
Ecklonia maxima – marine algae		235 mg/g	Fenga and Aldrich (2004)
Oedogonium species		145 mg/g	Gupta and Rastogi (2008)
ZrPS-001	80 mg/L	>99%	Zhang et al. (2008)

certain pH ranges. This implies that charge behaviour of the contaminant and the adsorbent are equally important to determine the required pH adjustment for the selected treatment application. The adsorbent is selected depending on the oxidation state of the metal ion. The adsorption efficiency of some good adsorbents has been depicted in Fig. 2.10.

Activated coconut shell carbon powder (ACSCP) and activated charcoal powder (ACP) are used as adsorbent for the removal of lead from electrochemical industry effluent as shown by Nishigandha et al. (2015). Baari et al. (2008) studied the removal of Pb(II) using Tunisian smectite-rich clay (sampled in Jebel Aïdoudi in El Hammaarea (meridional Atlas of Tunisia)) in aqueous solution. Four smectite clay samples, untreated clay (UC), hydrochloric activated clay (HAC), sulphuric-activated clay (SAC) and thermic-activated clay (TAC), were used. HAC and SAC samples enhanced the adsorption capacity under the same conditions compared to the untreated clay minerals due to the increased surface area. The removal of Pb(II) by SAC was observed to be very high when compared to HAC because clay minerals are more soluble in sulphuric acid than hydrochloric acid. HAC and SAC removed as much as 50.1 and 65.1% of Pb(II), respectively, whereas UC could remove only 41.3%. The removal of lead by the TAC sample calcined at 100 °C was 54.2%, but the efficiency decreased with increase in temperature. A comparative study between activated carbon and SAC showed that the adsorption capacity of SAC was better than that for activated carbon.

2.3.6 *Adsorbents Used for Removal of Zinc*

The adsorption for the removal of Zn^{2+} includes the use of natural materials such as bagasse, moss, bentonite and mixed mineral; microbial and algal biomass including seaweed, yeast, fungi and bacteria; and industrial and agricultural wastes such as

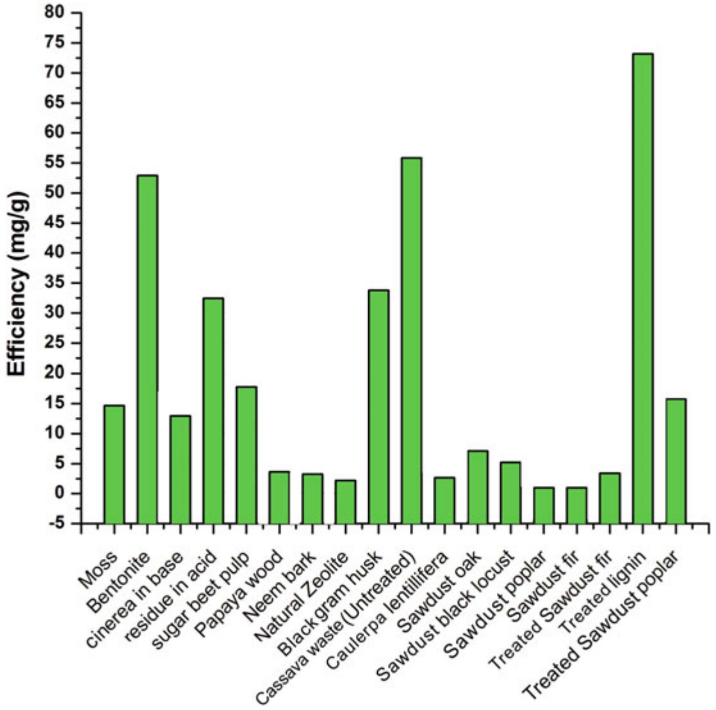

Fig. 2.10 Some adsorbents that show good efficiency of lead removal using treated lignin [Moss (Martins et al. 2004); bentonite (Mellah and Chegrouche 1997); *Botrytis cinerea* (Tunali and Akar 2006); sea nodule residue in acid (Agrawal et al. 2004); sugar beet pulp (Reddad et al. 2002); papaya wood (Saeed et al. 2005a, b); neem bark (Bhattacharya et al. 2006); natural zeolite (Motsi et al. 2009); black gram husk (Saeed et al. 2005); cassava waste (untreated) (Horsfall et al. 2003); *Caulerpa lentillifera* (Pavasant et al. 2006); sawdust oak, sawdust black locust, sawdust poplar, sawdust fir and NaOH-treated sawdust fir (Sciban et al. 2006a, b); HCl + ether + benzene-treated lignin (Srivastava et al. 1994); NaOH-treated sawdust poplar (Sciban et al. 2006a, b)]

corncobs, peanut hulls, hazelnut shells, corn starch, waste tea leaves, sea nodule residue, blast furnace slag, sugar beet pulp, lignite, lignin and powdered waste sludge as listed in Table 2.11. The chemical modification of plant wastes poses several problems such as low adsorption capacity, high chemical oxygen demand (COD), biological chemical demand (BOD) and total organic carbon (TOC) due to the release of soluble organic compounds contained in the plant materials. The increase of the COD, BOD and TOC can cause depletion of the oxygen content in water and can threaten the aquatic life. Thus, according to Gaballah et al. (1997), plant wastes need to be chemically treated or modified before being applied for the decontamination of heavy metals. Also pretreatment of plant wastes can extract soluble organic compounds and enhance the chelating efficiency.

Babel and Kurniawan (2003a, b) state that numerous studies have so far been discussing the importance of low-cost adsorbents in water pollution control, many of them are generally either adsorbate specific (metals, dyes and phenols) or

Table 2.11 Adsorptive removal of zinc using synthesized adsorbents

Adsorbent used	Efficiency of the adsorbent	References
Zero-valent irons	10^{-5} M	Suponik et al. (2015)
Sawdust	90%	Pragati et al. (2015)
Powdered waste sludge	128.8 mg/g	Zwain et al. (2014)
Clarified sludge	168 mg/g	Zwain et al. (2014)
Rice husk ash + coal fly ash + palm oil fuel ash	16.9 mg/g	Zwain and Dahlan (2012)
Dried marine green macroalgae	15.5 mg/g	Saeed et al. (2005)
Sea nodule residue in acid	32.4 mg/g	Agrawal et al. (2004)
H_2O_2-modified powdered waste sludge	168 mg/g	Kargi and Cikla (2006)
Waste-activated sludge	36.9 mg/g	Norton et al. (2004)
Activated alumina	13.6 mg/g	Bhattacharya et al. (2006)
Acid-treated saltbush leaves	32.7 mg/g	Sawalha et al. (2007)
Coal fly ash	6.5–13.3 mg/g	Mohan and Singh (2002)
Fe impregnated fly ash ($FeCl_3$ 30°–60°)	7.5–15.5 mg/g	Banerjee et al. (2003)
Al impregnated fly ash (($Al(NO_3)_2$ 30°–60°)	7.0–15.4 mg/g	Banerjee et al. (2003)
Cassava waste (thioglycolic acid + nitric acid)	559.7 mg/g	Horsfall and Abia (2003)
Acid-modified bagasse	31.1 mg/g	Mohan and Singh (2002)
Formaldehyde-treated sawdust oak	6.1 mg/g	Sciban et al. (2006a, b)
Formaldehyde + NaOH-treated sawdust oak	9.3 mg/g	Sciban et al. (2006a, b)
Formaldehyde-treated sawdust black locust	5.3 mg/g	Sciban et al. (2006a, b)
HCHO + NaOH-treated sawdust black locust	9.0 mg/g	Sciban et al. (2006a, b)

adsorbent specific. Hence, different forms of inexpensive and nonliving plant material have been studied as potential adsorbent, such as black gram husk by Saeed et al. (2005) as shown in Fig. 2.9, eggshell by Park et al. (2007), sugar beet pectin gels by Mata et al. (2009) and citrus peels by Schiewer and Patil (2008).

Adsorption of divalent heavy metal ions, particularly Cu^{+2}, Zn^{+2}, Co^{+2}, Ni^{+2} and Pb^{+2} onto acid- and alkali-treated banana and orange peels was performed by Annadurai et al. (2003). Residues of banana and orange peels are cellulose-based wastes. Hence, they can be processed and converted to be adsorbents, because they have a large surface area, high swelling capacity and excellent mechanical strength. Thus, they are convenient to use and have great potential to adsorb harmful contaminants such as heavy metals. In addition, the acid and alkali solutions used for modification of adsorbents were HNO_3 and NaOH. Generally, the adsorption capacity decreases in the order of $Pb^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+}$ for both adsorbents. Banana peel exhibits a higher maximum adsorption capacity for heavy metals compared to orange peel. The reported maximum adsorption capacities can be summarized as follows: 7.97 (Pb^{2+}), 6.88 (Ni^{2+}), 5.80 (Zn^{2+}), 4.75 (Cu^{2+}) and 2.0 (Co^{2+}) mg/g using banana peel and 7.75 (Pb^{2+}), 6.01 (Ni^{2+}), 5.25 (Zn^{2+}), 3.65 (Cu^{2+}) and 1.82 (Co^{2+}) mg/g using orange peel, respectively. Acid-treated peels showed better adsorption capacities followed by alkali- and water-treated peels. Based on regeneration studies, it was reported that the peels could be used for two regenerations of heavy metal ions removal and recovery.

Rice husk pretreatment can remove hemicellulose, and lignin reduces the cellulose crystallinity and increases the surface area or porosity. In general, unmodified rice husk showed lower adsorption capacities on heavy metal ions than untreated or chemically modified rice husk. It was reported by Kumar and Bandyopadhyay (2006) that rice husk treated with sodium carbonate, sodium hydroxide and epichlorohydrin enhanced the adsorption capacity of heavy metals. Also it was reported that adsorption properties by the base treatment (NaOH) remove base soluble materials from the rice husk surface. Bhattacharya et al. (2006) studied pretreated rice husk ash for the removal of Zn^{2+}. An efficiency of 96.8% of Zn^{2+} removal was obtained at pH 5. The Langmuir and Freundlich adsorption isotherm models were used to represent the experimental data, wherein both models fitted well. The adsorption capacity was obtained as 14.3 mg/g at optimum pH 5.0.

In another study by Montanher et al. (2005), rice bran was evaluated for its potential use as an adsorbent for Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}. Rice bran adsorbent is able to successfully adsorb the metal ions from aqueous solutions. Maximum efficiency of 72% for Zn^{2+} removal was observed in chloride medium, and 0.1 mol/L NaCl has been used throughout the work. The experimental data were well fitted to the Freundlich equation with good correlation coefficients.

2.4 Conclusion

This chapter shows that adsorption is a very promising and effective technology as a remediation to toxic metals present in groundwater. The technology involves the use of various adsorbents, including natural and chemical/synthesized ones that have effectively removed heavy metals from water. Besides the operating parameters of removal of heavy metal ions from water, the increasing costs and environmental considerations have in recent years led to the use of new low-cost adsorbents derived from renewable resources. Chemical modification of different wastes increases the adsorption capacity, but the technology cost and side pollution must be taken in consideration in order to produce real “low-cost” adsorbents.

The metal ions are attracted and bound to the sorbent due to high affinity through a complex process that depends on ion-exchange chemisorption, complexation, adsorption on the surface and pores, chelation and adsorption by physical forces due to a concentration gradient and diffusion through the biosorbent material. The presence of competitive cations and chelators reduces the metal removal capacity of an adsorbent due to which some adsorbents may show poor adsorption capacity, low efficiency/cost ratio and ineffectiveness for high or very low metal concentration. On the other hand, a decrease in sorbent particle size leads to an increase in the sorption of metal ions. This is overcome by chemical modification of the adsorbent that improves the adsorption capacity of adsorbents due to an increased number of active binding sites, better ion-exchange properties and formation of new functional groups. The initial metal ion concentration, initial solution temperature, solution pH, flow rate, sorbent mass and contact time are known to affect the metal removal efficiency from water. The operating temperature changes the rate of molecular interactions and solubility.

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