Review

Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water

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Abstract

Hexavalent chromium is a well-known highly toxic metal, considered a priority pollutant. Industrial sources of Cr(VI) include leather tanning, cooling tower blowdown, plating, electroplating, anodizing baths, rinse waters, etc. The most common method applied for chromate control is reduction of Cr(VI) to its trivalent form in acid (pH $\sim$ 2.0) and subsequent hydroxide precipitation of Cr(III) by increasing the pH to $\sim$9.0–10.0 using lime. Existing overviews of chromium removal only cover selected technologies that have traditionally been used in chromium removal. Far less attention has been paid to adsorption. Herein, we provide the first review article that provides readers an overview of the sorption capacities of commercial developed carbons and other low cost sorbents for chromium remediation.

After an overview of chromium contamination is provided, more than 300 papers on chromium remediation using adsorption are discussed to provide recent information about the most widely used adsorbents applied for chromium remediation. Efforts to establish the adsorption mechanisms of Cr(III) and Cr(VI) on various adsorbents are reviewed. Chromium's impact environmental quality, sources of chromium pollution and toxicological/health effects is also briefly introduced. Interpretations of the surface interactions are offered. Particular attention is paid to comparing the sorption efficiency and capacities of commercially available activated carbons to other low cost alternatives, including an extensive table.
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Contents

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1. Introduction

Chromium was discovered in 1797 by the French chemist Louis Vauquelin. It was named chromium (Greek chroma, "color") because of the many different colors found in its compounds. Chromium is the earth's 21st most abundant element (about 122 ppm) and the sixth most abundant transition metal. The principal chromium ore is ferric chromite, $FeCr_2O_4$, found mainly in South Africa (with 96% of the world's reserves), Russia and the Philippines. Less common sources include crocoite, $PbCrO_4$, and chrome ochre, Cr_2O_3. The gemstones emerald and ruby owe their colors to traces of chromium.

Chromium occurs in 2+, 3+ and 6+ oxidation states but Cr^{2+} is unstable and very little is known about its hydrolysis. The hydrolysis of Cr(III) is complicated. It produces mononuclear species $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_4^-$, neutral species $Cr(OH)_3^0$ and polynuclear species $Cr_2(OH)_2$ and $Cr_3(OH)_4^{5+}$ [1–3]. The hydrolysis of Cr^{6+} produces only neutral and anionic species, predominately CrO_4^{2-}, $HCrO_4^{2-}$, $Cr_2O_7^{2-}$ [2,3]. At low pH and high chromium concentrations, $Cr_2O_7^{2-}$ predominates while at a pH greater than 6.5, Cr(IV) exists in the form of CrO_4^{2-} [2]. Cr(III) is classified as a hard acid and forms relatively strong complexes with oxygen and donor ligands. Chromium(VI) compounds are more toxic than Cr(III) due to their high water solubility and mobility. On the other hand, trivalent chromium is insoluble and thus immobile under ambient conditions. The most soluble, mobile and toxic forms of hexavalent chromium in soils are chromate and dichromate. The hexavalent form is rapidly reduced to trivalent chromium under aerobic conditions [4]. Insoluble trivalent hydroxides and oxides form which cannot leach.

Chromium has both beneficial and detrimental properties. Chromium(III) is an essential trace element in mammalian metabolism. In addition to insulin, it is responsible for reducing blood glucose levels, and is used to control certain cases of diabetes. It has also been found to reduce blood cholesterol levels by diminishing the concentration of (bad) low density lipoproteins "LDLs" in the blood. Cr(III) is supplied in a variety of
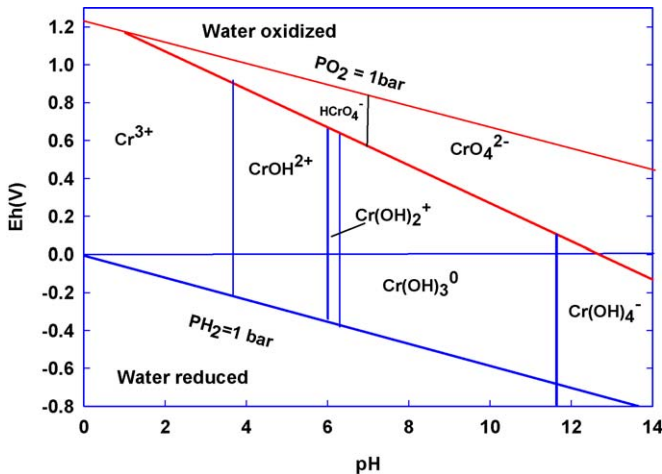
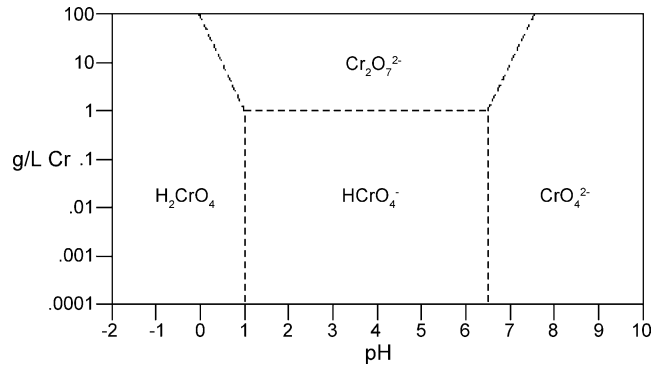Fig. 1. Eh–pH diagram for chromium. *Source*: Palmer and Puls [309].

Fig. 2. Speciation diagram of Cr(VI). *Source*: Dionex [6].

foods such as Brewer's yeast, liver, cheese, whole grain breads and cereals, and broccoli. Chromium is claimed to aid in muscle development. In fact, dietary supplements containing chromium picolinate (its most soluble form) are very popular with body builders. In contrast, Cr(VI) is hazardous by all exposure routes.

The redox potential Eh–pH diagram (Fig. 1) presents equilibrium data and indicates the different oxidation states and chemical forms which exist within specified Eh and pH ranges. Cr(III) is the most thermodynamically stable oxidation state under reducing conditions (Fig. 1). Cr(VI) can remain stable for significant periods of time. Cr(III) predominates at pH < 3.0. At pH > 3.5, hydrolysis of aqueous Cr(III) yields trivalent chromium hydroxy species [$CrOH^{2+}$, $Cr(OH)^{2+}$, $Cr(OH)_3^0$ and $Cr(OH)_4^-$]. $Cr(OH)_3^0$ is the only solid species, existing as an amorphous precipitate [5]. Hexavalent chromium exists primarily as salts of chromic acid (H_2CrO_4), hydrogen chromate ion ($HCrO_4^-$) and chromate ion (CrO_4^{2-}),

depending on the pH. H_2CrO_4 predominates at pHs less than about 1.0, $HCrO_4^-$ at pHs between 1.0 and 6.0, and CrO_4^{2-} at pHs above about 6.0 (Fig. 2) [6]. The dichromate ion ($Cr_2O_7^{2-}$), a dimer of $HCrO_4^-$, minus a water molecule, forms when the concentration of chromium exceeds approximately 1 g/L.

Acute exposure to Cr(VI) causes nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhage, and respiratory problems [3]. Inhalation may cause acute toxicity, irritation and ulceration of the nasal septum and respiratory sensitization (asthma) [2,3,7]. Ingestion may affect kidney and liver functions. Skin contact may result in systemic poisoning damage or even severe burns, and interference with the healing of cuts or scrapes. If not treated promptly, this may lead to ulceration and severe chronic allergic contact dermatitis. Eye exposure may cause permanent damage. The drinking water guideline recommended by Environmental Protection Agency (EPA) in US is 100 μg/L.

Industrial processes that produce aqueous effluents rich in chromium and other heavy metals are given in Table 1. Chromium compounds are widely used in electroplating, metal finishing, magnetic tapes, pigments, leather tanning, wood pro-

Table 1
Heavy metals in some major industries

Industry source	Al	Zn	As	Sn	Ag	Sb	Cd	Cr	Cu	Fe	Hg	Mn	Pb	Ni	Bi
Automobile		X		X			X	X		X			X	X	
Petroleum refining		X	X					X	X	X			X	X	
Pulp and paper		X						X	X		X		X	X	
Textile								X							
Steel		X	X			X	X	X		X			X	X	
Organic chemicals	X	X	X	X			X	X		X	X		X		
Inorganic chemicals	X	X	X				X	X		X	X		X		
Fertilizer	X	X	X				X	X	X	X	X	X	X	X	
Plastic and synthetics								X							
Leather tanning and finishing								X							
Steel power plants		X						X							
Mining			X				X		X		X	X	X		
Acid mine drainage	X	X							X	X		X			
Metal plating		X					X	X	X						
Glass			X												
Nuclear power															X
Coal and gasoline										X			X		X

Table 2
Global discharges of trace metals (1000 metric tonnes/year) [287]

Metals	Water	Air	Soil
Arsenic	41	19	82
Cadmium	9.4	7.4	22
Chromium	142	30	896
Copper	112	35	954
Lead	138	332	796
Mercury	4.6	3.6	8.3
Nickel	113	56	325
Selenium	41	3.8	41
Tin	ND	6.4	ND
Zinc	226	132	1372

tection, chemical manufacturing, brass, electrical and electronic equipment, catalysis and so on (Table 1) [7]. Contaminants from industrial wastewater rich in heavy metal ions remain an important environmental issue. Although control technologies have been applied to many industrial and municipal sources, the total quantity of these agents released to the environment remains staggering (see Table 2).

Several treatment technologies have been developed to remove chromium from water and wastewater. Common methods include chemical precipitation [8], ion exchange [9–14], membrane separation [15,16], ultrafiltration [17], flotation [18], electrocoagulation [19], solvent extraction [20], sedimentation [21], precipitation [22], electrochemical precipitation [22], soil flushing/washing [22], electrokinetic extraction [22], phytoremediation [22], reduction [23], reverse osmosis [24], dialysis/electrodialysis [25], adsorption/filtration [2,3,26–30], evaporation, cementation, dilution, air stripping, steam stripping, flocculation, and chelation [31]. Chemical precipitation has traditionally been the most used method. The most often used precipitation processes, include hydroxide precipitation, sulfide precipitation, carbonate precipitation and phosphate precipitation. The disadvantage of precipitation is the production of sludge. This constitutes a solid waste a disposal problem. Ion exchange is considered a better alternative. However, it is not economically appealing because of high operational costs.

Most remediation methods more effectively remove chromium from water/wastewater containing relatively high initial chromium concentrations (usually above 100 mg/L). Advantages and disadvantages of various treatment methods are summarized in Table 3 [32]. Adsorption has evolved as the front line of defense for chromium removal. Selective adsorption by biological materials, mineral oxides, activated carbons, or polymer resins has generated increasing excitement [1,26,30,32–39] In general, activated carbons are broadly applied effective adsorbents for wastewater treatment.

The origin of carbon use extends so far back into history that it is impossible to document. Charcoal was first used for drinking water filtration by ancient Hindus in India, and carbonized wood was used as a medical adsorbent and purifying agent by the Egyptians as early as 1500 B.C. [40].

A number of review articles have appeared on activated carbon adsorption, and the use of other low cost adsorbents

[1,33–35]. Allen et al. [34] reviewed the production and characterization of activated carbon from many carbonaceous sources. Characterization by porosimetry, sorptometry, topography, pore size distribution, isotherms, and surface area measurements was reviewed and the specific data from activated carbons derived from lignocellulosic materials (peat and lignite) were also presented. Pollard et al. [33], reviewed low cost alternatives to activated carbon for water/wastewater treatment. Carbon selection criteria and activation methods were discussed [33]. Similar types of review articles later appeared on low cost alternatives to activated carbons [30,32,36]. Davis et al. [37] presented an excellent review of the biochemistry of heavy metal biosorption by brown algae. Gavrilescu [41] discussed the removal of heavy metals by biosorption. Biosorption of heavy metals by fungal biomass and its modeling was also reviewed [39]. Mui et al. [42] reviewed the production of active carbons from waste tires. Kapoor and Viraraghvan [38] reviewed fungal biosorption as an alternate treatment option for heavy metal bearing wastewaters. However, to the best of our knowledge, no review exists of activated carbons or alternative adsorbents used for chromium adsorption from water/wastewater.

Compiling the research on chromium removal by adsorption is important because this topic has advanced significantly. A large number of publications appear every year. Many significant papers published during last two decades are reviewed herein. The term "significant" is, of course, our interpretation with which others may differ. Particular attention has been paid to comparing the sorption efficiency of commercially available activated carbons with other low cost alternatives. An extensive table summarizing the sorption capacities of various activated carbons and/or other adsorbents is included.

2. What is activated carbon?

The basis for modern industrial production of active carbons was established in 1900–1901 to replace bone char in the sugar refining process [43]. Powdered activated carbon was first produced commercially in Europe in the early 19th century, using wood as a raw material. The use of activated carbon for the water treatment in the United States was first reported in 1930, for the elimination of taste and odor from contaminated water [44]. Activated carbon is a crude form of graphite with a random or amorphous structure, which is highly porous, exhibiting a broad range of pore sizes, from visible cracks, crevices and slits of molecular dimensions [45]. Active carbons have been prepared from coconut shells, wood char, lignin, petroleum coke, bone char, peat, sawdust, carbon black, rice hulls, sugar, peach pits, fish, fertilizer waste, waste rubber tire, etc. (Table 4). Wood (130,000 tonnes/year), coal (100,000 tonnes/year), lignite (50,000 tonnes/year), coconut shell (35,000 tonnes/year), and peat (35,000 tonnes/year) are most commonly used [33]. Activated carbons adsorptive properties are due to such factors as surface area, a micro-porous structure, and a high degree of surface reactivity.

The starting material and the activation method used for activated carbon production determine surface functional

Table 3
Advantages and disadvantages of commercial activated carbons, synthetic ion-exchange resins and polysaccharide-based sorbents for solution remediation

Adsorbent	Advantages	Disadvantages

Activated carbon	• The most effective adsorbent
	• Very high surface areas
	• Porous sorbent
	• High capacity and high rate of adsorption
	• Great capacity to adsorb a wide range of pollutants
	• Fast kinetics
	• A high quality-treated effluent is obtained
		• Expensive
		• The higher the quality, the greater the cost
		  • Performance is dependent on the type of carbon used
		  • Requires complexing agents to improve its removal performance
		• Non-selective
		• Problems with hydrophilic substances
		• Ineffective for disperse and vat dyes
		• High reactivation costs
		• Reactivation results in a loss of the carbon

Ion-exchange resin	• Wide range of pore structure and physicochemical characterization • Good surface area • Effective sorbent • Excellent selectivity towards aromatic solutes • Regeneration: no adsorbent loss	• Expensive • Derived from petroleum-based raw materials • Sensitive to particle • Performance is dependent on the type of resin used • Not effective for all dyes • pH-dependence • Poor contact with aqueous pollution • Requires a modification for enhanced the water wetability
Chitosan-based material	• Low cost natural polymer • Environmentally friendly • Extremely cost-effective • Outstanding metal and dye-binding capacities • High efficiency and selectivity in detoxifying both very dilute or concentrated solutions excellent diffusion properties • High quality-treated effluent is obtained • Versatile sorbent • Easy regeneration if required	• Nonporous sorbent • The sorption capacity depends of the origin of the polysaccharide and the degree of N-acetylation • Variability in the bead characteristics • pH-dependence • Requires chemical modification to improve its performance • Low affinity for basic dyes
Starch-based material	• Very abundant natural biopolymer and widely available in many countries • Renewable resource • Economically attractive and feasible • Easy to prepare with relatively inexpensive reagents • A remarkably high swelling capacity in water • Good removal of wide range of pollutants • Important selectivity for different concentrations • Fast kinetics • Amphiphilic crosslinked adsorbent • Applicable to a wide variety of process • Easy regeneration if required	• Low surface area • Requires chemical derivatization to improve its sorption capacities • Variability in the bead characteristics • Its use in sorption columns is limited since the characteristics of the particles introduce hydrodynamic limitations and column fouling

Source: Crini [32], with permission from Elsevier.

groups. Carbon surface chemistry has been studied extensively [1,43,46]. The carbon surface chemistry depends upon the activation conditions and temperatures employed. Activation also refines the pore structure. Mesopores, micropores and ultramicropores are formed yielding large surface areas up to 2000 m^2/g [1,35].

2.1. Activation

During the activation process, the spaces between the elementary crystallites are cleared by removal of less organized loosely bound carbonaceous material. The resulting channels through the graphitic regions, the spaces between the elementary crystallites, together with fissures within and parallel to the graphite planes constitute the porous structure, with a large internal surface area [47]. Two types of activation, thermal/physical or chemical activation, impart a porous structure within a starting material of relatively low surface area.

2.1.1. Physical or thermal activation

Physical or thermal activation involves carbonization at 500–600 °C to eliminate the bulk of the volatile matter followed by partial gasification using mild oxidizing gas such as CO_2, steam or fuel gas at 800–1000 °C to develop the porosity and surface area [35,48].

2.1.2. Chemical activation

Chemical activation involves the incorporation of inorganic additives, metallic chlorides such as zinc chloride or phos-

Table 4
Alternative feedstocks proposed for the preparation of activated carbons [33,35]

Bones	Lampblack
Bagasse	Leather waste
Bark	Municipal waste
Beat-sugar sludges	Molasses
Blood	Nut shells
Blue dust	News paper
Coal	Oil shale
Coffee beans	Olive stones
Coconut shell	Petroleum acid sludge
Coconut coir	Pulp-mill waste
Cereals	Palm tree cobs
Carbohydrates	Petroleum coke
Cottonseed hulls	Petroleum acid sludge
Corn cobs	Potassium ferrocynide residue
Distillery waste	Rubber waste
Fuller's earth	Rice hulls
Fertilizer waste slurry	Refinery waste
Fish	Reffination earth
Fruit pits	Scrap tires
Graphite	Sunflower seeds
Human hairs	Spent Fuller's earth
Jute stick	Tea leaves
Kelp and seaweed	Wheat straw
Lignin	Wood
Lignite	

Table 5
List of low cost adsorbents used in wastewater treatment [33,35]

Bagasse	Red mud
Bagasse fly ash	Rubber waste
Bark	Rice hulls
Coal	Refinery waste
Coconut shell	Scrap tires
Corn cobs	Slag
Clay minerals	Sludge
Fuller's earth	Sunflower seeds
Fertilizer waste slurry	Spent Fuller's earth
Ferrocynides	Tea leaves
Fly ash	Old tires
Lignin	Wheat straw
Lignite	Wood
Lampblack	Wool waste
Leather waste	Zeolites
Olive stones	

phoric acid into the precursor before the carbonization [34]. Carbons with well-developed meso- and microporous structure can be produced by $ZnCl_2$ incorporation. KOH activation successfully increased active carbon surface area and pore volume [49]. Ammonium salts, borates, calcium oxide, ferric and ferrous compounds, manganese dioxide, nickel salts, hydrochloric acid, nitric acid and sulfuric acid have also been used for activation.

The basic differences between physical and chemical activation is the number of stages required for activation and the activation temperature. Chemical activation occurs in one step while physical activation employs two steps, carbonization and activation. Physical activation temperatures (800–1000 °C) are higher than those of chemical activation (200–800 °C).

According to Steenberg's classification [50], acidic and basic activated carbons exist:

(a) Carbon activated at 200–400 °C, called L carbons, generally develop acidic surface oxides and lower solution pH values. They adsorb bases, are hydrophilic, and exhibit a negative zeta potential.

(b) The carbons activated at 800–1000 °C, termed H carbons, develop basic surface oxides and raise solution pH. They adsorb acids and exhibit a positive zeta potential. However, cooling H carbons in contact with air changes the zeta potential to a negative value due to the formation of acidic surface oxides.

The acidic groups on activated carbons adsorb metal ions [51]. The L carbons are stronger solid acids than the H carbons and more efficiently adsorb metal ions. Surface area may not be a primary factor for adsorption on activated carbon. High surface area does not necessarily mean high adsorption capacity [52] due to the following factors:

(a) Only the wetted surface adsorbs ions. The total surface area is seldom wetted.

(b) Sometimes the material to be adsorbed is too large to enter the smallest pores where the bulk of the surface area may exist.

(c) Surface area, pore volume and surface chemistry are not usually correlated with species adsorbed.

The adsorption of metal ions on carbon is more complex than uptake of organic compounds because ionic charges affect removal kinetics from solution. Adsorption capacity depends on activated carbon properties, adsorbate chemical properties, temperature, pH, ionic strength, etc. Many activated carbons are available commercially but few are selective for heavy metals. They are expensive.

Despite carbon's prolific use to treat wastewater, it remains expensive, requiring vast quantities of activated carbon. Improved and tailor-made materials are sought. Substitutes should be easily available, cheap and, above all, be readily regenerated, providing quantitative recovery.

Industrial or agricultural by-products can be converted into activated carbons or low cost adsorbents. Table 5 lists various materials, which have been investigated.

3. Evaluation/comparison of adsorptive properties

Adsorption equilibrium measurements are used to determine the maximum or ultimate adsorption capacity. Six types of adsorption isotherms [35,53] exist including types I–VI. Equilibrium isotherm data are formulated into an adsorption isotherm model.

Feed solution is contacted in stirred vessels with a definite quantity of activated carbon/adsorbent in batch experiments. The important design parameters are calculated from batch adsorption isotherms, which model full-scale batch processes. The most commonly used models include Freundlich, Langmuir, and BET isotherms. The batch adsorption processes are inefficient and capital intensive so column adsorption processes are used commercially.

3.1. Freundlich isotherm

This isotherm developed by Freundlich [54] describes the equilibrium on heterogeneous surfaces and does not assume monolayer capacity.

The Freundlich equation is

$$q_e = K_F C_e^{1/n} \quad \text{(nonlinear form)} \tag{1}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{(linear form)} \tag{2}$$

where q_e is the amount of solute adsorbed per unit weight of activated carbon (mg/g), C_e the equilibrium concentration of solute in the bulk solution (mg/L), K_F a constant indicative of the relative adsorption capacity of the adsorbent (mg/g) and the constant $1/n$ indicates the intensity of the adsorption.

3.2. Langmuir isotherm

The Langmuir adsorption isotherm describes the surface as homogeneous assuming that all the adsorption sites have equal adsorbate affinity and that adsorption at one site does not affect adsorption at an adjacent site [55,56]. The Langmuir equation may be written as

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad \text{(nonlinear form)} \tag{3}$$

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{1}{Q^0} C_e \quad \text{(linear form)} \tag{4}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e the equilibrium concentration of solute in the bulk solution (mg/L), Q^0 the monolayer adsorption capacity (mg/g) and b is the constant related to the free adsorption energy. b is the reciprocal of the concentration at which half saturation of the adsorbent is reached.

3.3. BET isotherm

The BET (Brunauner, Emmett, Teller) isotherm assumes the partitioning of a compound between liquid and solid phases. This isotherm assumes multi-layer adsorption of solute occurs [56,57]:

$$q_e = \frac{BCQ^0}{(C_s - C)[1 + (B - 1)(C/C_s)]} \quad \text{(nonlinear form)} \tag{5}$$
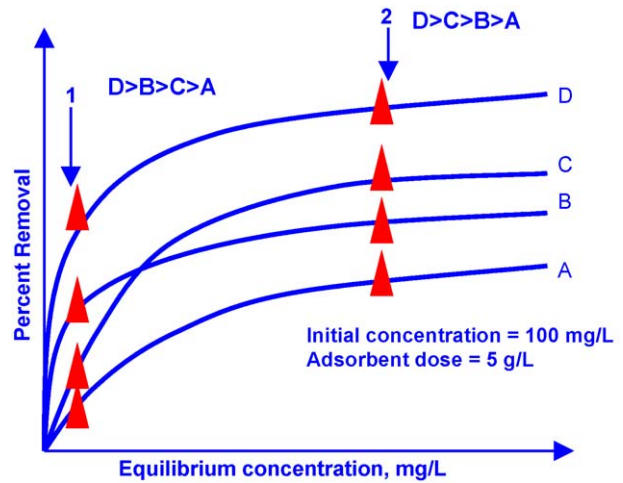
Fig. 3. Comparative evaluation of adsorbents.

$$q_e = \frac{C}{(C_s - C)q_e} = \frac{1}{BQ^0} + \frac{B - 1}{BQ^0} \frac{C}{C_s} \quad \text{(liner form)} \tag{6}$$

where q_e is the amount of adsorbate adsorbed per unit weight of activated carbon, B the constant related to the energy of interaction with the surface, C the equilibrium concentration of adsorbate in solution (mg/L or mol/L), Q^0 the number of moles of adsorbate per unit weight of carbon to form a complete monolayer, and C_s is the saturation concentration of the adsorbate.

Various sorbents have been compared based on percent removal. This is a crude and rather inaccurate misleading approach. Isotherms are always (Langmuir) more accurate than percentage removal to compare two sorbents because isotherms have more experimental points.

Fig. 3 shows four different adsorption experiments. Each curve gives different results depending upon equilibrium concentration where the percent removal was calculated. If the sorption capacities were calculated at point 1, the capacity order is D > B > C > A while at point 2 the order is D > C > B > A. Thus, it is difficult to compare various sorbents in terms of percent removal. Sorption capacity should be calculated in mg/g using sorption models, particularly the Langmuir adsorption model.

Activated carbons, waste materials, industrial by-products, agricultural waste products, biosorbents, etc., have been used for the removal and recovery of chromium [Cr(III) and Cr(VI)] from water/wastewater. For simplicity, in this review article, adsorbents are divided into two classes:

(1) activated carbons;
(2) other low cost adsorbents.

4. Activated carbons

Activated carbons can be further subdivided into commercial activated carbons and synthetic activated carbons.

4.1. Commercial activated carbons

Many commercial activated carbons have been used as received and also after chemical modifications for Cr(VI) and Cr(III) adsorption. Important contributions in this direction were made by Huang and coworkers [58–61] and also by other groups [62–74]. The dominating mechanism for Cr(VI) removal in most of the studies is surface reduction of Cr(VI) to Cr(III) followed by adsorption of Cr(III).

Cr(VI) adsorption from aqueous solutions by lab-made high surface area (HSA)-activated carbons exhibited higher sorption capacities than commercial carbons [63]. A pH of ∼3.0 was optimum for Cr(VI) adsorption. Both micropores and mesopores make important contributions to Cr(VI) adsorption but desorption is more dependent on the mesoporosity. Thus, regeneration was easier for carbons having high mesoporosity. Cr(VI) adsorption mechanism was not discussed.

Huang and Wu [61] showed that Cr(VI) adsorption by activated carbon, filtrasorb 400 (Calgon), occurred by two major interfacial reactions: adsorption and reduction. Cr(VI) adsorption reached a peak value at pH 5.0–6.0. Carbon particle size and the presence of cyanide do not change the magnitude of chromium removal. Cr(III) is less adsorbable than Cr(VI). The free energy of specific chemical interaction, ΔG^{chem}, was computed by the Gouy–Chapman–Stern–Grahame model. ΔG^{chem} was −5.57RT and −5.81RT, respectively, for Cr(VI) and CN. These values were large enough to influence the magnitude of both Cr(VI) and CN adsorption. $HCrO_4^-$ and $Cr_2O_7^{2-}$ were the major Cr(VI) species involved in surface association.

Rivera-Utrilla and Sanchez-Polo [67] analyzed the effect of oxygenated surface groups on Cr(III) sorption using a series of ozonized activated carbons [carbon F, carbon F10, carbon F120 (Calgon Carbon Corp.)]. The adsorption capacity of the oxidized carbon was greater than that of the original carbon. This effect is due to the formation of surface oxygen groups that, through their ionization, increase the attractive electrostatic interactions between the surface of the activated carbon and the metallic cations present. At pH 2.0, almost all the Cr(III) was found as Cr^{3+} cation (hexahydrated), whereas at pH 12.0 it was found as $Cr(OH)_4^-$ anion. At pH 6.0 where the adsorption isotherms were obtained, the predominant species were: $Cr(OH)^{2+}$ (60.61%) and $Cr(OH)_2^+$ (38.24%). The adsorption of cationic Cr(III) species on basic carbons with surface positive charge density was explained by Cπ–cation interactions. In these processes, the ionic interchange of Cπ–H_3O^+-interaction protons for metallic cations plays a determinant role. According to the pH_{PZC} values of the carbon samples, the mean surface charge density at pH 6.0 is positive (carbon F), near zero (carbon F10) or negative (carbon F120). The attractive electrostatic interactions between the Cr(III) species and the carbon would increase in the order: F < F10 < F120; which is also the order of their increase in adsorption capacity.

Park and Jang [64] studied hydrochloric acid- and sodium hydroxide-treated activated carbons (ACs) for Cr(VI) reduction. The surface pH and acid–base values were measured and FT-IR, and X-ray photoelectron spectrometer (XPS) analyses were performed. Porosity was characterized by N_2/77 K adsorp-

tion. Cr(VI) adsorption and reduction depended on both microporous structure and surface functionality. Cr(VI) was more effectively adsorbed by acid-treated activated carbons. However, base-treated activated carbons were not effective Cr(VI) adsorbents, probably due to the decrease of specific surface area. Fluka carbons (particle size of 100–150 μm; specific surface area 1100 m^2/g) were modified by immobilizing tetrabutylammonium iodide (TBAI) and sodium diethyl dithiocarbamate (SDDC) on their surfaces [68]. These carbons were used for copper, zinc, chromium and cyanide removal. TBAI (417 μmol/g) and SDDC (295 μmol/g) were adsorbed. TBAI and diethyl dithiocarbamate-treated carbons adsorbed more CN^-, Cu, Zn and Cr than unmodified carbon.

The effect of anodic surface treatment of activated carbons on their Cr(VI) adsorption properties under reaction-treatment time conditions with 35 wt.% HCl solution was investigated [75]. The acidic surface functional groups increased with increasing HCl reaction-treatment time. Specific surface area, total pore volume, net heat of adsorption, and BET's, slightly decreased during anodic surface treatments of activated carbons. Adsorption was controlled more by the acid–base interactions between electron-donor substances and acidized activated carbons as electron acceptor than by the pore structures.

Aggarwal et al. [65] reported Cr(III) and Cr(VI) adsorption on activated carbon fibers and activated carbons in 20–1000 mg/L concentration range. Activated carbon surfaces further modified by oxidation with nitric acid, ammonium persulfate, hydrogen peroxide or oxygen gas at 350 °C were used after degassing at different temperatures. Cr(III) removal increased when the oxidized carbons were used decreased on degassing. Conversely, adsorption of Cr(VI) ions decreased on oxidized carbons and increased on degassing. The increase of Cr(III) and the decrease of Cr(VI) on oxidized carbons was due to acidic groups on the carbon surface. The decrease of Cr(III) and the increase of Cr(VI) on degassed carbons occurred because degassing removed these acidic groups. Acidic surface groups enhanced the Cr(III) adsorption and suppressed Cr(VI) adsorption. Chromic ions exist in aqueous solutions as $[Cr(H_2O)_6]^{3+}$. These associated water molecules are exchanged with the hydroxyl ions. The number exchanged depends on the pH of the solution as shown in Fig. 4. pH changes are caused by changes in amount of acidic carbon–oxygen surface groups. These, in turn, change the extent of the positive charge on the chromic ion. These changes in the surface negative charge resulting from oxidation and the changes in the positive charge on the Cr(III) ions in solution favor the adsorption of Cr(III) ions because attractive electrostatic interactions between the carbon surface and the chromium ions present in the solution are enhanced. Degassing reduces electrostatic attractive interactions, resulting in a decrease in the Cr(III) adsorption. When all the surface oxy-

Fig. 4. Aqueous Cr(III) species present versus pH.

gen complexes are thermally desorbed on degassing at 950 °C, little or no Cr(III) adsorption occurs.

Commercial activated carbon was treated with HNO_3 to introduce surface oxygen complexes, and subsequently heated up to 873 K in N_2 to eliminate some of the these complexes [76]. The three samples used for Cr(III) and Cr(VI) adsorption gave enhanced removal. Leyva-Ramos et al. [70] investigated Cr(III) adsorption on commercial activated carbon in the pH range of 2.0–6.0. At pH < 2.0 Cr(III) was not adsorbed and at pH values >6.4 Cr(III) precipitated as $Cr(OH)_3$. Maximum adsorption occurred at pH 5.0. The adsorption capacity increased by about 20% as the temperature was raised from 25 to 40 °C. Cr(VI) removal by two commercial granular activated carbons (GACs) in batch and continuous-flow modes was investigated [72]. Cr(VI) removal decreased with increase in pH from 4.0 to 7.5. Dissolved oxygen (DO) removal from experimental systems enhanced GAC performance, but pretreatment of the GACs with reductants (ferrous iron or dithionite) did not improve Cr(VI) removal. Regeneration of spent carbons was accomplished by equilibration with 0.01 M dibasic potassium phosphate to extract adsorbed Cr(VI) followed by a wash with 0.02N sulfuric acid to remove precipitated-sorbed Cr(III).

Cr(VI) removal from water by coconut shell, wood and coal dust based activated carbons was studied [77]. The coconut shell and coal dust activated carbons have protonated hydroxyl groups on the H-type carbons surface, while the surface of the wood-based activated carbon has ionized hydroxyl groups (L-type carbons). The optimum pH was 2.0 for wood-based activated carbon, while for coconut shell and coal dust activated carbons, the optimum pH was ∼3.0–4.0. Babel and Kurniawan [73] investigated coconut shell charcoal (CSC) and commercial coconut shell activated carbon (CAC) for Cr(VI) removal. Surface modifications of CSC and CAC with chitosan and/or oxidizing agents (such as sulfuric acid and nitric acid) were carried out. The oxidized adsorbents performed better. Nitric acid oxidized CSC and CAC had higher Cr adsorption capacities (CSC: 10.88 mg/g, CAC: 15.47 mg/g) than sulfuric acid oxidized (CSC: 4.05 mg/g, CAC: 8.94 mg/g) and non-treated CSC coated with chitosan (CSCCC: 3.65 mg/g) carbons, respectively. It was assumed that the following physicochemical interactions occurred during chromium removal

$$M^{n+} + n(\text{–COOH}) \rightleftharpoons (\text{–COO})_n M + nH^+ \qquad (7)$$
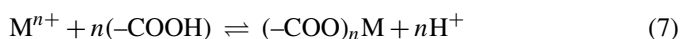
where (–COOH) represents the CSC surface functional groups and n is the coefficient of the reaction component, depending on the oxidation state of metal ions, while M^{n+} and H^+ are Cr(III) and hydrogen ions, respectively.

Thus, reduction of Cr(VI) oxyanions is accompanied by a large amount of proton consumption in the acidic solution. This confirms the decisive role played by H^+ in Cr(VI) removal. It was also reported that the Cr(VI)/Cr(III) redox potential strongly depends on pH. At pH ≈ 1.0, $E^0 \approx 1.3$ V and at pH ≈ 5.0, $E^0 \approx 0.68$ V, indicating that improving the redox potential of the oxidant extends the oxidation towards the more resistant surface functionalities. The pH of synthetic wastewater ranges from 5.0 to 6.0, where Cr(III) mostly exists as $[Cr(OH)]^{2+}$, formed by the
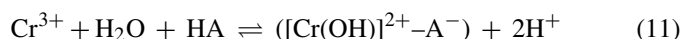
hydrolysis of Cr(III) as follows

$$Cr^{3+} + H_2O \rightleftharpoons [Cr(OH)]^{2+} + H^+ \quad (pK_1 = 3.85) \qquad (8)$$
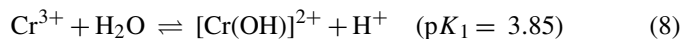
The second mechanism controlling the adsorption of Cr(III) on the carbon surface of CSC is represented as

$$Cr^{3+} + H_2O \rightleftharpoons [Cr(OH)]^{2+} + H^+ \qquad (9)$$

$$HA + [Cr(OH)]^{2+} \rightleftharpoons ([Cr(OH)]^{2+}\text{–}A^-) + H^+ \qquad (10)$$
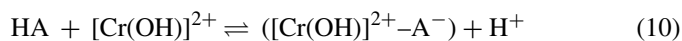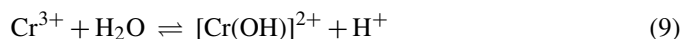
where A represents an adsorption site on the acidic surface of CSC.

Combining these two equations gives on overall Cr(III) adsorption reaction:

$$Cr^{3+} + H_2O + HA \rightleftharpoons ([Cr(OH)]^{2+}\text{–}A^-) + 2H^+ \qquad (11)$$

Chromium(VI) adsorption from dilute aqueous solutions onto modified activated carbons at natural pH values was achieved [69]. As expected surface reduction of Cr(VI) to Cr(III) appeared to be the principal chromium adsorption mechanism for the activated carbons studied. Oxidizing agents changed the adsorption capacity of Cr(VI) on the carbons. Cr(VI) removal from water on a commercial activated carbon occurred through reduction Cr(VI) to Cr(III) and adsorption, resulting in predominant attachment of Cr(VI) species with less Cr(III) species [60].

4.2. Synthetic activated carbons

As discussed in Sections 2.1.1 and 2.1.2, the production of activated carbon involves carbonization and activation. Carbonization consists of slow heating in the absence of air to the pyrolysis temperature, usually below 600 °C, where volatiles are removed. Then chemical or physical activation is performed. Physical activation involves of treating chars with steam, carbon dioxide, or oxygen at elevated temperature. Chemical activation is carried out in the presence of chemical activants such as $ZnCl_2$, H_2PO_4, H_2SO_4, KOH, K_2S, and KCNS [33,35]. These chemical activants promote the formation of cross-links giving a rigid matrix less prone to volatilization and volume contraction when heated to a high temperature. Zinc chloride is the most widely used chemical dehydrating agent (catalyst) [33,35]. Post-activation is also required to remove residual catalyst, which may be reclaimed for the subsequent reuse. Some important feedstocks containing an activant and other conditions used for activated carbons development are listed in Table 6. The most commonly used feed stocks include fertilizer waste [28,78,79], coconut shells and coconut shell fibers [2,3], wood [80], nuts [81], sawdust [82–85], waste tires [85], cow dung [86]; rice hulls [87] bagasse [88], coir pith [89] and lignin [66].

Waste carbon slurry generated in fertilizer plants in India was converted into a low cost activated carbon [28,78,79] and utilized for the removal of heavy metals from water/wastewater. Kinetic studies were also conducted to determine various parameters necessary to design fixed bed reactors [79]. To establish optimum deign parameters, mini column adsorption studies were performed and a mass transfer kinetic approach was successfully applied [28]. The length of the primary adsorption zone

(δ), total time involved for the establishment of primary adsorption zone (t_x), mass rate of flow to the absorber (F_m), time for primary adsorption zone to move down its length (t_δ), amount of adsorbate adsorbed in the primary adsorption zone from breakpoint to exhaustion (M_s), fractional capacity (f), time for initial formation of adsorption zone (t_f) and per cent saturation of column at break point were all studied. Chemical regeneration was achieved with 1 M HNO_3.

A variety of low cost activated carbons were developed from coconut shell fibers and coconut shells [2,3]. The carbons are designated as FAC (activated carbon derived from coconut fibers), SAC (activated carbon derived from coconut shells), ATFAC (activated carbon derived from acid-treated coconut fibers), and ATSAC (activated carbon derived from acid-treated coconut shells). These were characterized, and utilized for hexavalent chromium removal [2]. A commercial activated carbon fabric cloth was also tested. Trivalent chromium adsorption from water was restricted to ATFAC and ACF [3]. The optimum pHs for Cr(VI) and Cr(III) adsorption were 2.0 and 5.0, respectively. The Langmuir adsorption model fitted the Cr(III) and Cr(VI) adsorption data better than the Freundlich model. At 25 °C, Cr(VI) removal followed the order ACF (96.30 mg/g) > FAC (21.75 mg/g) > ATSAC (11.51 mg/g) > ATFAC (9.87 mg/g) > SAC (9.54 mg/g) [2] while the maximum adsorption capacities of ATFAC and ACF at 25 °C were 12.2 and 39.56 mg/g, respectively [3]. Overall, the activated carbon fabric cloth performed best. The adsorption capacities of these carbons and the activated carbon fabric cloth were comparable to those of the available adsorbents/activated carbons (Table 7).

Aqueous Cr(VI) uptake onto activated carbons (AC) produced from wood was investigated [80]. A KOH-activated carbon and a commercial H_3PO_4-activated carbon (Acticarbone CXV) were tested. Cr(VI) removal was maximized at pH 3.0 and increased with temperature for both adsorbents. The KOH-activated carbon had a higher Cr(VI) sorption capacity than Acticarbone. Favorable adsorption at low pH was due to the neutralization of negative surface charges by excess hydrogen ions. This facilitates diffusion of hydrogen chromate ions ($HCrO_4^-$) and their subsequent adsorption. $HCrO_4^-$ was the dominant Cr(VI) anion between pH 1.0 and 4.0. This ion was preferentially adsorbed on the carbon surface. The negative charges could result from basic oxygenated functions, chemisorbed at pore surfaces. Under acidic conditions, Cr(VI) could be reduced to Cr(III) in the presence of activated carbon. The authors failed to explore the dominating mechanism.

Several activated carbons were prepared from *Terminalia arjuna* nuts, an agricultural waste, by chemical activation with zinc chloride and then tested for aqueous Cr(VI) remediation [81]. The most important chemical activation parameter was the activating agent/precursor (g/g). A high surface area (1260 m^2/g) was obtained at a chemical ratio of 3, after 1 h of carbonization at 500 °C. The isotherm equilibrium data fit well to both the Langmuir and Freundlich models. The maximum Cr(VI) uptake was obtained at pH 1.0. Authors failed to explain the dominating Cr(VI) adsorption mechanism.

Table 6
Some chemical activant–feedstock couples to prepare activated carbon for chromium removal from water/wastewater

Feed stock	Carbonization	Activation		Reference
		Agent	Conditions	
Coconut shells	H_2SO_4, 150–65 °C, 24 h	–	600 °C/1 h	[2,3]
Coconut shell fibers	H_2SO_4, 150–65 °C, 24 h	–	600 °C/1 h	
Leather	N_2/900 °C/5 h	CO_2	825 °C/8 h	
	N_2/900 °C/5 h	CO_2	825 °C/45 h	
	N_2/900 °C/2 h	H_3PO_4	480 °C/3 h	
Olive stone	N_2/900 °C/2 h	$ZnCl_2$	725 °C/3 h	
	N_2/900 °C/2 h	H_2O	860 °C/2 h	[95]
	N_2/900 °C/2 h	CO_2	820 °C/72 h	
Almond shell	N_2/900 °C/2 h	$ZnCl_2 + CO_2$	(3:1) agent:raw material; 820 °C/69 h	
Norit CA-1	–	H_3PO_4	–	
Proquifi Andujar 39	–	H_3PO_4	–	
Casurina equisetifolia leaves	H_2SO_4 and 10% Na_2HPO_4 (1:1) 425 °C for 1 h in the absence of air	–	850 °C/30 min	[92]
	$ZnCl_2$/425 °C for 1 h in the absence of air	–	850 °C/30 min	
Hazelnut shell (*Corylus avellana*)	H_2SO_4/150 °C for 24 h	–	–	[90]
Eucalyptus grandis sawdust	800 °C in a N_2 atmosphere	CO_2 (D); air (A)	800/400 °C	[84]
Cornelian cherry (CC), apricot stone (AS) and almond shells (ASC)	1:1 (w/w) with concentrated H_2SO_4 for 24 h	–	200 °C/24 h	[91]
Fertilizer slurry	H_2O_2/H_2O	N_2	450 °C, 1 h	[28,78,96]
Used tires/sawdust	900 °C/N_2/2 h	CO_2	900 °C/2 h	[85]
Cow dung	1:1 (w/w) with concentrated H_2SO_4 for 24 h	–	–	[86]
Hevea brasiliensis sawdust	1:2 (w/w) with phosphoric acid/24 h/110 °C	–	400 °C/1 h	[82]
Lignin	H_3PO_4		350–600 °C	[66]

Table 7
Comparison of activated carbons and other low cost adsorbents for chromium [Cr(III) and Cr(VI)] removal

Adsorbents	pH	Temperature (°C)	Model used to calculate adsorption capacities	Adsorption capacity (mg/g)		Reference
				Cr(VI)	Cr(III)	
	2.0	20	Langmuir	27.1	8.9	
	3.0	20	Langmuir	23.4	20.7	
Composite alginate–goethite beads	4.0	20	Langmuir	20.5	30.4	[169]
	3.0	40	Langmuir	27.1	24.1	
	3.0	60	Langmuir	29.5	25.3	
Raw rice bran	5.0	25	Freundlich	0.07	0.1	[112]
Hevea brasiliensis (rubber wood) sawdust activated carbon	2.0	30	Langmuir	44.1	–	
	2.0	40	Langmuir	59.2	–	[82]
	2.0	50	Langmuir	65.8	–	
Coir pith	3.3	27	Langmuir	–	11.6	[103]
Palygorskite clay	7.0	25	Langmuir	58.5		[164]
	3.0	25	Langmuir	180.3		
	6.0	25	Langmuir	95.1		
Activated carbons (CKW)	9.0	25	Langmuir	33.4		
	3.0	33	Langmuir	281.3		
	3.0	40	Langmuir	315.6		
						[80]
	3.0	25	Langmuir	124.6		
	6.0	25	Langmuir	32.4		
Activated carbon (Acticarbone CXV)	9.0	25	Langmuir	17.5		
	3.0	33	Langmuir	144.4		
	3.0	40	Langmuir	186.1		
	2.5	22.5	Freundlich	7.8	–	
	3.5	22.5	Freundlich	6.3	–	
	5.0	22.5	Freundlich	3.4	–	
	8.0	22.5	Freundlich	1.9	–	
Maghemite nanoparticles	10.0	22.5	Freundlich	1.5	–	[126]
	2.5	10.0	Freundlich	1.4	–	
	2.5	22.5	Freundlich	1.4	–	
	2.5	35.0	Freundlich	1.4	–	
Soybean hulls	3.0	25	Langmuir	58.2	–	
Sugarcane bagasse	3.0	25	Langmuir	103	–	[136]
Corn stover	3.0	25	Langmuir	83.7	–	
Native saltbush (stems)	5.0	–	Langmuir	0.00	16.3	
Native saltbush (leaves)	5.0	–	Langmuir	0.1	22.7	
Native saltbush (flower)	5.0	–	Langmuir	0.1	27.0	
Esterified saltbush (stems)	5.0	–	Langmuir	3.4	5.5	
Esterified saltbush (leaves)	5.0	–	Langmuir	4.1	6.1	[255]
Esterified saltbush (flower)	5.0	–	Langmuir	3.1	7.1	
Hydrolyzed saltbush (stems)	5.0	–	Langmuir	0.0	20.8	
Hydrolyzed saltbush (leaves)	5.0	–	Langmuir	0.4	25.1	
Hydrolyzed saltbush (flower)	5.0	–	Langmuir	0.3	26.2	
Cross-linked (glutaraldehyde)	4.0	–	Langmuir	215	6	[275]
A. flavus biomass (live)		30	Langmuir	0.2	–	
A. flavus biomass (autoclaved)		30	Langmuir	0.3	–	
A. flavus biomass (acid-treated)		30	Langmuir	0.1	–	[273]
A. flavus biomass (alkali-treated)		30	Langmuir	0.2	–	
A. flavus biomass (detergent-treated)		30	Langmuir	0.2	–	
Native biomass of N. crassa (ATCC 12526)	1.0	25	Freundlich	0.4	–	
Heat inactivated of N. crassa (ATCC 12526)	1.0	25	Freundlich	9.2	–	
Sodium hydroxide of N. crassa (ATCC 12526)	1.0	25	Freundlich	7.4	–	[234]
Acetic acid of N. crassa (ATCC 12526)	1.0	25	Freundlich	15.9	–	
Ground nut shell (GS)	4.0	10	Langmuir	5.9	–	
	4.0	10	Langmuir	–	–	
Walnut shell (WS)	4.0	10	Langmuir	2.3	–	
	4.0	10	Langmuir	18.4	–	
Almond shell (AS)	4.0	10	Langmuir	22.0	–	
	4.0	10	Langmuir	2.4	–	[115]
	2.0	50	Langmuir	98.0	–	
	4.0	50	Langmuir	55.3	–	
T. indica seed (TS)	6.0	50	Langmuir	80.0	–	

Table 7 (*Continued*)

Adsorbents	pH	Temperature (°C)	Model used to calculate adsorption capacities	Adsorption capacity (mg/g)		Reference
				Cr(VI)	Cr(III)	
	8.0	50	Langmuir	23.0	–	
Native algae (*Chlamydomonas reinhardtii*)	2.0	25	Langmuir	25.0	–	
Heat-treated algae (*Chlamydomonas reinhardtii*)	2.0	25	Langmuir	30.2	–	[288]
Acid-treated algae (*Chlamydomonas reinhardtii*)	2.0	25	Langmuir	25.6	–	
Activated carbon prepared from *Terminalia arjuna* nuts	1.0	25	Langmuir	28.4	–	[81]
Isparta–Yalvaç–Yarikkaya (YK) coal	4.5	25	Langmuir	–	16.2	[152]
Kasikara (KK) coal	4.5	25	Langmuir	–	5.4	
	2.0	10	Langmuir	25.9	–	
Agave lechuguilla biomass	2.0	22	Langmuir	34.6	–	[253]
	2.0	40	Langmuir	35.6	–	
	2.0	27	Langmuir	47.4	–	
M. hiemalis	2.0	40	Langmuir	51.0	–	[235]
	2.0	50	Langmuir	53.5	–	
B. thuringiensis (vegetative cell)	2.0	25	Langmuir	28.6	–	[247]
B. thuringiensis (spore–crystal mixture)	2.0	25	Langmuir	34.2	–	
Lewatit MP 62 anion exchange resin	5.0	25	Langmuir	21.6	–	[131]
Lewatit M 610 anion exchange resin	5.0	25	Langmuir	22.1	–	
Lentinus sajor-caju (untreated)	2.0	25	Langmuir	19.6	–	
Lentinus sajor-caju (heat-treated)	2.0	25	Langmuir	33.1	–	[230]
Lentinus sajor-caju (HCl-treated)	2.0	25	Langmuir	25.8		
Lentinus sajor-caju (NaOH-treated)	2.0	25	Langmuir	27.7		
Carrot residues	4.5	25	Langmuir	–	45.1	[116]
Ferric chloride impregnated-sponified sugar beet pul	4.4	25	Langmuir	5.1	–	[289]
	4.4	35	Langmuir	4.9	–	
	4.4	45	Langmuir	4.6	–	
Carboxymethylcellulose (CMC)	2.0	25	Langmuir	5.1	–	
Free mycelia of *Lentinus sajor-caju*	2.0	25	Langmuir	18.9	–	[212]
Immobilized mycelia (in carboxymethylcellulose (CMC)) of *Lentinus sajor-caju*	2.0	25	Langmuir	32.3	–	
Sawdust	–	–	Freundlich	1.5	–	
Rice husks	–	–	Freundlich	0.6	–	[102]
Coir pith	–	–	Freundlich	0.2	–	
Raw stevensite	3.0	25	Dubinin–Radushkevich	0.7	–	[159]
Fe-stevensite	3.0	25	Dubinin–Radushkevich	2.6	–	
Cone biomass of *Thuja oriantalis*	1.5	17	Langmuir	49	–	[256]
Quaternary chitosan salt (QCS)	4.5	25	Langmuir	68.3	–	[276]
	9.0	25	Langmuir	30.2	–	
Uncalcined hydrotalcite	2.0–2.1	25	Freundlich	4.6	–	[35]
Amberlite IR-120 resin	–	20	Langmuir	–	67.7	[129]
Pantoea sp. TEM18	3.0	25	Langmuir	204.1	–	[248]
	2.0	20	Langmuir	0.5	–	
Bauxite	2.0	35	Langmuir	0.5	–	[167]
	2.0	50	Langmuir	0.4	–	
Hydrous titanium(IV) oxide	2.0	25	Langmuir	5.0		[165]
Aeromonas caviae, a gram-negative bacteria	2.5	20	Langmuir	284.4	–	[245]
	2.5	40	Langmuir	181.5	–	
	2.5	60	Langmuir	169.1	–	
Activated carbon from co-mingled natural organic wastes	3.7	30	Langmuir	–	56.7	
	3.7	35	Langmuir	–	56.2	
	3.7	40	Langmuir	–	56.6	
	3.7	45	Langmuir	–	43.5	[95]
Norit carbon (oxidized)	3.7	22	Langmuir	–	25.6	
	3.7	30	Langmuir	–	52.5	
	3.7	40	Langmuir	–	53.0	
	3.7	50	Langmuir	–	45.9	
Beech (*Fagus orientalis* L.) sawdust	∼1.0	25	Langmuir	16.1	–	[252]

Table 7 (*Continued*)

Adsorbents	pH	Temperature (°C)	Model used to calculate adsorption capacities	Adsorption capacity (mg/g)		Reference
				Cr(VI)	Cr(III)	
	4.0	20	Langmuir	–	10.5	
Wine processing waste sludge	4.0	30	Langmuir	–	13.5	[186]
	4.0	40	Langmuir	–	15.4	
	4.0	50	Langmuir	–	16.4	
Polyacrylonitrile fibers (APANFs)	5.0	–	–	~16	~5	[137]
Peat	4.0	22–25	Extended Langmuir	–	22.4	[267]
Bio-polymeric beads of cross-linked alginate and gelatin	8.9	25	Langmuir	0.8	–	[169]
Ocimum basilicum seeds	1.5	25	Langmuir	205	–	[119]
	5.0	30	Langmuir	–	2.5	
Bagasse fly ash	5.0	40	Langmuir	–	2.3	[176]
	5.0	50	Langmuir	–	2.1	
Protonated dry alginate beads	3.5	25	Langmuir	–	57.0	[170]
	4.5	25	Langmuir	–	77	
Fe-modified steam exploded wheat straw	3.0	25	Langmuir	9.1	–	[105]
Solvent impregnated resins	4.0	25	Langmuir	50.4	–	[134]
Persimmon tannin (PT) gel	3.0	25	Langmuir	274.0	–	[172]
Distillery sludge	3.0	25	Langmuir	5.7	–	[187]
Ion exchange resin 1200H	3.8	25	Langmuir	84.0	–	
Ion exchange resin 1500H	3.8	25	Langmuir	188.7	–	[12]
Ion exchange resin IRN97H	3.8	25	Langmuir	58.1	–	
Hydrotalcite	6.0	25	Freundlich	120.0	–	[158]
Maple sawdust	6.0	25	Langmuir	5.1	–	[101]
Pitch-based activated carbon fibers, ACF30M	3.0	25	Langmuir	23.7		[138]
Pitch-based activated carbon fibers, ACF45M	3.0	25	Langmuir	24.9	–	
Activated carbon, FS-100	3.0	–	Langmuir	69.3	–	
Activated carbon, GA-3	3.0	–	Langmuir	101.4	–	
Activated carbon, SHT	3.0	–	Langmuir	69.1	–	
Activated carbon, CZ-105	3.0	–	Freundlich	40.4	–	[63]
Activated carbon, CZ-130	3.0	–	Freundlich	44.9	–	
Activated carbon, CK-22	3.0	–	Freundlich	47.4	–	
Activated carbon, CK-26	3.0	–	Freundlich	45.6	–	
Free biomass	2.0	30	Freundlich	27.6	–	
Polysulfone entrapped biomass	2.0	30	Freundlich	17	–	
Polyisoprene immobilized biomass	2.0	30	Freundlich	15.6	–	[231]
PVA immobilized biomass	2.0	30	Freundlich	13.4	–	
Calcium alginate entrapped biomass	2.0	30	Freundlich	9.6	–	
Polyacrylamide biomass	2.0	30	Freundlich	2.3	–	
SI resin prepared using HP-20	4.0	30	Langmuir	38.0	–	[133]
SI resin prepared HP-2MG	4.0	30	Langmuir	40.0	–	
Dunaliella alga (sp. 1)	2.0	25	Langmuir	111.0	–	[213]
	2.0	25	Langmuir	102.5	–	
Inorganic–organic silicon hybrid matrices	–	–	–	–	29.12	[156]
Cone biomass of *Pinus sylvestris*	1.0	25	Freundlich	38.4	–	[257]
PAC	2.0	25	Langmuir	0.03	–	
Bagasse	6.0	25	Langmuir	0.0005		[177]
Flyash	6.0	25	Langmuir	0.001		
Immobilized dried activated sludge	1.0	25	Langmuir	18.9		[197]
Granular activated carbon	1.0	25	Langmuir	147.1	–	
Wool	2.0	30	Langmuir	41.2	–	
Olive cake	2.0	30	Langmuir	33.4	–	
Sawdust	2.0	30	Langmuir	15.82	–	
Pine needles	2.0	30	Langmuir	21.5	–	[100]
Almond	2.0	30	Langmuir	10.6	–	
Coal	2.0	30	Langmuir	6.78	–	
Cactus	2.0	30	Langmuir	7.08	–	
Soya cake	<1.0	20	Langmuir	0.00028	–	[120]
Activated sludge	1.0	25	Langmuir	294.0	–	[188]
Activated sludge	4.5	25	Langmuir	95.2	–	
Cation-exchange resin, IRN77	3.5	25	Freundlich	35.4	–	[11]

Table 7 (*Continued*)

Adsorbents	pH	Temperature (°C)	Model used to calculate adsorption capacities	Adsorption capacity (mg/g)		Reference
				Cr(VI)	Cr(III)	
Untreated *R. nigricans*	2.0	30	Langmuir	123.5	–	
CTAB-treated R. nigricans	2.0	30	Langmuir	140.8	–	
PET-treated *R. nigricans*	2.0	30	Langmuir	161.3		[232]
APTS-treated *R. nigricans*	2.0	30	Langmuir	200.0		
Biomass of filamentous algae *Spirogyra* species	2.0	18	Langmuir	14.7	–	[211]
	2.0	22	Langmuir	48.1	–	
Carbonaceous adsorbent from waste tires (TAC)	2.0	30	Langmuir	55.3	–	
	2.0	38	Langmuir	58.5	–	
	2.0	22	Langmuir	1.9	–	
Carbonaceous adsorbent from sawdust (SPC)	2.0	30	Langmuir	2.2	–	[85]
	2.0	38	Langmuir	2.3	–	
	2.0	22	Langmuir	44.4	–	
Carbon, F-400	2.0	30	Langmuir	48.5	–	
	2.0	38	Langmuir	53.2	–	
IRN77 resin	3.5	25	Freundlich	–	35.4	[10]
SKN1 resin	3.5	25	Freundlich	–	46.3	
Dried anaerobic activated sludge	1.0	25	Langmuir	577.0	–	[198]
	2.0	30	Langmuir	22.7	–	
Red mud	2.0	40	Langmuir	21.6	–	[29]
	2.0	50	Langmuir	21.1	–	
Tannin gel (66% water content)	2.0	30	–	192.0	20.0	
Tannin gel (72% water content)	2.0	30	–	224.0	28.0	
Tannin gel (75% water content)	2.0	30	–	235.0	38.0	[173]
Tannin gel (77% water content)	2.0	30	–	287.0	50.0	
Cow dung carbon	3.4	30	Langmuir	10.0	–	[86]
Carbon C3	3.0	25	Langmuir	35.0	–	[92]
Carbon C4	3.0	25	Langmuir	15.0	–	
Algae, *Chlorella vulgaris*	2.0	25	Langmuir	27.3	–	[214]
Insoluble straw xanthate (ISX)	3.6–3.9	25	Langmuir	–	1.9	[118]
Alkali-treated straw (ATS)	3.6–3.9	25	Langmuir	–	3.9	
Algae, *C. vulgaris*	2.0	25	Langmuir	79.3	–	
Algae, *S. obliquus*	2.0	25	Langmuir	58.8	–	[215]
Algae, *Synechocystis* sp.	2.0	25	Langmuir	153.6	–	
Algae, *C. vulgaris*	2.0	25	Freundlich	6.0	–	[217]
	2.0	25	–	30.7	–	[268]
Peat	4.0	25	–	–	14.0	
Free biomass of *R. arrhizus*	2.0	–	Freundlich	11.0	–	[226]
Immobilized biomass of *R. arrhizus*	2.0	–	Freundlich	8.6	–	
GAC-S	–		Langmuir	–	13.3	
GAC-E	–		Langmuir	–	10.5	[65]
ACF-307	–		Langmuir	–	7.1	
ACF-310	–		Langmuir	–	3.5	
	3.0	30	Langmuir	12.2	–	
Polymer-grafted sawdust	3.0	40	Langmuir	9.4	–	[97]
	3.0	50	Langmuir	7.6	–	
	3.0	60	Langmuir	6.2	–	
Dithizone-anchored poly(EGDMA-HEMA) microbeads	5.0	25	Langmuir	–	62.2	[171]
Aspergillus biomass	5.0	28	Langmuir	23.6	15.6	[229]
R. arrhizus	2.0	25	Langmuir	58.1	–	[227]
Leaf mould	2.5	25	Column capacity	25.9	–	[107]
Activated carbon	2.5	25		75.6	–	
Biogas residual slurry	1.50	30	Langmuir	5.87	–	[193]
Peat moss	2.0	25	Column capacity	65.8	–	[269]
Irish sphagnum peat	2.5	25	Column capacity	35.5	–	[270]
	2.0	25	Column capacity	43.9	–	
	3.5	30	Langmuir	61.4	–	
Chitosan impregnated with a microemulsion	3.5	40	Langmuir	81.9	–	[277]
	3.5	50	Langmuir	85.6	–	
Lignocellulosic substrate	2.1	–	Langmuir	35.0	–	[108]
Chitosan	4.0	25	Langmuir	154	–	[278]

Table 7 (*Continued*)

Adsorbents	pH	Temperature (°C)	Model used to calculate adsorption capacities	Adsorption capacity (mg/g)		Reference
				Cr(VI)	Cr(III)	
Sargassum wightii Seaweed	3.5–3.8	25	Langmuir	35.0	–	[220]
Surface-modified jacobsite (MnFe₂O₄)	2.0	25	Langmuir	31.5	–	[127]
Protonated brown seaweed *Ecklonia* sp.	2.0	20–25	–	233.5	–	[294]
Aeromonas caviae biomass	2.5	20	Langmuir	284.4	–	[245]
Activated carbon, FAC	2.0	10	Langmuir	16.0	–	
Activated carbon, SAC	2.0	10	Langmuir	1.4	–	
Activated carbon, ATFAC	2.0	10	Langmuir	1.1	–	
Activated carbon, ATSAC	2.0	10	Langmuir	1.6	–	
Activated carbon fabric cloth	2.0	10	Langmuir	116.9	–	
Activated carbon, FAC	2.0	25	Langmuir	21.8	–	
Activated carbon, SAC	2.0	25	Langmuir	9.5	–	
Activated carbon, ATFAC	2.0	25	Langmuir	10	–	[2]
Activated carbon, ATSAC	2.0	25	Langmuir	11.5	–	
Activated carbon fabric cloth	2.0	25	Langmuir	96.3	–	
Activated carbon, FAC	2.0	40	Langmuir	24.1	–	
Activated carbon, SAC	2.0	40	Langmuir	32.6	–	
Activated carbon, ATFAC	2.0	40	Langmuir	15.6	–	
Activated carbon, ATSAC	2.0	40	Langmuir	16.4	–	
Activated carbon fabric cloth	2.0	40	Langmuir	42.1	–	
	5.0	10	Langmuir	–	11	
Activated carbon, ATFAC	5.0	25	Langmuir	–	12.2	
	5.0	40	Langmuir	–	16.1	
	5.0	10	Langmuir	–	36.1	[3]
Activated carbon fabric cloth	5.0	25	Langmuir	–	39.6	
	5.0	40	Langmuir	–	40.3	
Activated carbon, A	3.0	30	Langmuir	–	0.8	
Activated carbon, D	3.0	30	Langmuir	–	0.4	
Activated carbon, OA	3.0	30	Langmuir	–	31.5	[84]
Activated carbon, OD	3.0	30	Langmuir	–	26.3	
PEI-modified biomass of *P. chrysogenum*	4.6	25	Langmuir	279.2	–	[228]
Fleshing from animal hides/skins	4.0	25	Langmuir	51.0	–	[202]
Treated fleshing from animal hides/skins	4.0	25	Langmuir	9.0	–	
	2.5	30	Langmuir	24.1	–	
Carbon slurry	2.5	45	Langmuir	25.2	–	[290]
	2.5	60	Langmuir	25.6	–	
Biogas residual slurry	2.5	30	Langmuir	–	7.8	[194]
Coniferous leaves	3.0	30	Freundlich	6.3	–	[262]
	3.0	20	Langmuir	68.0	–	
London leaves	3.0	30	Langmuir	75.8	–	[261]
	3.0	40	Langmuir	83.3	–	
Brown seaweed (*Turbinaria* spp.)	3.5	30	Langmuir	–	31	[223]
Cork powder	4.0	22	Langmuir	–	6.3	[109]
Hazelnut shell activated carbon	1.0	30	Langmuir	170	–	[90]
Kendu fruit gum dust (KGD)	1.0	30	Freundlich	218	–	[110]
		30	Langmuir	24.1	–	
Carbon slurry		45	Langmuir	25.2	–	[195]
		60	Langmuir	25.6	–	
Cationic surfactant-modified yeast	4.5–5.5	20	Langmuir	94.3	–	[244]
	3.0	20	Langmuir	127.3	–	
Amine-modified polyacrylamide-grafted coconut coir pith		30	Langmuir	123.4	–	
		40	Langmuir	111.4	–	[104]
		50	Langmuir	108.4	–	
Dowex	3.0	30	Langmuir	109.3	–	
	3.0	20	Langmuir	144.2	–	
Sawdust (SD) of rubber wood (*Hevea brasiliensis*) was grafted with polyacrylamide	3.0	30	Langmuir	153	–	
	3.0	40	Langmuir	158.7	–	[99]
	3.0	50	Langmuir	166.7	–	
	3.0	60	Langmuir	172.4	–	
As received CSC	6.0	25	Langmuir	2.2	–	
CSC coated with chitosan	6.0	25	Langmuir	3.7	–	
CSC oxidized with sulfuric acid	6.0	25	Langmuir	4.1	–	[73]

Table 7 (*Continued*)

Adsorbents	pH	Temperature (°C)	Model used to calculate adsorption capacities	Adsorption capacity (mg/g)		Reference
				Cr(VI)	Cr(III)	
CSC oxidized with sulfuric acid and coated with chitosan	6.0	25	Langmuir	9	–	
CSC oxidized with nitric acid	6.0	25	Langmuir	11	–	
As received CAC	6.0	25	Langmuir	4.7	–	
CAC oxidized with sulfuric acid	6.0	25	Langmuir	8.9	–	
CAC oxidized with nitric acid	6.0	25	Langmuir	10.4	–	
	2.0	10	Langmuir	2.5	–	
Agave lechuguilla biomass	2.0	22	Langmuir	3.3	–	[259]
	2.0	40	Langmuir	3.4	–	
Fly ash	2.0	30	Langmuir	1.4		
Fly ash impregnated with aluminum	2.0	30	Langmuir	1.8	–	[179]
Fly ash impregnate with iron	2.0	30	Langmuir	1.7	–	
	3.0	30	Langmuir	71.9	–	
Japanese ceder (*Cryptomeria japonica*)	3.0	40	Langmuir	80.0	–	[263]
	3.0	50	Langmuir	90.9	–	
Larch bark	3.0	30	Langmuir	31.3	–	[264]
Fly ash-wollastonite	2.0	25	Langmuir	2.9		[291]
Sawdust	2.0	25	Langmuir	39.7	–	
Sugar beet pulp	2.0	25	Langmuir	17.2	–	[292]
Maize cob	1.5	25	Langmuir	13.8	–	
Sugarcane bagasse	2.0	25	Langmuir	13.4	–	
Dried *Chlorella vulgaris*	2.0	25	Langmuir	27.8	–	[217]
Chitosan cross-linked with epichlorohydrin	3.0	25	Langmuir	11.3	–	[293]
Chitosan coated on perlite	4.0	25	Langmuir	153.8	–	[280]
Metal ion imprinted chitosan	5.5	25	Langmuir	51.0	–	
Chitosan cross-linked with epichlorohydrin	5.5	25	Langmuir	52.3	–	[281]
Metal ion imprinted chitosan cross-linked with epichlorohydrin	5.5	25	Langmuir	51.0	–	
Chitosan cross-linked with ethylene glycol diglycidyl ether	5.5	25	Langmuir	56.8	–	
Bagasse fly ash	1.0	30	Langmuir	259.0	–	[27]
	1.0	40	Langmuir	123.7	–	
Activated carbon developed from fertilizer waste slurry	2.0	27	Langmuir	371.0	–	[78]
	2.0	45	Langmuir	173.0	–	
Blast furnace slag	1.0	30	Langmuir	1.45	–	[181]
	1.0	40	Langmuir	1.76	–	
Activated carbon obtained from black liquor lignin	7.0	25	Langmuir	40.0–56.0		[66]
	3.0	25	Langmuir	80.0–92.6		
Cement kiln dust	–	–	Langmuir	33.3	–	[204]
Activated carbon, F	6.0	25	Langmuir	7.3		
Activated carbon, F10	6.0	25	Langmuir	10.7		[67]
Activated carbon, F120	6.0	25	Langmuir	19.2		
Brown coal, YK	3.0	25	Langmuir	47.83		[153]
Brown coal, KK	3.0	25	Langmuir	50.95		

Hazelnut shell activated carbon was developed from Corylus avellane species for Cr(VI) removal from water [90]. Cr(VI) adsorption was best achieved in the pH range of 1.0–2.0. The maximum adsorption capacity calculated using Langmuir model was 170 mg/g at pH 1.0. Under acidic conditions Cr(VI) reduced to Cr(III). Cornelian cherry (CC), apricot stone (AS) and almond shells (ASC) were converted into activated carbons and used for Cr(VI) removal from aqueous solution [91]. The optimum pH was 1.0. Sorption capacities for various activated carbons were not reported.

Rubber wood sawdust [82], sawdust [83], eucalyptus sawdust [84] were converted to activated carbons. Sawdust carbons were characterized and used for Cr(VI) [82,83] and Cr(III) [84] reme-

diation. Karthikeyan et al. [82] examined Cr(VI) adsorption onto activated carbon from *Hevea brasiliensis* (rubber wood) sawdust. Cr(VI) removal peaked at pH 2.0. Langmuir, Freundlich and Temkin isotherms were used to describe the adsorption equilibrium data. Maximum adsorption in acidic pHs indicated that an increase in the surface H^+ ion concentration resulted in strong electrostatic attractions between the surface and chromate ions. No consideration was given to the reduced Cr(III). Bishnoi et al. [83] concluded that the improved chromium removal at low pH (2.0) by sawdust activated carbon was due to Cr(VI) reduction to trivalent chromium. No adsorption capacity was reported.

Eucalyptus sawdust was converted into activated carbon by CO_2 [84]. These carbons were then treated with concentrated

70 wt.% HNO_3 at 80 °C to obtain and the corresponding oxidized carbons were used for Cr(III) remediation. HNO_3 oxidation enhanced the ability to retain Cr(III) due to a significant increase in oxygenated surface groups. Other non-acidic functions, which evolve CO upon temperature programmed desorption, contributed to Cr(III) uptake. Significant adsorption into the micropores took place although oxidation of the active carbons leads to a narrowing of the average micropore widths.

Casurina equisetifolia leaves. *C. equisetifolia* leaves were carbonized and then activated with sulfuric acid (1:1), a phosphate salt (10%) or zinc chloride (25%) [92]. Different temperatures were employed to get these activated carbons [92], which were then used to remove Cr(VI). Data were fitted with the Freundlich model. Adsorbed chromium was 65–80% desorbed by alkali followed by acid treatments. Carbon recycling was achieved without changing in the sorption efficiency. Rice husk-based activated carbons were prepared using KOH and NaOH as activation agents [93]. The porous carbon prepared with KOH (RHCK) had higher surface area ($3000 \, m^2/g$) than the carbon ($2500 \, m^2/g$) prepared using NaOH. Reduction of Cr(VI) into Cr(III) was not considered at low pH. Neither data set was modeled by Langmuir/Freundlich equations nor were the maximum sorption capacities (monolayer) determined. Chromium removal by rice hull-based activated carbon (RHAC) and Calgon's F-400 was investigated [87]. Chromium was successfully removed only by F-400.

A variety of activated carbons in powder and granular form were developed from leather, olive stone, almond shells by different activation procedures [94]. These carbons were used for Cr(VI) removal. The porous texture of the activated carbons was characterized by adsorption of N_2/77 K and methylene blue/298 K. Cr(VI) adsorption increased with increasing pH and initial Cr(VI) concentration. At pH < 1.0, the retention of Cr(VI) was due to its reduction to Cr(III). The lower the pH the greater the reduced tendency. The extent of adsorption and reduction depended on the porous texture, and procedure used to prepare the activated carbons. Physical activation gives the best performance. Cr(VI) removal by carbonaceous adsorbents produced from pyrolysis/activation of waste tires (TAC), pyrolysis of sawdust (SPC) and a commercially available carbon (F400) was investigated [85]. Pyrolysis was carried out at a heating rate of 20 °C/min for 2 h to reach the pyrolysis temperature (900 °C). After pyrolysis, the product was activated by CO_2 at 900 °C for 2 h. The sawdust was pyrolyzed at 650 °C at the same conditions used for tires. Maximum adsorption occurred at pH 2.0 for all carbons (Table 7) because Cr(VI) was adsorbed as $HCrO_4^-$ which predominates between pH 1.0 and 4.0. Reduction of Cr(VI) to Cr(III) was not considered. The sorption data were modeled using the Langmuir isotherm.

Activated carbons prepared from co-mingled natural organic wastes [95] and a commercially available carbon (Norit) were used for Cr(III) removal. Total chromium uptake by the co-mingled waste activated carbon was higher then by Norit activated carbon under similar conditions (1.09 and 1.01 mmol/g, respectively, at 30 °C) (Table 7). The operating adsorption mechanism at pH 3.7 was a rapid ion exchange of aqueous chromium ions followed by their surface hydrolysis and slow chemisorption and/or an outer-sphere complexation. The first hydrolytic species probably converts to inner-sphere complexation with time. Cr(VI) removal from aqueous medium by cow dung activated carbon was achieved [86]. Cow dung was carbonized and activated by treating with concentrated H_2SO_4 and heating for 24 h at 120 °C. At lower pH (<3.5), this carbon removed ~90% of Cr(VI) present at 5 ppm in a synthetic aqueous solution. No adsorption mechanism was explored.

Activated carbon produced by graphite electrode arcing in an inert atmosphere was employed for aqueous Cr(VI) and Cr(III) removal [96]. This carbon selectively removed hexavalent chromium anions from solution, whereas, little or no uptake of [Cr(III)] was observed versus solution pH.

High BET surface area activated carbons with well-developed porosity by pyrolysis of H_3PO_4-impregnated lignin precipitated from kraft black liquors. These lignin-derived carbons were used for Cr(VI) remediation [66]. H_3PO_4/lignin (w/w) impregnation ratios between 1 and 3 and activation temperatures of 350–600 °C were used. Higher activation temperatures and the impregnation ratios widen the pore structure, producing a higher contribution of mesoporosity. Impregnation ratios of ~2 and activation temperatures around 425 °C were recommended as the best operating conditions to prepare activated carbons for chromium remediation.

5. Low cost adsorbents

5.1. Agricultural by-products and seeds

Agricultural wastes have been applied as adsorbents for hexa and trivalent chromium remediation from water. The most commonly used agricultural by-products include sawdust [97–100,102], coir pith [102–104] straw [105], husks [106], leaf mould [107], wheat bran [108], cork powder [109], fruit gum dust [110], sugar beet pulp [111], rice bran [112], rice hulls [113], bark [114], and nut shells [115].

Tamarindus indica seeds (TS), crushed coconut shells (CS), almond shells (AS), ground nut shells (GS) and walnut shells (WS) were used for Cr(VI) removal [115]. Hexavalent chromium sorption capacity followed the sequence (TS) > (WS) > (AS) > (GS) > (CS) (Table 7). Cr(VI) sorption by TS decreased with rising pH, and dropped slightly with higher ionic strengths. Cr(VI) removal occurred by chemisorption on TS. Desorption of Cr(VI) from Cr(VI) laden TS was quite favored by NaOH versus distilled water and HCl. Whether Cr(VI) adsorption occurred as chromate anions or reduced Cr(III) at low pH is not known. Recently, baggase, charred rice husks, activated charcoal and eucalyptus bark (EB) were tested for chromium removal [114]. EB provided the highest Cr(VI) removal capacity. The maximum Cr(VI) adsorption occurred at pH 2.0. The sorption capacity was 45 mg/g of adsorbent at a Cr(VI) concentration of 250 mg/L in the effluent.

The anion exchange properties of soybean hulls after quaternizion with *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride, in a strongly alkaline environment was inves-

tigated [113]. This modification converted the hulls to an anion exchanger. Modified hulls exhibited a larger uptake of anions compared with the unmodified hulls.

Raw rice bran adsorbed chromium and nickel from aqueous solutions [112]. Capacities were calculated using the Freundlich isotherm (Table 7). Cr(III), Cu(II) and Zn(II) were all removed from aqueous solution by carrot residues [116]. These lignocellulosic residues contained up to 12% of the weight of the original fruit. Metals cations were bound by carboxylic acid and phenolic groups. The Freundlich and Langmuir models described the sorption equilibria of Cr(III), Cu(II) and Zn(II). No adsorption mechanism was discussed.

An adsorbent from sugar beet pulp by iron(III) hydroxide loading was used for Cr(VI) removal [111]. Sugar beet pulp was subjected to saponification, ferric chloride impregnation, hydrolysing and heating. Cr(VI) adsorption and reduction to Cr(III) occur using sugar beet pulp-based materials. Cr(VI) reacts with organic matter leached from pulp to produce Cr(III). The following reduction mechanism was proposed

$$HCrO_4^- + \text{organic matter} + H^+ \rightarrow Cr^{3+} + H_2O \tag{12}$$

or

$$CrO_4^{2-} + CO_2 \quad \text{(and/or oxidized products)} \tag{13}$$
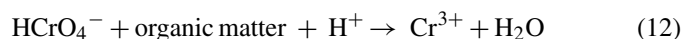
Sawdust, rice husks, coir pith, charcoal and vermiculite were used for aqueous Cr(VI) removal [102]. Cr(VI) adsorption capacities followed the order sawdust = coir pith > rice husks > charcoal and vermiculite (Table 7). Chromate anions and reduced Cr(III) both adsorbed but no quantification of Cr(VI) and Cr(III) was attempted. Formaldehyde and sulfuric acid-treated Indian Rosewood sawdust, a timber industry waste, was employed for Cr(VI) adsorption [117]. Maximum removal occurred at an initial pH of 3.0. Neither sorption capacities nor the sorption mechanisms were reported.

Heavy metals removal using alkali-treated straw (ATS) and insoluble straw xanthate (ISX) were explored [118]. Insoluble straw xanthate consisting of 4.1% total sulfur was also applied for the simultaneous removal of several metal ions. Potentiometric data from alkali-treated straw and xanthated straw confirmed their polyfunctionality. Diffuse reflectance IR (DRIFT) spectra of ISX exhibited characteristic xanthate peaks. Removal of Cr^{3+} from aqueous solutions using ATS and ISX followed the Langmuir model and both the materials removed >80% of the chromium. Pore adsorption preceded the surface adsorption with chromate and dichromate. Detailed spectroscopic (DRIFT and EPR) and sodium release studies conducted on ISX suggested that Cr^{3+} is removed through an adsorption-exchange mechanism involving alkoxide or xanthate groups. Xanthate groups bind Cr^{3+} aqua complexes via unidentate monosulfur chelation. Basic groups on ATS and ISX participated in the interaction with Cr^{3+}. Removal of Cr^{3+} via an ion-exchange route takes place according to the following reactions:

$$3(-CH_2O-Na^+) + Cr^{3+} \rightarrow (-CH_2O)_3Cr + 3Na^+ \tag{14}$$

$$3(-CH_2OCS_2^-Na^+) + Cr^{3+} \rightarrow (-CH_2OCS_2)_3Cr + 3Na^+ \tag{15}$$

$$-CH_2O^-Na^+ + Cr^{3+} \rightarrow -CH_2OCr^{2+} + Na^+ \tag{16}$$

$$-CH_2OCS_2^-Na^+ + Cr^{3+} \rightarrow -CH_2OCS_2Cr^{2+} + Na^+ \tag{17}$$

$$-CH_2O^-Na^+ + [Cr(H_2O)_6]^{3+}$$
$$\rightarrow -CH_2O^-Cr(H_2O)_5^{2+} + Na^+ + H_2O \tag{18}$$

$$-CH_2OCS_2^-Na^+ + [Cr(H_2O)_6]^{3+}$$
$$\rightarrow -CH_2OCS_2-Cr(H_2O)_5^{2+} + Na^+ + H_2O \tag{19}$$
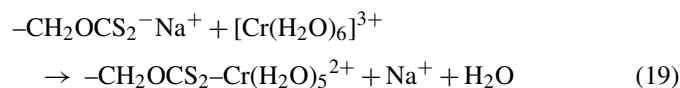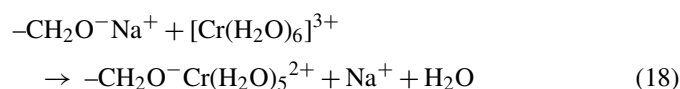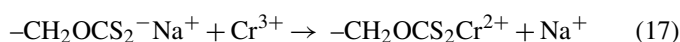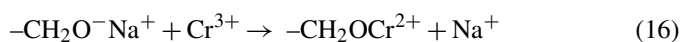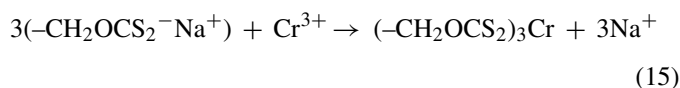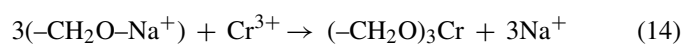
Three equivalents of Na^+ are released into solution (Eq. (15)) for each Cr^{3+} exchanged. One equivalent of Na^+ was released for each Cr^{3+} exchanged (Eqs. (16) and (17)). However, the exchange ratio for ATS and ISX was close to one. This indicates that exchange took place according to Eqs. (16) and (17). If Cr^{3+} is considered to exist as $[Cr(H_2O)_6]^{3+}$ in aqueous solutions, Eqs. (16) and (17) can be rewritten as Eqs. (18) and (19). $[Cr(H_2O)_6]^{3+}$ was exchanged as a dicationic aqua species with the participation of $-CH_2O^-Na^+$ or $-CH_2OCS_2^-Na^+$.

Polymer-grafted sawdust was synthesized and used it for Cr(VI) removal from aqueous solution [97]. An empirical relationship was obtained to predict the percentage Cr(VI) removal at any time for known values of adsorbent and initial adsorbate concentration. Other ions had little effect on the sorption of Cr(VI). The data fitted the Freundlich model. This adsorbent was effectively regenerated using 0.2 M NaOH and 0.5 M NaCl. Variations in adsorption were explained by taking into account this adsorbent's affinities for the different Cr(VI) species of coexisting at acidic pH ($Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$). Above pH 8.0, only CrO_4^{2-} is stable. As the pH decreased to 3.0–6.0, the equilibrium shifts to dichromate according to the overall equilibrium:

$$2CrO_4^{2-} + 2H^+ \Leftrightarrow Cr_2O_7^{2-} + H_2O \tag{20}$$
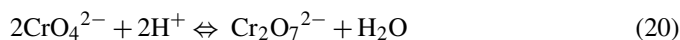
At lower pH values, $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ species are formed. In summary, decreasing of the pH resulted in the formation of more polymerized chromium oxide species.

At the pH of highest sorption efficiency (pH 3.0), the dominant species were $HCrO_4^-$ and $Cr_2O_7^{2-}$. Thus, $HCrO_4^-$ and $Cr_2O_7^{2-}$ are most easily exchanged with Cl^- from the peripheral $-NH_3^+Cl^-$ groups present in the polymer-grafted sawdust. $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ were also formed at highly acidic pH (<2.5) but were difficult to exchange with Cl^- ions from the adsorbent surface with difficulty. The adsorption capacities decreased with increase in temperature (Table 7).

Maple sawdust was also utilized for Cr(VI) remediation [101]. Adsorption increased in the pH range of 3.0–10.0. Sorption was explained in terms of the pH_{zpc} (zero point of charge) of the adsorbent. The pH_{zpc} of sawdust was 6.0. Surface charge of the adsorbent is positive at pH < 6.0. At pH < pH_{zpc}, the predominant metal species [M^{n+} and $M(OH)^{(n-1)+}$] are positively charged. Therefore, uptake of metals at pH between 2.0 and 6.0

is a H^+–M^{n+} exchange process. The possible sites on sawdust for specific adsorption include groups which are the source of H^+ ions ($\cdots C_6H_5\cdots OH$ and $\cdots COOH$ functional groups) where protons can be exchanged for cations:

$$S\cdots COOH + M^{n+} \rightarrow S\cdots COOM^{(n-1)+} + H^+ \tag{21}$$

$$S\cdots C_6H_5\cdots OH + M^{n+} \rightarrow S\cdots C_6H_5\cdots OM^{(n-1)+} + H^+ \tag{22}$$

$$S\cdots COOH + M(OH)^{(n-1)+}$$
$$\rightarrow S\cdots COOM(OH)^{(n-2)+} + H^+ \tag{23}$$

$$S\cdots C_6H_5-OH + M(OH)^{(n-1)+}$$
$$\rightarrow S\cdots C_6H_5\cdots OM(OH)^{(n-2)+} + H^+ \tag{24}$$
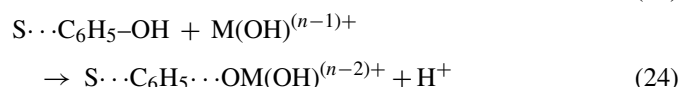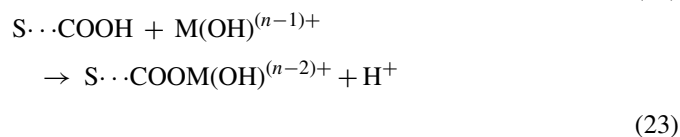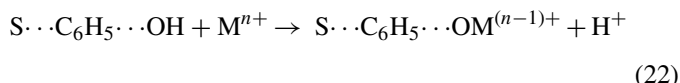
S denotes the surface. Adsorption is not exclusively due to the $\cdots COOH$ and phenolic –OH groups. Other sites also contribute. In an acidic medium, sawdust's amide group's protonate, generating net surface positive charge. Surface protons are also exchanged with positively charged sorbate species leading to metal ion coordination. A small increase in adsorption occurred at $pH > pH_{zpc}$. The surface becomes negatively charged while the sorbate species are still positively charged. Thus, the electrostatic attraction between sorbate and adsorbent causes metal ion adsorption. At lower pH, the higher proton concentration competes with the M^{2+} ions for adsorption sites. This reduces metal ion sorption. The decrease in adsorption at still higher pH was due to the formation of soluble hydroxyl complexes. Phosphate-treated and -untreated sawdust was exploited [98] for aqueous Cr(VI) removal. Almost 100% Cr(VI) removal was achieved in the pH range <2.0 for the initial Cr(VI) concentration of 8–50 mg/L. Furthermore, 100% removal of Cr(VI) from synthetic wastes as well as from electroplating waste containing 50 mg/L Cr(VI) was achieved by both batch and column processes. The Cr(VI) adsorbed on phosphate-treated sawdust was recovered (87%) using 0.01 M sodium hydroxide.

The iron(III) complex of a carboxylated polyacrylamide-grafted sawdust proved to be an effective adsorbent for the removal of aqueous Cr(VI) [99]. Sawdust of rubber wood (*Hevea brasiliensis*) was grafted with polyacrylamide. About 20.0 g of dried sawdust (1) was treated with 300 mL of a solution containing 5.0 g of *N,N'*-methylenebisacrylamide (2) and peroxydisulfate (2.0 g). Next, 7.5 g of acrylamide (3) was added, and the mixture was refluxed at 70 °C. The polyacrylamide-grafted sawdust (PGSD) was washed with water and dried at 80 °C. The desired carboxylate-functionalized polymer product was produced by refluxing PGSD with ethylenediamine [$(en)_2$] in toluene and then with succinic anhydride in 1,4-dioxane at pH 4.0 After reaction, carboxylic-acid-bound PGSD (PGSD-COOH) was separated, washed with 1,4-dioxane and ethanol and dried. PGSD-COOH was sieved to obtain −80 to +230 mesh size particles. The production of and structure of PGSD-COOH is represented in Fig. 5.

The carboxylate group loading in PGSD-COOH was 2.03 mmol/g. Maximum Cr(VI) removal (>99.0%) by PGSD-COOH took place at an initial Cr(VI) concentration of 25.0 mg/L in the pH range 2.0–3.0. Unsaturated coordination sites on the polymeric Fe(III) complex were the adsorption sites for Cr(VI) species (predominant species was $HCrO_4^-$). Adsorption isotherm data were interpreted by the Langmuir and Freundlich equations. Cr(VI) uptake increased from 144.20 mg/g at 20 °C to 172.74 mg/g at 60 °C. Kendu fruit gum dust (KGD) was also
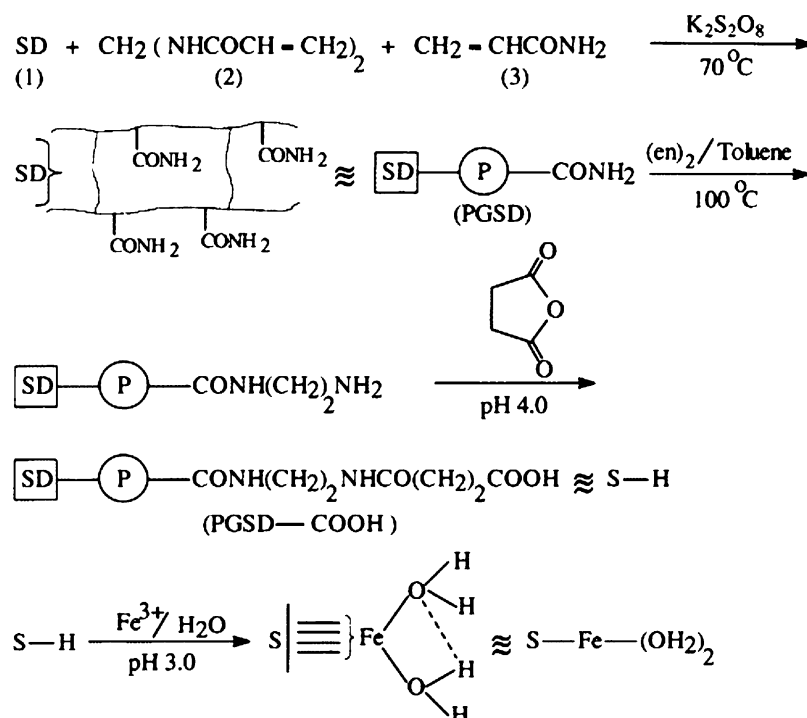
Fig. 5. Preparation of carboxylated polyacrylamide-grafted sawdust and its iron(III) complex. *Source*: Unnithan and Anirudhan [99] with permission.

tested for Cr(VI) removal from aqueous solutions [110]. As expected, at low pH Cr(VI) adsorption was high. The presence of cyanide ion decreased the Cr(VI) adsorption efficiency of the KGD. Only ~20% loss of efficiency occurred after six cycles. Thermogravimetric analysis of original KGD and the frust KGD with adsorbed Cr(VI) suggested the thermal stability of KGD increased due to metal ion adsorption.

Coir pith solid waste was investigated for Co(II), Cr(III) and Ni(II) adsorption in both single and multicomponent systems [103]. The optimum pH value for maximum chromium removal was 3.3. The Langmuir model fit the data better than Freundlich model. The maximum coir pith sorption capacity was 11.56 mg Cr/g. The amine-modified polyacrylamide-grafted coconut coir pith carrying $-NH_3^+Cl^-$ functional groups at the chain end (PGCP–$NH_3^+Cl^-$) was also examined for aqueous batch Cr(VI) removal [104]. Grafting polyacrylamide onto the coir pith improved this adsorbent's thermal stability and enhanced the apparent activation energy for the thermal degradation of PGCP–$NH_3^+Cl^-$. Adsorbent crystallinity and morphology were examined using XRD and SEM. The decrease in crystalline domains in PGCP–$NH_3^+Cl^-$ results in the loss of tensile strength of the grafted chain. This enhances the free mobility grafted chain. Maximum Cr(VI) adsorption (99.4%; 12.43 mg/g) was achieved at an initial concentration of 25.0 mg/L Cr(VI) at 30 °C, pH 3.0, and an adsorbent concentration of 2.0 g/L. The Cr(VI) sorption kinetics were described by a pseudo-second-order kinetic model. Quantitative removal of 22.7 mg/L Cr(VI) in 50 mL of electroplating industry wastewater by 125 mg of PGCP–$NH_3^+Cl^-$ was achieved at pH 3.0.

Polysaccharides bound to bacteria or in isolated form can bind heavy metals. *Ocimum basilicum* seeds, which swell upon wetting, could serve as natural immobilized source of agriculturally based polysaccharides [119]. The seeds consist of an inner hard core and a pectinous fibrillar outer layer. Pre-treating the seeds with acid, alkali, periodate or boiling in water altered the metal binding capacity. Of these various treatments, seeds boiled in water were superior in terms of mechanical stability and exhibited optimal Cr(VI) uptake kinetics. The maximum adsorption capacity at pH 1.5 as calculated from the Langmuir isotherm was 205 mg Cr/g dry seeds. Sorption was not affected by the presence of other metal ions such as Cd^{2+}, Cu^{2+}, Ca^{2+} and Na^+. Daneshvar et al. [120] reported the reduction of Cr(VI) to Cr(III) followed by Cr(III) adsorption. A high efficiency for reduction of Cr(VI) to Cr(III) took place at pH < 1.0. Cr(VI) also adsorbed on soya cake at pH < 1.0.

Cr(VI) from synthetic and actual electroplating wastewaters was removed by Fe-modified steam exploded wheat straw (Fe-SEWS) [105]. Removal of Cr(VI) was higher at pH ≤ 3.0. The removal was ~96%. No attempts were made to explain the sorption mechanism. Wool, olive cake, sawdust, pine needles, almond shells, cactus leaves and charcoal were employed to remove Cr(VI) [100]. The influence of pH, contact time, metal concentration, adsorbent nature and concentration on the selectivity and sensitivity of the removal process was investigated. Cr(VI) adsorbed as $HCrO_4^-$. No measurements were made to check if there was any reduction of Cr(VI) into Cr(III). Further, Cr(III) was not adsorbed at pH ≤ 3.0 because positive Cr(III)

ions were repulsed by positively charged active centers on the adsorbents. Therefore, Cr(III) adsorption was carried out at pH 5.0. At this pH, the number of negatively charged groups on the adsorbent matrix increased and enhanced the Cr(III) removal by columbic attraction. Cr(III) adsorption capacities were not reported.

Eromosele et al. [106] utilized shea butter (*Butyrospermum parkii*) seed husks for aqueous Cr(III) removal. The effects of agitation and counter-ions on the sorption process were investigated. Sorption was enhanced by a factor of 2 by agitation but was independent of its speed. Addition of isopropanol to aqueous solutions of Cr(III) ions depressed Cr(III) adsorption. Carboxymethylation of the seed husk reduced its adsorptive capacity for Cr(III) ion by 60%. Sharma and Forster [107] tried using leaf mould as biosorbent for the treatment of wastewaters contaminated with Cr(VI) in a column system. The results were compared with an activated carbon column. Both columns were operated at a pH of 2.5 and a flow-rate of 74 mL/min. Cr(VI) adsorption capacities of the leaf mould were only 26 mg/g compared to 76 mg/g for the activated carbon. The leaf mould caused little or no reduction of Cr(VI) and produced an effluent with very low concentration of Cr(III). The activated carbon, on the other hand, reduced a lot of chromium.

Dupont and Guillon [108] utilized a lignocellulosic substrate derived from the industrial treatment of wheat bran as an adsorbent. The air-dried, coarsely powdered wheat bran (30 g) was subjected to acid hydrolysis by 2 mol/L H_2SO_4 (1:1 (w/w) dry matter, at 100 °C for 30 min) to remove starch, proteins, and sugars. This was followed by alkali treatment with 0.5 mol/L NaOH (5:1 ratio of bran/sodium hydroxide, stirring for 24 h at room temperature) to remove the low molecular weight lignin compounds after filtration. The solid was stirred with 0.04 mol/L HNO_3 in order to protonate all acidic sites and then it was washed with deionized water until the pH reached a constant value close to neutrality. Adsorption consumed a large number of protons accompanying the reduction of Cr(VI) into Cr(III). Concurrent oxidation of lignin moieties took place during chromium reduction. This led to the formation of hydroxyl and carboxyl functions. The latter contribute to an increase in the number of ion-exchange sites for the reduced chromium. The maximum adsorption capacity for Cr(VI) was ~35 mg/g in an acidic medium.

Trivalent chromium biosorption was investigated on cork powder [109]. Chromium was reduced from 10 mg/dm to less than 1.5 mg/dm in 2 h at 22 °C using a solid–liquid ratio of 4 g/dm. Fifty percent of the chromium bound to the cork was eluted using 0.5 mol/dm H_2SO_4 and that cork maintained its binding capacity over four biosorption/elution cycles.

5.2. Zeolites

Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations, having infinite, three-dimensional structures [121,122]. Zeolites have been received increasing attention for pollution control. There are more than 30 natural zeolites known. Only seven (mordenite, clinoptilolite, chabazite, erionite, ferrierite, phillipsite, and analcime) occur in sufficient

quantity and purity to be considered exploitable. Kesraoui-Ouki et al. [123] published a review of natural zeolite utilization in metal effluent treatment applications. Zeolites, modified by ion exchange, can be used for adsorption of different metal ions. Covarrubias et al. [124] examined Cr(III) removal by columns packed with zeolite and activated carbon. Cr(III) exchange in $13\times$ zeolite was optimized using the mass transference approach [124]. Cr(III) exchange in the zeolite was predominantly controlled by diffusion into the particle. The optimum pH was 3.5. A mixed system of columns in series (activated carbon + zeolite) increased the removal, principally due to the adsorption of dissolved organic matter (COD) onto the carbon column and to a lesser extent to the retention of chromium and interfering ions.

5.3. Nano-technology

Nanoporous materials are defined as those materials having pore diameters less than 100 nm. Nanoporous materials, a subset of nanostructured materials possess unique surface, structural and bulk properties that underline their important uses in various fields such as ion exchange, separation, catalysis, sensor, biological molecular isolation and purifications [125]. During the last decade, considerable effort has been made in the synthesis, characterization, functionalization, molecular modeling and design of nanoporous materials due to their extremely small size and large specific surface area. Nano-adsorbents [126–128] were also studied for aqueous chromium remediation.

Hu et al. [126] developed a method combining nanoparticle adsorption and magnetic separation for the removal and recovery of Cr(VI) from wastewater. Maghemite nanoparticles were prepared by developing the existing sol–gel method from [128]. Equilibrium was reached within 15 min and was independent of initial Cr concentration. The maximum adsorption occurred at pH 2.5. The adsorption data were fitted well by Freundlich isotherm. Competition from common coexisting ions such as Na^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, NO_3^-, and Cl^- was insignificant, which illustrated the selectivity towards aqueous Cr(VI). Maghemite nanoparticles were used for six-successive adsorption–desorption cycles. An analysis of the chromium contents in solution and on the particle surface was performed to see if any chemical redox reaction occurred during adsorption. Dissolved hexavalent chromium was determined by the diphenylcarbazide method. Then the concentration of any existing Cr(III) was taken to be the difference between the total chromium and Cr(VI). Specifically, an aqueous sample was injected onto a high capacity anion exchange column where Cr(VI) as CrO_4^{2-} was retained and then eluted with an alkaline sulfate eluent. After this separation, a diphenylcarbazide color indicator was added to the eluent system, which flowed through a photometric detector. The reagent formed a colored complex with Cr(VI), detected by photoadsorbance at 530 nm. Cr(VI) was measured in this way and total Cr was determined by ICP. The concentration of Cr(VI) always equaled that of total Cr (Table 8), demonstrating that the chromium oxidation state in solution never changed after adsorption. This conclusion contradicts other mechanisms where Cr(VI) reduction into Cr(III), followed by adsorption, was the dominant mechanism. The Cr-

Table 8
Concentration of chromium after adsorption on maghemite nanoparticles at pH 2.5 and desorption [126]

C_0	After adsorption		After desorption	
	$C_{e,Cr}$	$C_{e,Cr(VI)}$	$C_{ed,Cr}$	$C_{ed,Cr(VI)}$
50	2.8	2.8	34.8	34.1
100	34.3	34.2	53.5	53.0

C_0 represents the initial concentration of adsorbate; C_e represents the equilibrium concentration after adsorption; C_{ed} represents the equilibrium concentration after desorption. All units are expressed in mg/L.

loaded maghemite particles were characterized by XRD, XPS, and Raman spectroscopy techniques after Cr(VI) adsorption at different pHs. XRD showed that Cr-adsorbed particles matched well with standard γ-Fe_2O_3. Other crystalline phases did not appear after adsorption. XPS study confirmed the Cr $2p_{3/2}$ and Cr $2p_{1/2}$ peaks, respectively, centered at 579.8 and 587.2 eV, belonged only to Cr(VI). Thus, no chemical redox to Cr(III) occurred.

The effectiveness of surface-modified jacobsite ($MnFe_2O_4$) nanoparticles for Cr(VI) removal and recovery from synthetic wastewater was examined [127] examined. Ten nanometer diameter modified $MnFe_2O_4$ nanoparticles were produced using a co-precipitation method followed by a surface redox reaction. The equilibrium time for Cr(VI) adsorption onto modified $MnFe_2O_4$ nanoparticles was 5 min. The adsorption data fit the Langmuir model well. The maximum uptake of 31.5 mg Cr(VI)/g of modified $MnFe_2O_4$ was obtained at pH 2.0. The adsorption mechanisms for Cr(VI) onto modified $MnFe_2O_4$ nanoparticles were a combination of electrostatic interactions and ion exchange. This was determined by X-ray diffraction and X-ray photoelectron spectroscopy.

5.4. Organic resins

Both commercial [10–12,129–135] and synthetic organic resins [136] were investigated for chromium remediation.

Wartelle and Marshall [136] converted soybean hulls, sugarcane bagasse and corn stover to functional anion exchange resins using dimethyloldihydroxyethylene urea (DMDHEU) and choline chloride. The modification method was optimized using soybean hulls as a substrate. This optimized method was additionally used to modify sugarcane bagasse and corn stover. Chromate ion adsorption suggested that modification with both DMDHEU and choline chloride was required for the highest efficiencies. Adsorption capacities of the modified by-products were 1.97, 1.61 and 1.12 mmol/g for sugarcane bagasse, corn stover and soybean hulls, respectively (Table 7). Competitive adsorption experiments were performed at 10 and 50 times the US Environmental Protection Agencies (US EPA) concentration limits for chromium in a simulated wastewater at pH 7.0. Estimated product costs for the three resins ranged from \$ 0.88 to $0.99 \, kg^{-1}$ were considerably lower than the market costs for the two commercial anion exchange resins QA-52 and IRA-400 also used in this study. No mechanism was provided.

Gode and Pehlivan [131] explored Cr(VI) adsorption on macroporous resins containing tertiary amine groups (Lewatit MP 62 and Lewatit M 610). As expected, the sorption increased with the decrease in pH and slightly decreased with the increase in temperature. The maximum sorption capacity of 0.40 mmol Cr(VI)/g for Lewatit MP 62 and 0.41 mmol Cr(VI)/g for Lewatit M 610 was achieved at pH of 5.0. Cr(VI) adsorption on the resin was attributed to chromate adsorption. No attempts were made to quantify the reduced Cr(III) and chromates at low pH.

Uncalcined hydrotalcite ($[Mg_2Al(OH)_6]_2CO_3 \cdot 3H_2O$), an ion exchange resin was used for Cr(VI) remediation [135]. A Freundlich isotherm, was used to describe sorption equilibrium (Table 7). As expected the process was highly pH dependent, only yielding significant Cr(III) removal at pH 2.0–2.1. Alguacil et al. [129] used amberlite IR-120 resin [a sulfonic acid functionalized styrene–DVB resin with an exchange capacity of 4.4 mequiv./g (dry)]. Amberlite IR-120 has a maximum operating temperature of 120 °C and a particle size of 0.45–0.60 mm; swelling: 5–7%. Cr(III) was removed from acidic waste solution by batch and column methods. A maximum adsorption of 67.7 mg/g Cr(III) was achieved. The Langmuir isotherm adequately described the equilibrium relation between the resin and liquid phases, whereas the chromium adsorption kinetics was film-diffusion controlled.

Solvent impregnated resin (SIR) was prepared by impregnating Amberlite XAD-7 with Aliquat 336 as an extractant and acetone as the solvent. A wet impregnation technique was used. The SIR was investigated for Cr(VI) remediation [134]. Three different concentrations, 0.5, 1.0 and 2.0 g Aliquat 336 g^{-1} Amberlite XAD-7, were prepared in two different size ranges: 300–401 and 553–711 μm. Cr(VI) removal decreased at an equilibrium pH below 4.0. Two solvent impregnated resins have also been prepared by wet-impregnation using Diaion HP-20 and HP-2MG matrices [133]. Diaion HP-20 possessed a hydrophobic styrene–divinylbenzene resin structure whereas HP-2MG was a hydrophilic methacrylic-based resin. Aliquat 336 was employed as the extractant and acetone as the impregnation solvent. Impregnated resins containing Aliquat 336 were effectively used for Cr(VI) removal. The data were fitted to the Langmuir adsorption model. Increasing the impregnation ratio from 0.5 to 1.0 (g Aliquat 336 g^{-1} polymer adsorbent) increased the breakthrough capacity in a column-mode sorption study. The Cr(VI) adsorbed by these SIRs was quantitatively desorbed using aqueous 0.1 M NaOH–0.1 M NaCl mixture.

Ion exchange resins 1200H, 1500H, IRN97H, IRN77 and SKN1 were utilized for Cr(VI) remediation [11,13]. IRN77 was also used for Cr(III) adsorption [12]. The sorption process exhibited maximum removal in the pH range 2.0–6.0. The metal ion adsorption followed linear, Langmuir and Freundlich isotherms. The reported Freundlich sorption capacities were 35.38 and 46.34 mg/g for IRN77 and SKN1 resins, respectively. The uptake by these ion exchange resins was reversible so they exhibit good potential for the removal/recovery of chromium from aqueous solutions.

Similarly, Gode and Pehlivan [130] remediated Cr(III) with macroporous resins containing iminodiacetic acid (IDA) groups
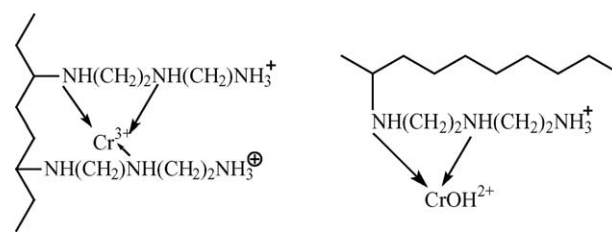
Fig. 6. Adsorption of Cr(III) species on the APANFs. *Source*: Denga and Bai [137].

(Lewatit TP 207 and Chelex-100). Both of these sorbents had high bonding constants with Lewatit TP 207 showing stronger binding. Maximum sorption capacities of 0.288 mmol Cr(III)/g for Chelex-100 and 0.341 mmol Cr(III)/g for Lewatit TP 207 were achieved at pH of 4.5.

5.5. Fibers

Cr(III) and Cr(VI) were removed using synthesized aminated polyacrylonitrile fibers (APANFs) [137]. Significant amounts of Cr(III) and Cr(VI) species were adsorbed by the APANFs. The adsorptions were dependent on solution pHs. Cr(III) adsorption increased and Cr(VI) decreased with the increase of the solution pH values. X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy suggested that Cr(III) adsorption on APANFs was attributed to the formation of surface complexes between the nitrogen atoms on the APANFs and the Cr(III) species adsorbed. On the other hand Cr(VI) adsorption on the APANFs was effected through the formation of hydrogen bonds at high solution pH values or through both electrostatic attraction and surface complexation at low solution pH values (Figs. 6 and 7). Cr(VI)-adsorbed APANFs was regenerated in a basic solution and reused almost without any loss of the sorption efficacy while the Cr(III)-adsorbed APANFs needed regeneration in an acidic solution and it was less effective.

Sorption properties of activated and oxidized pitch-based activated carbon fibers (ACFs) were applied to Cr(III) and Cr(VI) removal [138]. Steam activation was conducted at 900 °C for 30 min (ACF30M) and 45 min (ACF45M), respectively (H_2O/N_2 volume ratio: 0.44). Oxidation of dry ACFs with boiling 1 M nitric acid was carried for 2 h. Surface carboxyl groups were created by nitric acid oxidation. The affinity for chromium ions increased with increasing specific surface area, micropore volume, and surface functionalities of ACFs as the activation time increases. Cr(VI) adsorption mechanisms on ACFs were not proposed. The sorption capacities were evaluated (Table 7).
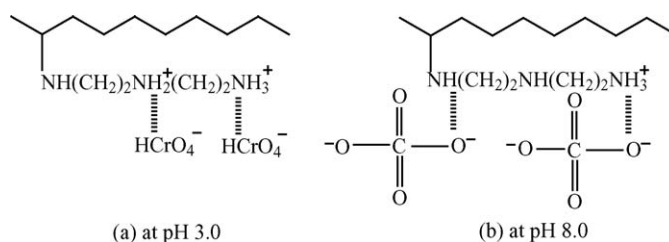
Fig. 7. Adsorption of Cr(VI) species on the APANFs. *Source*: Denga and Bai [137].

Cr(III) and Cr(VI) adsorption on electrolyses Cu-plated activated carbon fibers (ACFs) was performed [139]. ACFs were characterized by pH, acid/base values, and BET (N$_2$/77 K) isotherm adsorption. Electroless copper plating significantly decreased the surface acidity in well-developed micropores of ACFs. The Cr(III) adsorption increased with the introduction of copper on ACFs, whereas Cr(VI) adsorption decreased. This was attributed to the formation of copper oxides on the ACFs which increased the surface basicity. This enhanced Cr(III) adsorption and suppressed Cr(VI) adsorption. The Cr(III) and Cr(VI) sorption capacities were not reported.

5.6. Carbon steel

Carbon steel powder together with granular activated carbon (PCS–GAC) was explored for Cr(VI) removal from drinking water [140]. Authors reported that granular activated carbon could not be used for chromate removal from water. This was very surprising. There are very many reports discussed in this review where activated carbons possessed high chromate sorption capacities. The adsorption capacity of the carbon steel powder was deemed high due to ferro-chromium electrochemical redox processes at carbon steel surface sites.

5.7. Lignite, peat, chars, and coals

Lignite and peat use for wastewater treatment has received increasing attention [141,142]. They may be good substitutes for activated carbons. They are plentiful, inexpensive and locally available. Lignite's properties fall between those of peat and bituminous coal. Consolidation of peat and lignite increases as coalification proceeds. Lignite's densities range from 1.0 to 1.35 g/cm^3. Lignites are usually amorphous and fibrous or woody in texture. The 'as mined' lignite possesses water-filled pores and capillaries and exhibits high moisture contents (30–70%). Pore diameters vary; micropores are present, leading to highly porous typical surface areas of 100–200 m^2/g [143–146]. Lignite has organic and inorganic portions. A carbonaceous continuous organic matrix contains inorganic mineral matter distributed throughout.

Peat, a complex composed contains lignin, cellulose, fulvic and humic acids as its major constituents and has been recognized as a natural humic substance which can trap cations. All these constituents carry polar functional groups such as alcohols, aldehydes, carboxylic acids, ketones, and phenolic hydroxides which play roles in ion exchange and complexation during metal ion fixation from solution. Peat is generally dark brown and exhibits a spongy texture. It is partially fossilized plant matter, formed in wet areas under partially anaerobic conditions where the rate of accumulation of plant matter is greater than of decomposition. Decomposition is incomplete leading to the build up of peat over time. A generalized chemical structure for a portion of peat is given in Fig. 4.

Review articles have appeared [147–151] on the properties, availability, and use of peat in the control of industrial wastewater pollution. Viraraghavan and Ayyaswami [151] reported that peat is comparable to carbon, silica, alumina, etc., in both
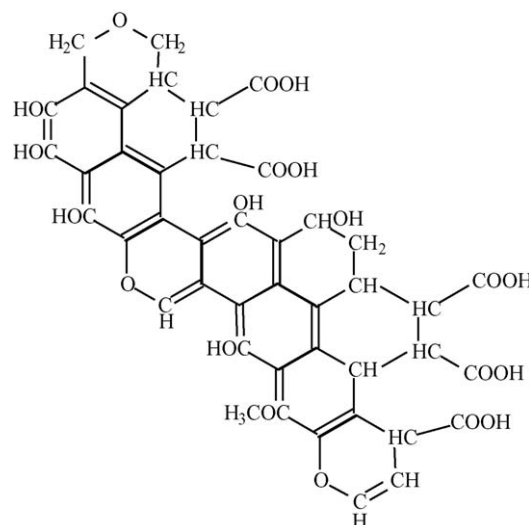
Fig. 8. Chelating structure of peat.

adsorption capacity and cost. The cost of peat ($\sim$US\$ 0.09 kg^{-1}) is lower than commercial ion exchange resins which cost US\$ 4.40–22.00 kg^{-1} and activated carbon which costs around US\$ 1.10 kg^{-1}. Since peat is highly polar, it adsorbs large quantities of metals, which makes it competitive with other adsorbents [148,149].

Equilibrium and kinetic adsorption of Cr(III) by two brown coals (Isparta–Yalvaç–Yarikkaya (YK) and Kasikara (KK)) were investigated [152]. The Cr(III) ions were able to form complexes with carboxylic acid and phenolic groups of brown coals. Cr(III) remained bonded with phenolic groups even at pH < 3.0. Ion exchange, complexation and adsorption to coal surfaces were the general mechanisms in the sorption process. High adsorption at higher pH values was due to chelation of the metal ions with coal functional groups. Equilibrium sorption data fitted the linear Langmuir isotherm. The maximum equilibrium uptake was 0.05 mmol Cr(III)/g for KK, and 0.26 mmol Cr(III)/g for YK, respectively, at a pH of 4.5 (Table 1).

The ability of brown coals (leonardites) to remove chromium(VI) from aqueous solutions was studied as a function of pH, contact time, adsorbent nature, and concentration of metal solutions [153]. The adsorption of Cr(VI) was higher between pH 2.0 and 3.0 for all brown coals and maximum sorption was observed at pH 3.0. The maximum adsorption capacity of 0.92 mmol Cr(VI)/g for YK, 0.98 mmol Cr(VI)/g for KK was obtained (Fig. 8).

5.8. Hydroxide/hydrotalcite

Hydrotalcites have the structural formula $[M_{1-x}^{II}M_x^{III}(OH)_2]^{x+}A_{x/n}^{n-} \cdot yH_2O$, where M^{II} and M^{III} denote divalent (e.g. Mg, Ni, and Zn) and trivalent metals (e.g. Al, Fe, and Cr), respectively [154]. A^{n-} represents interlayer anions, such as NO_3^-, SO_4^{2-}, and CO_3^{2-}, and x typically ranges from 0.17 to 0.33. These materials consist of positively charged, brucite-like octahedral layers and a negatively charged interlayer region contain-

ing anions and water molecules. The presence of large interlayer spaces and a significant number of exchangeable anions cause hydrotalcites to be good ion-exchangers and adsorbents. Various hydroxide/hydrotalcite compositions [155–158] were tested for chromium remediation.

Das et al. [155] developed hydrotalcite-like compounds (layered double hydroxides, LDHs) containing varying amounts of Al^{3+}, Zr^{4+}, and Zn^{2+} or Mg^{2+} in the metal hydroxide layer. Uncalcined (as-synthesized) and calcined LDHs were explored for $Cr_2O_7^{2-}$ and SeO_3^{2-} removal. The mixed oxides, obtained on calcination at 450 °C, exhibited high sorption capacities for $Cr_2O_7^{2-}$ (1.6–2.7 mequiv./g) and SeO_3^{2-} (1.1–1.5 mequiv./g). The adsorption occurred through rehydration. Substitution of Zr^{4+} in the LDHs, for either M^{2+} or Al^{3+} ions, increased the removal capacity up to 20%.

de Farias et al. [156] synthesized a hybrid inorganic–organic matrix with 4.0 mmol/g of pendant organic moiety by the solgel condensation of tetraethylorthosilicate (TEOS) and *n*-[3(trimethoxysilyl)propyl]-ethylenediamine. The hybrid matrix was used as a substrate for Cr(III) and Fe(III) adsorption from their aqueous chloride solutions. A maximum sorption capacity of 0.56 mmol/g was achieved. No sorption mechanism was explored.

Cr(VI) adsorption by uncalcined and calcined Mg–Al, Ni–Al and Zn–Cr layered double hydroxides was investigated [157]. Sorption of $Cr_2O_7^{2-}$ by the uncalcined LDH was slower and smaller amounts were removed than using the calcined LDHs. Uncalcined LDHs sorbed via ion exchange whereas calcined LDHs removed Cr(VI) by rehydration. Bi- and trivalent metal ions in the LDHs influence the adsorption. Calcined Mg–Al LDH containing higher Al^{3+} contents exhibited higher adsorption capacities. Adsorption was higher using Mg–Al LDH than with Ni–Al and Zn–Cr LDHs. The $Cr_2O_7^{2-}$ solution's pH has no affect on sorption by calcined LDH. Release of $Cr_2O_7^{2-}$ from the adsorbent was dependent upon the types of anions present in the aqueous phase. CO_3^{2-} was the most effective at promoting release. Sorptive removal of aqueous Cr(VI) by calcined hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$) was also achieved. Hydrotalcite's adsorptive capacity was 120 mg Cr/g [158].

5.9. Clay minerals and oxides

Clay minerals and oxides are widespread and abundant in both aquatic and terrestrial environments. Finally divided clay minerals and oxides exhibit large surface areas. Clay minerals and oxides adsorb cationic, anionic, and neutral metal species. They also take part in cationic and anionic exchange processes. Their sorption capacities, cation and anion exchange properties and binding energies vary widely. Many studies of Cr(III) and Cr(VI) removal from water by oxides and clay minerals were reported [159–166].

Benhammou et al. [159] investigated aqueous Cr(VI) adsorption onto Moroccan stevensite. Adsorption capacity of stevensite was improved by saturating it with ferrous iron Fe(II) and reduction with $Na_2S_2O_4$. The adsorption isotherms were described by the Dubinin–Radushkevich model. The sorption capacity for Cr(VI) increased from 13.7 (raw stevensite) to 48.86 mmol/kg

(modified stevensite) (Table 7). Higher Cr(VI) adsorption at low pH (2.0–5.0) was due to the reduction of Cr(VI) to Cr(III) by Fe(II) released from Fe-stevensite, and adsorption of Cr(III) onto the negatively charged stevensite.

Khan et al. [162] reported Cr(III) and Cr(VI) adsorption on bentonite. Sorption data were interpreted in terms of Freundlich, Langmuir and Dubinin–Raduskevich (D–R) equations. Lehmann et al. [163] studied chromate sorption from aqueous solutions using synthetic granulated goethite packed-bed columns. The bed-depth-service-time model was applied in order to model the column operation. The presence of EDTA decreased the removal efficiency of Cr(VI) due to competition for the same sorption sites.

Aqueous lead, nickel, chromium and copper adsorption on Palygorskite clay, mined in the Dwaalboom area of the Northern Province of South Africa, was studied [164]. The data fitted better to the Langmuir model than to the Freundlich model. The adsorption capacity was 58.5 mg Cr(VI) g^{-1} at a pH of 7.0 at 25 °C for clay particles of 125 μm. CrO_4^{2-} was the predominant form of Cr(VI) that was adsorbed by palygorskite.

5.9.1. Bauxite
Bauxite is an abundant minerals, widely used for alumina production by the Bayer process. Erdem et al. [167] tested heat-treated bauxite for Cr(VI) adsorption. The maximum removal of 64.9% was achieved at pH 2.0. At pH 2.0, the adsorbents surfaces were highly protonated, favoring the uptake of Cr(VI) as $HCrO_4^{-}$. Authors failed to quantify reduced form of Cr(VI).

5.9.2. Titanium(IV) oxide
Tel et al. [165] explored a hydrous titanium(IV) oxide for Cr(III) and Cr(VI) removal in batch mode. More than 99% of Cr(VI) was removed whereas less than 1% Cr(III) was adsorbed at pH 2.0. The Cr(VI) sorption data on hydrous TiO_2 at pH 2.0 was fitted with the Langmuir isotherm. The maximum sorption capacity of Cr(VI) was 5 mg/g (Table 7) but the Cr(III) sorption capacity was not reported. The adsorption mechanism was not determined. Cr(VI) adsorption on TiO_2 in presence and absence of humic acids was investigated [166]. Chromium adsorption capacity of TiO_2 was influenced by the presence of humic acid indicating a competitive adsorption on the active sites of titanium dioxide.

5.9.3. Aluminum oxide
Cr(III) adsorption on aluminum oxide was analyzed using the surface complexation model to describe the acid–base behavior of adsorbents and Cr(III) sorption [160]. Sorption increased with solution pH and was dependent on the initial chromium concentration. Increasing the ionic strength suppressed sorption onto silica and enhanced sorption onto aluminum oxide.

5.10. Alginate–goethite beads

Alginate–goethite beads were prepared by adding a dispersion of sodium alginate (1%, w/v) and goethite (2%, w/v) into a continuously stirred calcium chloride solution (0.3 mol/L) and these beads were used for Cr(VI) and Cr(III) removal from
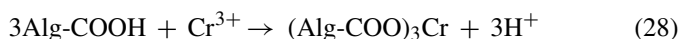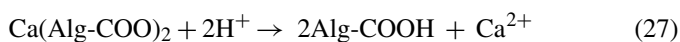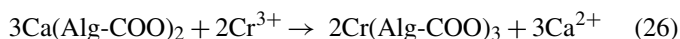
binary aqueous solutions [168]. Hexavalent chromium adsorption was favored at pH 2.0. The sorption capacity increased from 20.5 to 27.1 mg Cr/g sorbent by lowering the pH value from 4.0 to 2.0. This is due to the surface charge of goethite, which becomes more positive at pH values well below the point of zero charge (PZC). Contrary to Cr(VI), trivalent chromium loading was greater at higher pH values and increased by raising pH. The Cr(III) sorption capacity increased from 8.8 to 30.4 mg Cr/g sorbent by increasing pH from 2.0 to 4.0. Since the pK_H of alginate carboxyl groups is 4.6, at low pH these sites are neutral (–COOH, not –COO$^-$), so chromium is not easily bound to them.

The mechanism of hexavalent chromium uptake was explained by the following reaction:

$$\equiv SOH + HCrO_4^- + H^+ \rightarrow \equiv SOH_2^+ HCrO_4^- \quad (25)$$
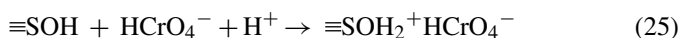
Cr(III) sorption by single alginate beads was governed by ion exchange. Ca-alginate beads at pH 3.0 undergo partial substitution of the calcium ions with protons. After exposure to low pH, calcium ions only remained in the electronegative cavities

of the G-blocks. The following mechanisms were proposed for Cr(III) sequestration:

$$3Ca(Alg\text{-}COO)_2 + 2Cr^{3+} \rightarrow 2Cr(Alg\text{-}COO)_3 + 3Ca^{2+} \quad (26)$$

$$Ca(Alg\text{-}COO)_2 + 2H^+ \rightarrow 2Alg\text{-}COOH + Ca^{2+} \quad (27)$$

$$3Alg\text{-}COOH + Cr^{3+} \rightarrow (Alg\text{-}COO)_3Cr + 3H^+ \quad (28)$$

The adsorption capacities at different temperatures and pH were calculated (Table 7).

Cr(VI) removal was also achieved by bio-polymeric beads prepared in two steps. By adding a mixture of sodium alginate (0.4 g) and gelatin (1.0 g) into a 0.05 M CaCl$_2$ solution under constant stirring [169]. The resulting beads were then allowed to harden in the CaCl$_2$ solution for 24 h. The beads were filtered, washed with distilled water and placed in a gluteraldehyde bath for overnight. They were again filtered and washed with distilled water. The optimum removal pH was 8.9 which is very unusual for Cr(VI) adsorption.
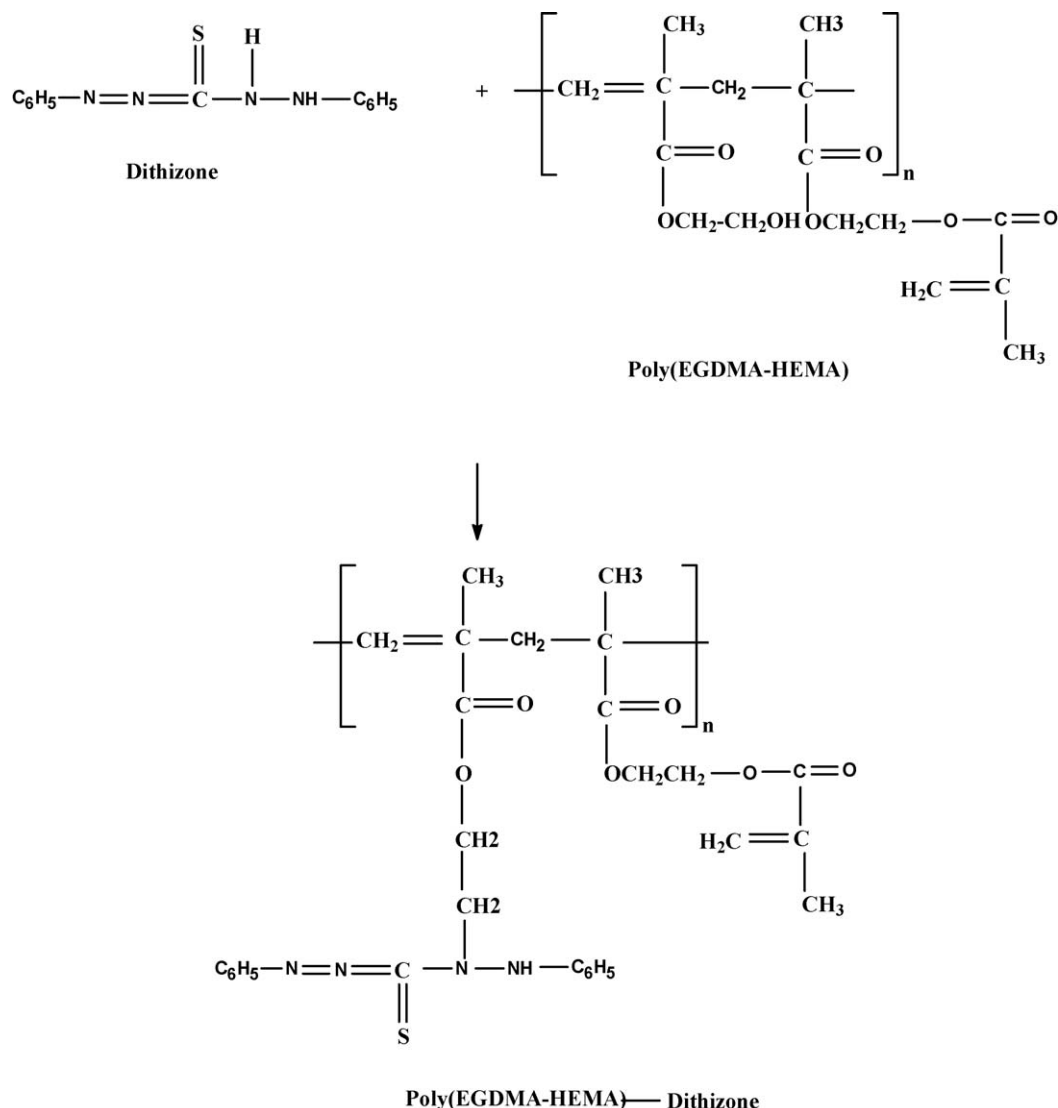
Fig. 9. Synthesis of dithizone-anchored poly(EGDMA-HEMA) microbeads.
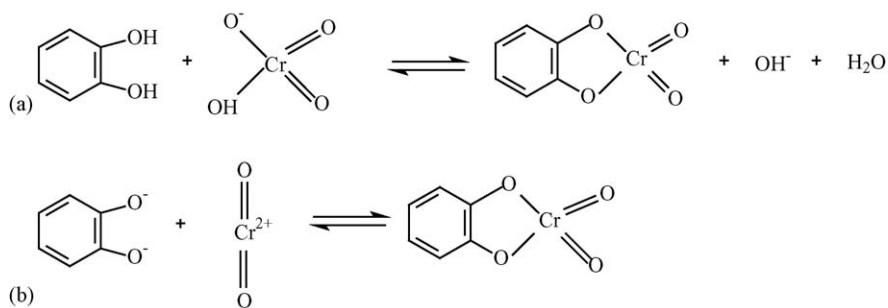
Fig. 10. Schematic structures of hexavalent chromium–catechol coupling in the PT gel: (a) the esterification between catechol and $HCrO_4^-$ and (b) the coupling between catechol anion and CrO_2^{2+}. *Source*: Nakajima and Baba [172].

Cr(III) uptake from water by protonated dry alginate beads was investigated [170]. The differences between the mechanisms which form the alginate beads and with metal uptake were demonstrated. Uptake was coupled with a release of protons, conforming ion exchange. The uptake was strongly dependent on solution pH up to ~4.5. At this pH the uptake was 112 mg Cr(III)/g of alginate beads (dry wt.). EPMA–EDX analysis of Cr-loaded beads showed a uniform distribution of chromic species throughout the structure of alginate beads, regardless of the solution pH. Dithiazone anchored to poly(EGDMA-HEMA) microbeads (Fig. 9) was prepared for chromium removal present at 25–500 ppm in the pH range from 2.0 to 8.0 [171]. The maximum Cr(III) adsorption capacity was 38.3 mg/g. Heavy metal ion desorption was achieved using 0.1 M HNO₃. The microbeads used repeatedly (>5 cycles) without noticeable loss of capacity.

5.11. Gels

Cr(VI) and Cr(III) adsorption by persimmon tannin (PT) gel [172] effectively removed Cr(VI) but smaller amounts of Cr(III). Maximum Cr(VI) adsorption occurred at pH 3.0. The gel which adsorbed Cr(VI) from solution (pH 1.0 and 3.0) showed no Cr(III) ESR signal, but this Cr(III) signal was observed in the residual solution at pH 1.0. Hexavalent chromium was adsorbed through chromate ester formation at catechol. Cr(VI) should combined with catechol as a hard acid, CrO_2^{2+} cation (Fig. 10).

Nakano et al. [173] explored Cr(VI) adsorption onto condensed-tannin gels derived from a natural polymer with many polyhydroxyphenyl groups for. The Cr(VI) sorption mechanism (Fig. 11) consists of four steps: (1) esterification of chromate with tannin molecules, (2) reduction of Cr(VI) to trivalent chromium Cr(III), (3) formation of carboxyl groups by tannin oxidation and (4) ion exchange of the reduced Cr(III) with the carboxyl and hydroxyl groups. A large proton consumption accompanied Cr(VI) reduction, permitting neutralization of the acidic Cr(VI) solution by choosing an appropriate initial pH. The carboxyl group created by tannin oxidation during reduction of Cr(VI) to Cr(III) contributed to an increase in the ion-exchange sites for the reduced Cr(III). Cr(VI) removal was optimized at 287 mg Cr/g dry tannin gel when the gel's water content was 0.77% and the initial pH 2.0.

Heitz et al. [174] examined chromium adsorption on cross-linked poly(acrylic acid) gels. Chromium adsorption increased with pH. Two adsorption mechanisms on the gel varied with pH.

At low pH chromium species are soluble. Adsorption occurred via ion binding throughout the gel. At higher pH, where insoluble chromium hydroxide particles are formed, surface adsorption occurred on the gel. Desorption depended on the retention mechanism and aging time of the polymer–chromium complex. Only partial desorption was achieved when retention occurred through ion-binding. Conversely, fast desorption took place where retention involved particle adsorption on the gel surface.

5.12. Polymers

Cellulosic graft copolymers were made by reacting bast fibers of the kenaf plant (*Hibiscus cannabinus*) with acrylonitrile
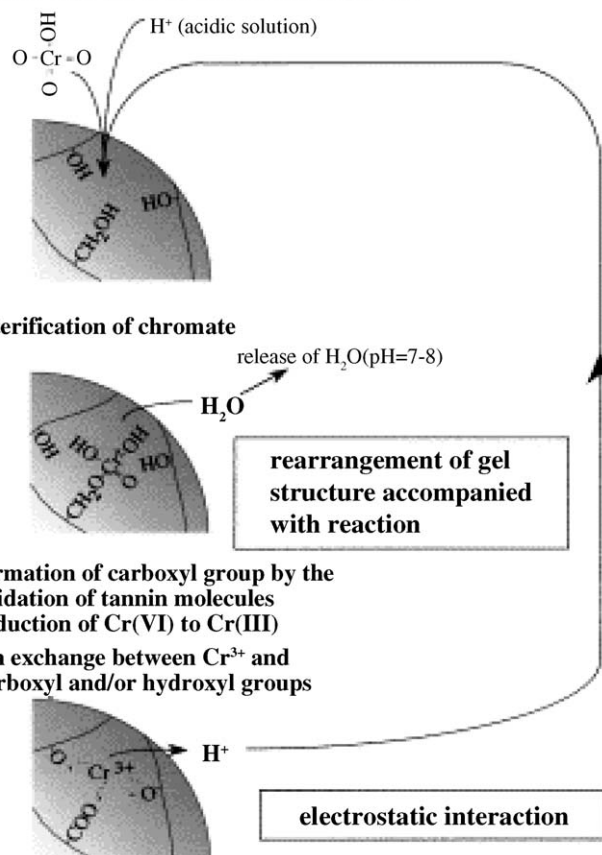
Fig. 11. Mechanism of removal of Cr(VI) by tannin gel particle. *Source*: Nakano et al. [173], with permission from Elsevier.
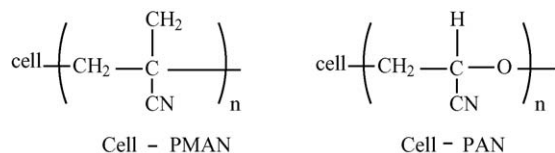
Fig. 12. *Source*: Eromosele and Bayero [175].

and methacrylonitrile monomers in aqueous media [175]. The cellulose–polyacrylonitrile (Cell–PAN) graft copolymer was a more effective Cr(III) sorbent than cellulose–polyacrylonitrile (Cell–PAN). The amount of Cr(III) sorbed decreased with an increase in the graft weight fraction. Increasing the graft percent from 38% to 149% lowered Cr(III) sorption in Cell–PAN by 56%.

The methyl groups in Cell–PMAN reduced the sorption affinity of the copolymer for Cr(III) (Fig. 12). The relative stabilities of the metal ion complexes with the hydroxyl and nitrile ligands appears to dominate the sorption processes. The maximum adsorption capacities were not calculated.

5.13. Industrial waste/by-products

Cr(III) and Cr(VI) adsorptive removal from water by Industrial waste/by-products has been explored. The most important of these adsorbents are fly ash [27,176–180], blast furnace slag [161,181], red mud [29,182], lignin [183–185], waste sludge [186–188], oil shale [189], tea factory waste [190], olive industry waste [191], waste tires [192] and residual slurry [193–195]. Some of the industrial by-products used for chromium remediation are discussed in the subsequent paragraphs.

5.13.1. Fly ash
For simplicity, fly ash used for chromium remediation has been subdivided based on its source.

5.13.1.1. Bagasse fly ash.
Bagasse fly ash, obtained from the sugar industry, was utilized for Cr(III) removal [176]. The waste bagasse fly ash costs about US$ $20.0\,t^{-1}$ including the cost of its purchase, transport, chemicals, electrical energy used in the adsorbent development and labor required. This cost is the lowest for any variety of carbon available in India. Activated carbon costs US$ $285.0\,t^{-1}$ in India for comparison. The optimum pH for Cr(III) adsorption on bagasse fly ash was 5.0. In an another study the bagasses fly ash was used for Cr(VI) remediation [27]. The sorption efficiency decreases with increase in pH. Adsorption of Cr(VI) on bagasse fly ash followed the Freundlich and Langmuir isotherms. The sorption capacity of this adsorbent for chromium removal was comparable to other low cost adsorbents.

Both raw bagasse and bagasse fly ash, a waste generated in sugar mills and boilers, respectively, and a powdered activated carbon were used for aqueous Cr(VI) removal in batch mode [177]. Raw bagasse was pretreated with 0.1N NaOH followed by 0.1N CH_3COOH before use. Various parameters were estimated and data were fitted to Langmuir, Freundlich and Bhattacharya and Venkobachar models [196] sorption models. Cr(VI) was strongly adsorbed at low pH and declined at higher pH range

in the case of powdered activated carbon (PAC). In case of raw and treated bagasse, maximum adsorption occurred at a pH of 6.0. Other studies carried out at bagasse fly ash gave maximum Cr(VI) adsorption in a very high acidic medium (pH 1.0–3.0).

5.13.1.2. Coal fly ash.
Coal combustion for power production produces huge amounts of by-product fly ash, whose disposal requires large quantities of land and water. Currently, coal fly ash applications are limited to civil engineering uses including cement and brick production and use in roadbeds. Resource recovery from coal fly ash is one of the most important issues in waste management worldwide. Since aluminosilicates are the components contained in fly ash, intensive efforts have been made to use it as an adsorbent.
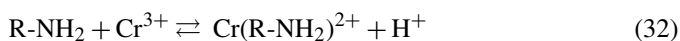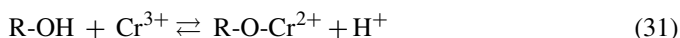
Bayat [178] studied aqueous Cr(VI) removal using two Turkish fly ashes; Afsin–Elbistan and Seyitomer. Cr(VI) adsorption was maximum at pH 4.0 for Afsin–Elbistan fly ash (25.46%) and pH 3.0 for Seyitomer fly ash (30.91%). The lime (crystalline CaO) content in fly ash seemed to significant influence Cr(VI) removal. The higher adsorption of Cr(VI) on fly ash at low pH was due to neutralization of negative surface charge by excess protons, facilitating the diffusion of dichromate ions and their adsorption on the adsorbent. No mention was made of any reduction of Cr(VI) into Cr(III). Banarjee et al. [179] also examined Cr(VI) removal by fly ash and impregnated fly ash. Impregnation of fly ash was carried out with 0.1 M $Al(NO_3)_3$ or 0.1 M $Fe(Cl)_3 \cdot Cr(VI)$ adsorbed on various fly ashes in the order fly ash < aluminum impregnated fly ash < iron impregnated fly ash. The most abundant surface functional group participating in the surface complexation reactions is the hydroxyl group. Surface hydroxyls are amphoteric and extremely reactive. The adsorption of Cr(VI) on hydrous metal oxide surface was explained on the basis of complex formation and ligand exchange reactions. The major adsorption schemes were given by the following reactions:

$$-SEOH + H^+ \leftrightarrow -SEOH_2^+ \tag{29}$$

$$-SEOH_2^+ + HCrO_4^- \leftrightarrow SEOH_2(HCrO_4)$$

$$\text{or } [SE(HCrO_4) + H_2O] \tag{30}$$
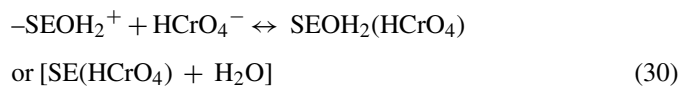
where, –SEOH is the surface hydroxyl site and SE = Si, Al, or Fe.

5.13.2. Waste sludges
Li et al. [186] utilized wine processing waste sludge as an effective adsorbent for aqueous Cr(III) removal. The sludge was characterized by scanning electron microscopy (SEM), energy dispersive X-rays (EDX) and IR spectroscopy. IR analysis identified R–COOH, R–OH and R–NH$_2$ functional groups, similar to those of the chitosan. The hydroxy and unprotonated amino groups served as coordination and electrostatic interaction sites to adsorb Cr(III). Following reactions were proposed for Cr(III) adsorption mechanism:

$$\text{R-OH} + Cr^{3+} \rightleftarrows \text{R-O-}Cr^{2+} + H^+ \tag{31}$$

$$\text{R-NH}_2 + Cr^{3+} \rightleftarrows Cr(\text{R-NH}_2)^{2+} + H^+ \tag{32}$$

Selvaraj et al. [187] explored distillery sludge for Cr(VI) removal. The Langmuir sorption capacity was 5.7 mg/g. Under acidic conditions, the protonated surface of the adsorbent (zeta potential pH$_{zpc}$ 5.9) attracts anionic Cr(VI) species. As the pH is increased above the adsorbent's zeta potential, the electrostatic attraction between the Cr(VI) species and the surface is reduced, with a consequent decrease in adsorption. The adsorbent efficiency was also tested in actual chromium plating wastewater.

Dried activated sludge immobilized on MowitalB30H resin was used to remove Cr(VI) in a continuous packed bed column [197]. The optimum pH was 1.0. The total adsorbed quantities, equilibrium uptakes and total Cr(VI) removal percents versus effluent volumes were determined by evaluating the breakthrough curves obtained at different flow-rates and inlet adsorbate concentrations for each sorbent. Cr(VI) uptakes dropped with rising flow-rates and rose with increasing Cr(VI) inlet concentrations for both immobilized dried activated sludge and granular activated carbon. Cr(VI) and Ni(II) adsorption, individually and in combination, by dried activated sludge was also studied [188]. The optimum initial pH for Cr(VI) adsorption alone was 1.0. The co-ion effect on the equilibrium uptake of Cr(VI) became more pronounced as the Ni(II) ion concentration increased and pH level increased. Sorption isotherms were developed for both single- and dual-metal ion systems. Cr(VI) adsorbed as an anionic form. Reduction of Cr(VI) into Cr(III) was not considered at low pH. Dried anaerobic activated sludge also adsorbed phenol and Cr(VI) individually and in combination [198]. The optimum initial adsorption pH for Cr(VI) was 1.0. Nonlinear Langmuir, Freundlich and Redlich–Peterson adsorption models were applied. Mono-component sorption equilibrium data were fitted to the non-competitive Freundlich and Redlich–Peterson models for both the components while the modified Freundlich model adequately predicted the multi-component sorption data.

5.13.3. Biogas residual slurry

Namasivayam and Yamuna [193,194] investigated Cr(VI) [193] and Cr(III) [194] removal from aqueous solutions using waste biogas residual slurry (BRS). The influence of metal ion concentration, contact time, adsorbent dosage, adsorbent particle size, temperature and pH on Cr(VI) removal was studied. The equilibrium data fitted both Langmuir and Freundlich isotherms. The optimum pH for Cr(VI) adsorption was 1.51. Cr(VI) did not reduce to Cr(III) at very low pH (highly acidic medium) (Table 9). The estimated concentrations of aqueous total chromium and Cr(VI) after adsorption were 30 and 40 mg/L Cr(VI) and 4.0 g/L adsorbed at pH 2.0 (Table 9). No reduction

from Cr(VI) to Cr(III) was observed at a Cr(VI) concentration of 40 mg/L. The concentration of Cr(III) formed (<4%) at 30 mg/L of Cr(VI) is not significant. The maximum adsorption capacity for Cr(III) (7.8 mg/g) occurred at pH 2.5.

5.13.4. Red mud

Red mud is a waste material formed during the alumina production when bauxite ore is subjected to caustic leaching [182]. A typical Bayer process plant generates a 1–2 tonnes red mud/t of alumina produced [29]. The toxicity, colloidal nature and large quantities of red mud particles create a serious pollution hazard. Improved disposal techniques are needed. There have been many proposals for red mud utilization. It is currently being used, in the manufacture of building materials and ceramics, as a filler in road asphalt and as a source of iron and various minerals. However, a large volume of red mud is dumped in holding ponds for which a large land area is required. Red mud has been explored as an alternate adsorbent for chromium [29]. The presence of other metal ions/surfactants effected the removal of Cr^{6+}. Freundlich and Langmuir models fit the sorption data. Column studies were also carried out. Cr^{6+} recovery and chemical regeneration of the spent columns have also been achieved. The maximum adsorption capacity for Cr(VI) by red mud was 22.67 mg/g.

5.13.5. Fertilizer waste or carbon slurries

A carbon slurry, generated as waste material in a naphtha-based ammonia plant, was tested for Cr(VI) removal from aqueous solution [195]. The optimum pH was 2.5. Cr(VI) adsorption increased at higher temperature (Table 7). Adsorbed chromium was recovered for reuse.

5.13.6. Blast furnace slag

Steel plants generate a large volume of granular blast furnace slag. It is being used as filler or in the production of slag cement. Recently this slag it was converted into an effective and economical scavenger and utilized for the remediation of aqueous chromium [161,181].

Slag was converted into an effective adsorbent for Cr(VI) removal [181]. Both batch and column studies were performed. Batch sorption and kinetic studies were investigated and the Langmuir and Freundlich constants and adsorption thermodynamics were evaluated. The bed-depth-service-time model (BDST) [199] was applied to column studies and parameters necessary for the design of a fixed bed reactor were evaluated. Metal recovery with simultaneous regeneration was also achieved. Erdem et al. [161] applied ferrochromium slag for Cr(VI) removal. The Cr(VI) concentration in water contacted with ferrochromium slag (W/FS = 10) was 0.61 mg/L after 50

Table 9
Aqueous concentrations of Cr before and after adsorption on biogas residual slurry (BRS) [193]

Before adsorption		After adsorption		
Initial [Cr(VI)] (mg/L)	Total [Cr] (mg/L)	[Cr(VI)] (mg/L)	[Cr(III)] (mg/L)	Percent Cr(III) formed
30	12.62	11.60	1.02	3.4
40	19.51	19.51	0	0

batches. Ten grams per liter ferrochromium slag dosage and 3.5 mL/L H_2SO_4 (5 M) were sufficient to reduce all Cr(VI) in the model solution containing 10 mg/L Cr(VI) during contact time of 60 min at 25 °C.

5.13.7. Lignin

Lignin is a major component of wood, accounting for 23–33% of softwood mass and 16–25% of hardwood mass [200]. It is an amorphous cross-linked resin which serves as main binder for the agglomeration of fibrous cellulosic components. Lignin also provides a shield against rapid microbial or fungal destruction of the cellulosic fibers. Lignin is a three-dimensional, highly branched, polyphenolic substance. It consists of an irregular array of variously bonded hydroxy- and methoxy-substituted phenylpropane units. Lignin is derived from photosynthesized glucose through a complicated enzymatic biosynthesis process. Lignins are very complex natural polymers with no precise single structure. A small representative section of lignin is presented (Fig. 13) illustrating typical chemical linkages and functional groups present. Physical and chemical properties of lignins differ depending on the extraction or isolation technology employed

to fragment and isolate them from cellulose/hemicellulose, etc.

Lignin, obtained as a by-product from the paper and pulp industry in the form of powder and beads was used for adsorption of Cr(III), Cr(VI), Pb(II) and Zn(II) from aqueous solutions [183,184]. Oxygen functionalities such as phenols, $-SO_3H$ groups present in lignin serve as sites for the metal cation exchange [183]. Adsorbed metals were desorbed using 10% sulfuric acid and then precipitated by adding alkali. Cr(III) and Cr(VI) adsorption on lignin was investigated [184]. Sorption was presumably due to the presence of multitude of ionic sites, both cations and anions (phenolic and carboxyl). No attempts were made to model the sorption data by Langmuir or Freundlich isotherms. Therefore, no adsorption capacity was reported. Ali et al. [185] also attempted to utilize waste lignin produced from the paper industry as a Cr(VI) removal adsorbent. The optimum pH was 3.0 with a 7 h contact time.

5.13.8. Miscellaneous

5.13.8.1. Residues from animal hides/skins.
Fathima et al. [202] used residues from animal hides/skins generated in leather processing for removing chromium. The residual flesh is high
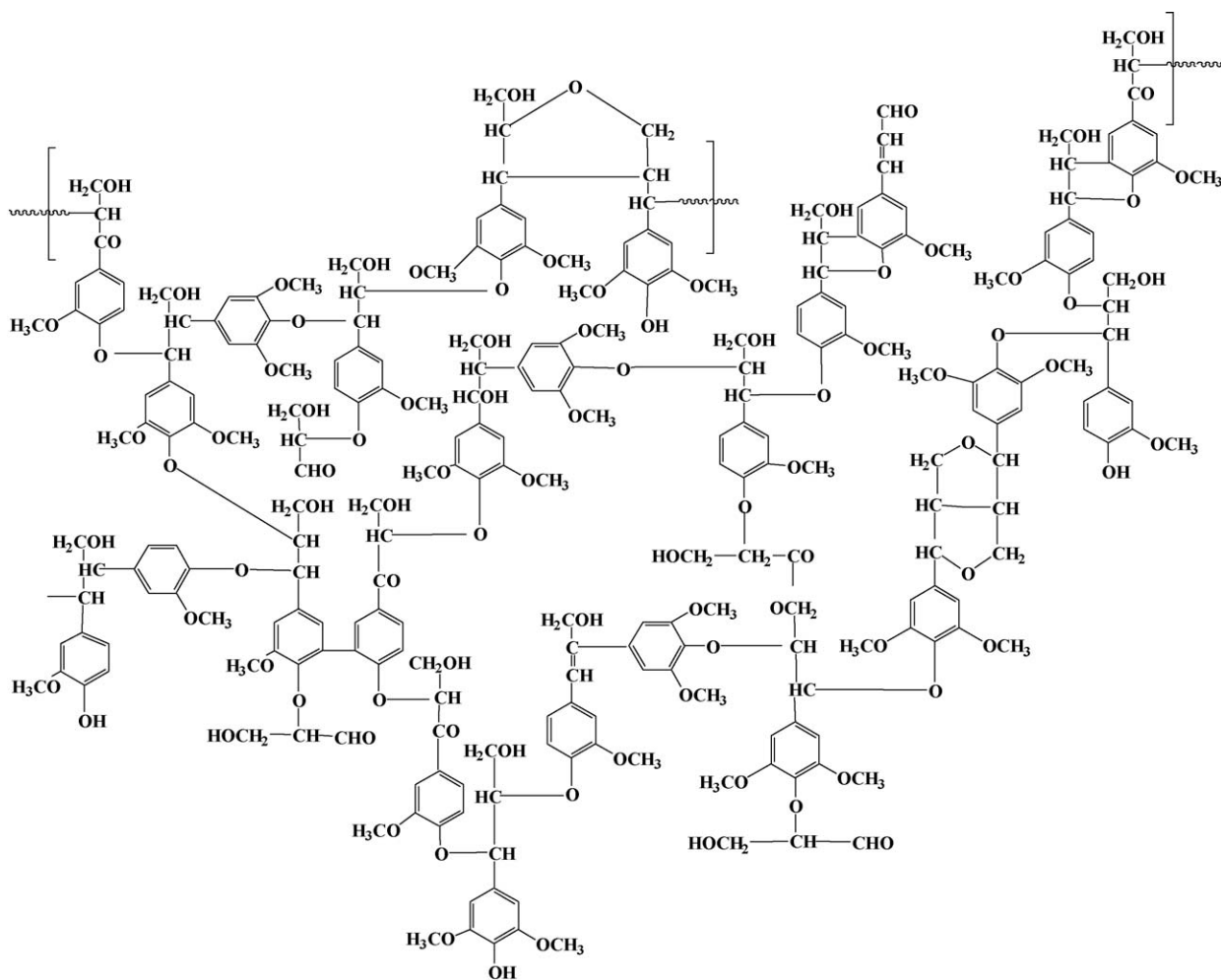
Fig. 13. Partial structure of a hardwood lignin molecule from European beech (*Fagus sylvatica*). The phenylpropanoid units that make up lignin are not linked in a simple, repeating way. The lignin of beech contains units derived from coniferyl alcohol, sinapyl alcohol, and *para*-coumaryl alcohol in the approximate ratio 100:70:7 and is typical of hardwood lignin. Softwood lignin contains relatively fewer sinapyl alcohol units. *Source*: Nimz [201].

in protein content. The raw residue was complexed with iron and utilized as an adsorbent for Cr(VI) removal. Iron treatment greatly improved Cr(VI) adsorption. The adsorption capacity of iron-treated residue was 51 mg chromium(VI)/g. This is much higher than that of the untreated residue (9 mg/g). X-ray photoelectron spectroscopic (XPS) studies verified iron was incorporated into the protein matrix. Shifts in XPS spectra suggested that dichromate binding occurred with iron at active adsorption sites and that iron-treated residues removed Cr(VI) without reducing it to chromium(III).

5.13.8.2. Pyrite fines. Studies of for aqueous Cr(VI) removal were conducted on dispersed pyrite fine particles [203]. Pyrite (an iron sulfide mineral), an efficient Cr(VI) reducing agent, produced hydroxo-Cr(III) species which precipitated onto the pyrite particles. The mechanism was examined by ζ-potential measurements and speciation studies. Promising results were obtained at pH $\sim$ 1.0–2.0.

5.13.8.3. Cement industry waste. Cement kiln dust was also used for chromium removal from tannery effluents [204]. The adsorption data were modeled by Langmuir, Freundlich and Redlich–Peterson isotherms. The maximum adsorption capacity of cement kiln dust was 33 mg/g. Industrial tannery effluent (22-mg/L chromium and COD 952 mg/L) was also treated by cement dust. The treated effluent (using 20 g cement dust/L) contains only 0.6 mg/L chromium and COD 200 mg/L. Thus, cement dust removed 98% of chromium and 80% of organic load.

5.14. Biosorbents

Biosorption is capable of removing traces of heavy metals from dilute aqueous solutions by living systems. Dead biomass can also be used. Algae, fungi and bacteria are examples of biomass-derived metal sorbents. Adsorption studies on several metals have produced encouraging results. Gadd [205] and Brierley [206] reviewed how bacteria, fungi and algae take up toxic metal ions. Heavy metal ion uptake into the cellular structure is followed by sorption onto biomolecule binding sites. This uptake is independent of biological metabolism and is known as "biosorption" or "passive uptake". Metal uptake can also involve active metabolic passage across the cell membrane into the cell. This is referred to as "active uptake". The combination of active and passive modes is called "bioaccumulation". Metal uptake by dead cells takes place only by the passive mode. Living cells employ both active and passive modes for heavy metal uptake. Living and dead fungi cell removal of may offer alternative methods for wastewater remediation.

The use of fungal biosorbents for heavy metals remediation has been reviewed [39]. A range of equilibrium sorption, and diffusion and sorption models in different reactor systems were reviewed to correlate fungal biosorption experimental data. Fungi are used in many industrial fermentation processes. Therefore, these processes could serve as an economical source of biosorbent for chromium [Cr(III) and Cr(VI)] removal. Fungi can also be easily grown in substantial amounts using unsophis-

ticated fermentation techniques and inexpensive growth media. Various chemical groups have been proposed to contribute to biosorption metal binding by algae, bacteria, fungi, etc. These include hydroxyl, carbonyl, carboxyl, sulfhydryl, thoether, sulfonate, amine, imine, amide, imidazol, phosphonate and phosphodiester groups [207].

Biosorption of chromium from aqueous solutions was investigated by passive binding to nonliving biomass. Different biosorbents including fungi, algae, bacteria, plants were explored for chromium and other heavy metals.

Reviews are available that deal with biosorption by different types of biomass including algae, fungi, bacteria, plants, etc. [37–39,41,208–210]. This section is devoted to biosorption of both Cr(VI) and Cr(III) on various biosorbents. Sorption mechanisms are discussed and capacities are compared. For simplicity the biosorbents have been subdivided into the following categories:

1. algae;
2. fungi;
3. bacteria;
4. plants;
5. wood, grasses, compost, peat moss.

5.14.1. Algae

Algae include a large and diverse assemblage of organisms that contain chlorophyll and carry out oxygenic photosynthesis. Algae are classified on the nature of the chlorophyll(s), the cell wall chemistry, and flagellation. All types of algae contain chlorophyll *a*. However, the presence of phytopigments other than chlorophyll *a* is characteristic of each particular algal division. Alge used for chromium remediation include *Spirogyra* [211], *Chlamydomonas reinhardtii* [212], *Dunaliella* [213], *Chlorella vulgaris* [214], *Chlorella vulgaris* [215], *C. vulgaris* [216,217], *Chlorella vulgaris*, *Clodophara crispata* [218,219], *Sargassum wightii* [220], *Ecklonia* sp. [221,222].

Gupta et al. [211] studied Cr(VI) biosorption by biomass of filamentous algae *Spirogyra* species. Equilibrium isotherms were obtained and maximum removal of Cr(VI) was $\sim$1.47 g metal/kg of dry weight biomass at pH of 2.0 (Table 7).

Arıca and Bayramoğlu [212] reported Cr(VI) biosorption onto native, heat- and acid-treated *Chlamydomonas reinhardtii*. The maximum Cr(VI) absorption was obtained at pH 2.0. The biosorption capacities of native, heat- and acid-treated algal preparations were 18.2, 25.6 and 21.2 mg Cr(VI)/g of dry biosorbents, respectively (Table 7). All algal preparations could be regenerated using 0.1 M NaOH solution, with up to 96% recovery of the adsorption ability. This microalgae cell wall contains a high amount of polysaccharides, some of which are associated with proteins and other components. These bio-macromolecules contain such functional groups as amino, carboxyl, thiol, sulfydryl, and phosphate groups. At pH 1.0–2.0, protonation of cell wall amino groups enhanced the biosorption capacities of the biosorbents to Cr(VI) ions. The increased binding of Cr(VI) containing anions at low pH was due to electrostatic binding to

the positively charged protonated amine groups. Authors did not establish if the Cr(VI) anions had been reduced to Cr(III).

The Cr(VI) biosorption from saline solutions on two strains of living *Dunaliella* algae were tested as a function of pH, initial metal ion and salt (NaCl) concentrations [213]. The biosorption capacity of both *Dunaliella* strains was obtained at pH 2.0 in both the absence and presence of increasing salt concentrations. Equilibrium uptakes of Cr(VI) decreased as salt concentrations went up for both the sorbents. Both the Freundlich and Langmuir models were used to describe Cr(VI) biosorption with and without salt present by both algal species.

Dönmez et al. [215] removed Cr(VI) by adsorption on dried *Chlorella vulgaris*, *Scenedesmus obliquus* and *Synechocystis* sp. algae. Optimum Cr(VI) adsorption occurred at pH 2.0 for all three algae. Both the Freundlich and Langmuir models suitably for described the short-term biosorption of copper(II), nickel(II) and Cr(VI) by all the algal species. Authors did not discuss any sorption mechanism by considering different forms of Cr(VI) existing at low pH.

Aksu and Açikel [214] explored the competitive biosorption of iron(III) and Cr(VI) on *Chlorella vulgaris* from a binary metal mixture in a single-staged batch reactor at pH 2.0. The sorption data was modeled by the competitive, multi-component Langmuir isotherm and this expression was used for calculating each residual or adsorbed metal ion concentration at equilibrium ($C_{eq,i}$ or $C_{ad,eq,i}$) for a constant V_0/X_0 ratio for a specific heavy metal ion combinations in a single-staged batch reactor. Experimental $C_{eq,i}$ and $C_{ad,eq,i}$ values were compared with calculated and graphically determined values. Aksu and Açikel [217] reported the simultaneous biosorption of Cu(II) and Cr(VI) by *C. vulgaris* at their optimum pH values of 2.0 and 4.0, respectively. The sorption phenomenon was expressed by competitive, multi-component Freundlich isotherm. Simultaneous biosorption of Cu(II) and Cr(VI) from binary metal ions mixtures was compared with the biosorption of each of the single metal ions [216]. Adsorption isotherms were developed for both single- and dual-metal ion systems at both pH 2.0 and 4.0 and expressed by the mono- and multicomponent Langmuir and Freundlich adsorption models. Model parameters were estimated by non-linear regression.

Nourbakhsh et al. [218] investigated Cr(VI) biosorption onto non-living biomass from *Chlorella vulgaris*, *Clodophara crispata*, *Zoogloea ramigera*, *Rhizopus arrhizus* and *Saccharomyces cerevisiae*. The optimum initial pH was 1.0–2.0 for all five microorganisms. Maximum metal ion adsorption rates onto microbial biomass were obtained from 25 to 35 °C.

Aravindhan et al. [220] utilized the abundant brown seaweed *Sargassum wightii* for chromium removal. A simulated chrome tanning solution was used for standardizing of experimental trials. Chemical modification of the seaweed through sulfuric acid, magnesium chloride, and calcium chloride pretreatment led to improved chromium uptake. Adsorption measurements on various quantities of seaweed have been fitted to Langmuir and Freundlich isotherms. The optimum pH was 3.5–3.8. The *Sargassum* species exhibited a maximum uptake of 35 mg chromium/g of seaweed (Table 1). The same group further investigated using brown seaweed (*Turbinaria* spp.), which had

been pre-treated with sulfuric acid, calcium chloride and magnesium chloride, to remove chromium from tannery wastewater [223]. Protonated seaweeds gave chromium uptake than seaweed treated with calcium and magnesium. Chromium uptake was optimal at pH 3.5. *Turbinaria* exhibited a maximum uptake of about 31 mg of chromium for 1 g of seaweed at an initial chromium concentration of 1000 ppm. Freundlich and Langmuir adsorption isotherm models described the biosorption of chromium(III) by *Turbinaria* spp.

Park et al. [221] utilized the protonated brown seaweed, *Ecklonia* sp., for remediating Cr(VI). When wastewater containing Cr(VI) was placed in contact with this biomass, the Cr(VI) was completely reduced to Cr(III). The converted Cr(III) appeared in solution or was partly bound to the biomass. The Cr(VI) removal efficiency was always 100% in the pH range of 1.0–5.0. A 1.15 mol protons/mol of Cr(VI) were consumed. The rate of Cr(VI) reduction increased with decreasing the pH. An optimum pH existed for total chromium (Cr(VI) plus Cr(III)) removal. This pH increased with contact time, eventually reaching approximately pH 4.0 when the reaction was complete. Cr(VI) reduction is accompanied by oxidation of the organic compounds in the biomass. The sorption capacity of *Ecklonia* sp. the was 4.49 mmol Cr(VI)/g.

Protonated *Ecklonia* sp. was also utilized for Cr(III) adsorption [222]. Protonated *Ecklonia* sp. contains at least three types of functional groups. Fourier transform infrared spectroscopy showed that the carboxyl group was the chromium-binding site within the pH range of 1.0–5.0. Cr(III) did not precipitate in this range. The pK_a value and the number of carboxyl groups were estimated as 4.6 and 2.2 mmol/g, respectively. A model describing chromium biosorption was also developed incorporating known chromium aqueous hydrolysis reactions.

Carmona et al. [224] studied Cr(III) and Cr(VI) removal separately using a 2^3 factorial experimental design. The three factors considered were pH, temperature, and metal concentration at two different levels: Cr(III), pH (2.0 and 6.0), temperature (29 and 55 °C), and metal concentration (10 and 1200 mg/L); Cr(VI), pH (1.0 and 3.0), temperature (29 and 55 °C), and metal concentration (10 and 1200 mg/L). Batch experiments were carried out. The results were analyzed statistically using the Student's t-test, analysis of variance, F-test, and lack of fit to define the most important process variables affecting the metal removal efficiency. The most significant effect on Cr^{3+} uptake was the interaction between metal concentration and pH. The most significant effect for Cr(VI) uptake was metal concentration. Factorial design allowed the identification of the most important Cr(III) and Cr(VI) biosorption parameters and within the range of conditions tested. The interaction between concentration and pH was most significant effect on Cr(III) adsorption.

5.14.2. Fungi

Fungi and yeast accumulate the non-nutrient metals cadmium, mercury, lead, chromium, etc., in substantial amounts. Both living and dead fungal cells possess a remarkable ability for toxic and precious metals uptake from water/wastewater. The fungi and yeast can be grown in substantial amounts using unso-

phisticated fermentation techniques and inexpensive growth media. Fungal biosorbent use in heavy metals removal has been reviewed [38,39]. Equilibrium sorption and diffusion models in different reactor systems were reviewed to correlate experimental fungal biosorption data. Fungi are used in a variety of industrial fermentation processes. These processes could serve as economical biomass supply sources for the removal of metal ions. Therefore, fungal biomass could serve as an economical means for metal ion removal/recovery of from aqueous solutions.

Various types of fungal biomass have been used for the removal and recovery of tri and hexavalent chromium from water/wastewater. These include unmethylated and methylated yeast [225], *R. arrhizus* [226], *R. arrhizus* [227], *Penicillium chrysogenum* [228], dead fungal biomass [229], *Lentinus sajorcaju* mycelia [212,230], *R. nigricans* [231–233], *Neurospora crassa* [234].

Seki et al. [225] applied unmethylated and methylated yeast (MeYE) to the adsorptive separation of Cr(VI) and As(V) anions from aqueous solutions. Cr(VI) and As(V) anions were scarcely adsorbed onto unmethylated yeast biomass at pH ∼ 7.0 but the amounts adsorbed increased with increasing methylation degree. The amount of Cr(VI) adsorbed onto MeYE was almost constant at pH 4.0–6.0 and decreased a pH was raised above pH 6.0. A metal-binding model described the adsorption characteristics of both Cr(VI) and As(V) on MeYE. Adsorption capacities were not reported.

Prakasham et al. [226] investigated Cr(VI) biosorption at pH 2.0 by non-living free and immobilized biomass from *R. arrhizus.* A biphasic Cr(VI) adsorption pattern was observed. Cr(VI) removal rates were slightly higher when employing the free biomass than the immobilized state. Free and immobilized *R. arrhizus* biomass adsorption capacities were 11 and 8.63 mg/g, respectively. Competitive biosorption of Cr(VI) and Fe(III) on *R. arrhizus* from binary mixtures was studied and compared to the single metal–ion systems [227]. Both Cr(VI) and Fe(III) were effectively adsorbed by the biomass at very low pH values. The optimum initial pH for Cr(VI) and Fe(III) ions by *R. arrhizus* was 2.0. Cr(VI) and Fe(III) adsorption increased as temperature increased (Table 7). Equilibrium data fitted the non-competitive Langmuir model when single ion adsorption was conducted. For multi-component adsorption, the competitive Langmuir model was consistent with the observed uptake of Cr(VI) and Fe(III) ions.

Deng and Ting [228] modified *Penicillium chrysogenum* fungal biomass by grafting polyethylenimine (PEI) onto the biomass surface in a two-step reaction. This adsorbent acquires a positive charge due to protonation of amine functions at low pHs. The presence of PEI on the biomass surface was verified by FT-IR and X-ray photoelectron spectroscopy (XPS) analyses. Schematic diagram illustrating the process of grafting branched PEI onto the biomass surface is presented in Fig. 14. The high density of amine groups in the PEI chains bound to the surface possessed a positive zeta potential at pH below 10.4. This led to a high sorption capacity for anionic Cr(VI). The maximum sorption capacity for Cr(VI) at pH 4.3–5.5 was 5.37 mmol/g. XPS confirmed Cr(III) on the biomass surface in the pH range 2.5–10.5, suggesting that Cr(VI) anions were reduced to Cr(III) during the sorption. Electrostatic interaction, chelation, and precipitation were likely to be involved in the chromium sorption on the PEI-modified biomass.

Sekhar et al. [229] explored dead fungal biomass for calcium, iron, nickel and Cr(III) removal in single and multicomponent systems. The maximum uptake was dependent on solution pH (4.0–5.0 for Fe, 4.0–7.0 for Ca, 6.0–7.0 for Ni and 6 for Cr) and increased with biomass loading up to 10 g/L. The adsorption capacity order was Ca > Cr(III) > Ni > Fe > Cr(VI). The presence of co-ions in binary, ternary and quarternary combinations decreased the each metal's metal uptake. Ni uptake was the most significantly affected while that of Cr(VI) the least.

Aqueous Cr(VI) biosorption onto untreated and heat-, acid- and alkali-treated *Lentinus sajor-caju* mycelia was studied [230]. Fungal mycelia particle sizes ranged from 100 to 200 μm. The effects of pH, temperature, biosorbent dose, initial Cr(VI) concentration and contact time were investigated. The surface charge density of the fungal preparations varied with pH, and the maximum Cr(VI) absorption on the fungal preparations occurred at pH 2.0. The maximum biosorption capacities of the untreated and heat-, HCl- and NaOH-treated fungal biomass were 0.36, 0.61, 0.48 and 0.51 mmol Cr(VI)/g of dry biomass, respectively.

Bai and Abraham [231] investigated Cr(VI) biosorption on immobilized *R. nigricans* The biomass was immobilized and evaluated for aqueous Cr(VI) adsorption, mechanical stability to desorbents, and reuse in successive cycles. Five different polymeric matrices, viz. calcium alginate, polyvinyl alcohol (PVA), polyacrylamide, polyisoprene, and polysulfone were employed to entrap finely powdered biomass. These sorbents were compared for biosorption efficiency and stability to desorbents. Physical immobilization onto polyurethane foam and coir fiber was less efficient than polymer entrapment methods. Different biomass dose combinations (%, w/v) for each matrix were compared. The optimum doses were 8% (calcium alginate), 6% (polyacrylamide and PVA), 12% (polyisoprene), and 10% (polysulfone). The Cr sorption capacity of all immobilized biomass samples was less than that of the native, powdered biomass and followed the order: free biomass > polysulfone
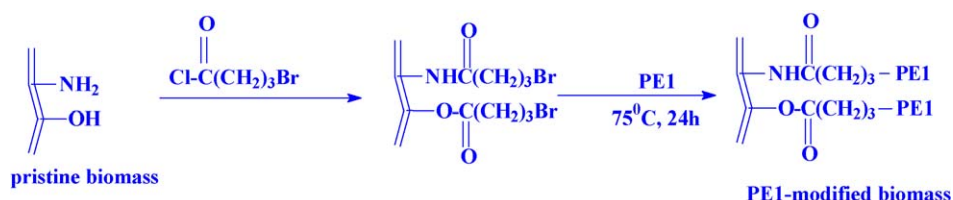

Fig. 14. Schematic diagram illustrating the grafting process of branched PEI on the biomass surface. *Source*: Ref. [228].

entrapped > polyisoprene immobilized > PVA immobilized > calcium alginate entrapped > polyacrylamide, at 500 mg/L concentration of Cr(VI). The mechanical stabilities and chemical resistances decreased in the order: polysulfone > polyisoprene > PVA > polyacrylamide > calcium alginate. Adsorbed Cr(VI) was eluted using 0.01N NaOH, NaHCO$_3$, and Na$_2$CO$_3$. Sorption data were analyzed using the Freundlich isotherm model. Biomass beads were regenerated and reused in more than 25-successive sorption–desorption cycles and the regeneration efficiency was 75–78%. No attempts were made to elucidate the Cr(VI) adsorption mechanism.

Chemically modified and polysulfone-immobilized *R. nigricans* fungal biomass samples were used for Cr(VI) removal in continuous systems. Packed bed, fluidized bed and stirred tank reactors were used [231]. Maximum removal efficiency (mg Cr/g biomass) was achieved in the stirred tank reactor (159.3), followed by the fluidized reactor (153.0) and the packed bed reactor (123.3). The same group [232], explored Cr(VI) biosorption onto chemically modified *R. nigricans* and the Cr complexation mechanism to the adsorbent. The cell wall of this fungus possesses strong complexing properties which effectively remove Cr(VI) anions from wastewater. The mechanism of Cr(VI) adsorption by *R. nigricans* was ascertained by chemically modifying of the dead biomass followed by FT-IR spectroscopic analysis the cell wall constituents. Treatment with mild alkalis (0.01N NaOH and aqueous ammonia) and formaldehyde (10%, w/v) deteriorated the biosorption efficiency. However, extraction of the biomass powder in acids (0.1N HCl and H$_2$SO$_4$), alcohols (50% (v/v), CH$_3$OH and C$_2$H$_5$OH) or acetone (50%, v/v) improved the Cr uptake capacity. Acetylation of cell wall amino groups with acetic anhydride reduced the biosorption potential drastically. Blocking –COOH groups by treatment with water-soluble carbodiimide also resulted in an initial lag in Cr binding. Biomass modifications using cetyl trimethyl ammonium bromide (CTAB), polyethylenimine (PEI), and amino propyl trimethoxy silane (APTS) each improved biosorption efficiency to exceptionally high levels. The FT-IR spectroscopic analysis of the native, Cr(VI) bound and the other types of chemically modified biomass indicated the involvement of amino groups of *Rhizopus* cell wall in Cr(VI) binding.

Tunali et al. [234] studied batch Cr(VI) removal from aqueous solutions by live and pretreated *Neurospora crassa* fungal biomass. Heat, sodium hydroxide and acetic acid pretreatments enhanced the biosorption capacity compared with the native biomass. Acetic acid pretreatment caused the largest increase of biosorption ability of all the pretreatments (Table 7). Surface bioaccumulation of Cr(VI) species was confirmed by FT-IR, SEM and EDAX analysis. Desorption and reusability studies demonstrated effective biosorbent regeneration using 10 mM NaOH up to 95% recovery in five successive biosorption–desorption cycles. The biosorption mechanism was studied by infrared spectroscopy, scanning electron microscopy and X-ray energy dispersion analysis.

The use of the free and immobilized *Lentinus sajor-caju* mycelia (in carboxymethylcellulose (CMC)) to remove aqueous Cr(VI) was evaluated [212]. The CMC immobilized fungus mycelia were incubated for the uniform growth on the bead sur-

faces at 30 °C for 3 days. The highest biosorption of Cr(VI) occurred at pH ∼ 2.0. The maximum biosorption capacities for the free and immobilized fungus were 18.9 and 32.2 mg/g dry weights, respectively (Table 7). The biosorbent was regenerated using 0.1 M NaOH, with more than 95% Cr(VI) recovery. These biosorbents were reused through five biosorption–desorption cycles with little loss of biosorption capacity.

A pure strain of *M. hiemalis* employed for aqueous Cr(VI) remediation exhibited an uptake of 53.5 mg/g at an initial pH of 2.0 (Table 7) [235]. Equilibrium data fitted well to Langmuir isotherm model. Cr(VI) biosorption onto *M. hiemalis* was endothermic. Nearly 99% of the adsorbed Cr(VI) was desorbed using 0.1N NaOH. *M. hiemalis* retained its adsorption activity after five batch sorption/desorption cycles. At pH 2.0, the negative chromate ions interact more strongly with the positively charged functional groups of *M. hiemalis* resulting in high Cr(VI) uptake. The authors did not quantify reduction of Cr(VI) into Cr(III) at low pH.

Most reports of aqueous Cr(VI) biosorption by dead fungal biomass have claimed that Cr(VI) was removed by "anionic adsorption" [218,226,227,231–233,236,237]. Zhao and Duncan [238] observed "partial reduction along with anion adsorption" in a column packed with formaldehyde cross-linked *Saccharomyces cerevisiae*. Park et al. [239] however, suggested that these findings were misinterpreted due to errors in measuring total Cr in aqueous solution and insufficient contact time required for equilibrium resulting from the lack of information about the valence state of Cr bound on the biomass. Park demonstrated that Cr(VI) is reduced to Cr(III), and completely removed from aqueous solution if sufficient experimental contact time is given. Furthermore, desorption and XPS studies indicated that most of the Cr bound to the biomass was Cr(III), implying that the Cr(VI) removal occurs via a "redox reaction". Park et al. [239] proposed a new Cr(VI) removal mechanism for the dead *A. niger* fungal biomass. Aqueous Cr(VI) can be removed through the two mechanisms: I and II in Fig. 15. In mechanism I, aqueous Cr(VI) is directly reduced to Cr(III) upon contact with the biomass. Mechanism II consists of three steps which include: (1) binding Cr(VI) to positively charged groups such as protonated amines present in the chitin and chitosan fungal cell wall components; (2) reduction of Cr(VI) to Cr(III) by adjacent functional groups having lower reduction potentials than that of Cr(VI); (3) the release of reduced Cr(III) into the aqueous solution by electronic repulsion between the positively charged groups and the Cr(III) ion. Since protons are consumed in each mechanism, the solution pH increases during Cr(VI) removal by the dead fungal biomass. Therefore, supplying protons promotes the rate and efficiency of Cr(VI) removal. Solution pH of water/wastewaters contaminated with chromium is generally very acidic in accord with this need [240].

Park et al. [241] also reported Cr(VI) removal by *A. niger*, *R. oryzae* and *P. chrysogenum*. *R. oryzae* completely removed Cr(VI) in 48 h, while the other species needed 218–254 h for the complete Cr(VI) removal. The initial Cr(VI) removal rate by *S. cerevisiae* was faster than that by *A. niger*, but the former required more contact time than the latter to completely remove Cr(VI) from aqueous solution. This suggests the design of a
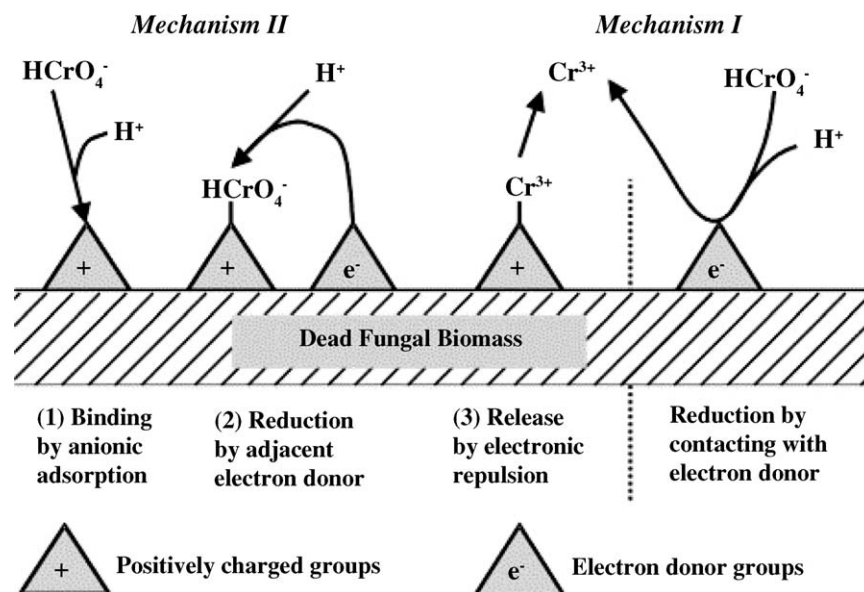
Fig. 15. Mechanism for Cr(VI) removal by the dead fungal biomass. *Source*: Park et al. [239] with permission from Elsevier.

two stage process where *S. cerevisiae* adsorption is followed by *A. niger* treatment. Park et al. [242] also studied the chromium biosorption by chemically treated brown seaweed biomass from *Ecklonia* sp., which was collected along the Pohang seashore in Korea. This biomass was treated acids, alkalis, formaldehyde (HCHO), formic acid and other chemicals. Acid-treatment produced the most favorable improvement of the aqueous Cr(VI) removal rate, while the organic solvent-treatment significantly improved the total chromium removal efficiency at equilibrium. FT-IR spectroscopy revealed that the amino and carboxyl groups were involved in Cr(VI) removal. The methylation of the amino groups significantly decreased the Cr(VI) removal rate, but amination of the carboxyl groups significantly increased the Cr(VI) removal rate. Amino groups enhance Cr(VI) removal. Meanwhile, esterification of the carboxyl groups and carboxylation of the amino groups to slowed Cr(VI) removal. Carboxyl group estrification produced a greater drop in rate than the latter. This suggests that carboxyl groups also contribute to Cr(VI) removal, but less strongly than amino groups. In conclusion, Cr(VI) is removed from the aqueous phase through both direct and indirect reduction mechanisms. Amino and carboxyl groups, take part in the indirect reduction, increasing the Cr(VI) removal rate. However, little information exists about the electron-donor and Cr-binding groups on the biomass. The components which reduce and bind Cr(VI) are now being studied. The effects of ionic strength, background electrolytes, heavy metals and redox-active species on the reduction of hexavalent chromium by *Ecklonia* biomass were also investigated by Park et al. [243].

Bingol et al. [244] reported CrO_4^{2-} removal from aqueous solution by a cationic surfactant-modified yeast. Cetyl trimethyl ammonium bromide (CTAB) was used for biomass modification. It substantially improved the biosorption efficiency. The biosorption of chromate anions by modified yeast was strongly affected by pH. The optimum pH for biosorption of CrO_4^{2-} onto modified yeast was 4.5–5.5.

5.14.3. Bacteria

The use of bacteria for bioadsorption is a fast growing field in metal remediation because of their ubiquity, ability to grow under controlled conditions and smaller size, which leads to high surface area and fast rates. *Zoogloea ramigera* [218], *Bacillus* sp. [219], *Aeromonas caviae* [245,246], *thuringiensis* [247], *Pantoea* sp. [248], *Aeromonas caviae* have been used for chromium remediation.

Nourbakhsh et al. [219] reported Cr^{6+}, Pb^{2+} and Cu^{2+} biosorption on *Bacillus* sp. in single and multi-component systems. In multicomponent solutions, lead biosorption increased widely while Cr(VI) and Cu(II) biosorption decreased versus their amounts in single metal ion systems. Loukidou et al. [245,246] explored aqueous Cr(VI) removal by *Aeromonas caviae* biomass particles, isolated from potable groundwater supplies. The optimum pH was 2.5 and the maximum adsorption capacity was 284.4 mg/g (Table 7).

Şahin and Öztürk [247] investigated Cr(VI) biosorption on a mixture of dried vegetative cells and spore–crystals of *Bacillus thuringiensis* var. *thuringiensis*. Batch studies were conducted as a function of pH, initial metal ion concentration and temperature. The optimum pH for Cr(VI) adsorption was 2.0. The sorption data fitted to both Langmuir and Freundlich isotherms. No attempt was made to elucidate a dominating mechanism.

Ozdemir et al. [248] and Ozdemir and Baysal [249] utilized a gram-negative bacterium *Pantoea* sp. TEM18 for Cr(VI), Cu(II), Cd(II) removal. Optimum Cr(VI) adsorption occurred at pH 3.0. Both the Freundlich and Langmuir sorption models were suitable for describing the short-term biosorption of Cr(VI) by *Pantoea* sp. TEM18. No sorption mechanism was provided.

Aeromonas caviae, a gram-negative bacteria, isolated from the water wells near Thessaloniki (North Greece), were employed for aqueous Cr(VI) removal [246]. Protonation of functional groups (e.g. carboxyl and amino groups) gives an overall biomass positive charge at 2.5 which enabled adsorption

of negatively charged heavy metal ions. No attempt at quantification of Cr(III) at low pH was reported.

Rabbani et al. [250] investigated 17 different bacterial strains isolated from Ramsar warm springs in Iran for Cr(III) remediation. A strain of gram-positive cocobacilli bacteria was highly efficient at Cr^{3+} biosorption. The maximum removal (100%) of 10 ppm Cr(III) occurred at pH 4.0 and 1 h contact time. An isolate (isolate TKW) of sulfate-reducing bacteria (SRB) was obtained from metal-contaminated marine sediments of Tokwawan, Hong Kong and utilized for the enzymatic reduction of hexavalent chromium into less toxic and insoluble trivalent chromium (Cr^{3+}) under anaerobic conditions. The enrichment consortium almost completely (98.5%) reduced 0.6 mM Cr^{6+} in 168 h and the reduction rate was $0.5 \, g \, (Cr^{6+}) \, g \, (protein)^{-1} \, h^{-1}$ [251].

Ozdemir and Baysal [249] examined Cr(VI) biosorption by *Chryseomonas luteola* TEM05. This optimum adsorption pH was 4.0. The adsorption capacity appears to be significantly higher for the Al(III) than for Cr(VI). Langmuir parameters from *C. luteola* TEM05 adsorption indicated a maximum adsorption capacity of 3.0 mg/g.

5.14.4. Plants

Chromium remediation was examined by various plants, including *Fagus orientalis* L. [252], *Agave lechuguilla* [253,254], *Atriplex canescens* [255], *Thuja oriantalis* [256], larrea tridentate [257], *Pinus sylvestris* [258].

Acar and Malkoc [252] explored the use of beech (*Fagus orientalis* L.) sawdust for aqueous Cr(VI) removal in batch experiments. Maximum Cr(VI) removal was achieved at a pH of ∼1.0, but no mechanism was discussed.

Cr(VI) biosorption onto *Pinus sylvestris* cone biomass was investigated by Ucun et al. [258]. The Cr(VI) biosorption was increased when the solution pH decreased from 7.0 to 1.0. An increase in chromium/biomass ratio caused a decrease in the biosorption efficiency. The authors postulated that Cr(VI) adsorption behaves like chromate anion uptake and not like reduced Cr(III) species.

Romero-González et al. [254] reported Cr(III) biosorption onto *Agave lechuguilla* biomass. The average adsorption capacities calculated from Freundlich (4.7 mg/g) and Langmuir (14.2 mg/g) isotherms showed *A. lechuguilla* to be effective for aqueous Cr(III) removal. Cr(III) binding was due to interactions with surface carboxyl groups of the biosorbent's cell tissue. Romero-González et al. [253] also used *Agave lechuguilla* for Cr(VI) bioadsorption. Cr(VI) binding at pH 2.0 could be due to either electrostatic attraction to Cr(VI) oxyanions by positively charged ligands such as protonated amines or through Cr(VI) to Cr(III) to reduction, subsequently resulting in the binding of Cr(III) to the biomass. Thermodynamic parameters (ΔG°, ΔH°, and ΔS°) for Cr(VI) adsorption were determined between 10 and 40 °C. They suggested that a portion of Cr(VI) may first bind to surface functional groups on the adsorbent and then be reduced to Cr(III). The Dubinin–Radushkevick equation indicated that the sorption of chromium species onto lechuguilla biomass mainly proceeds through binding to surface functional groups.

Gardea-Torresdey et al. [259] studied Cr(VI) bioadsorption and its possible reduction to Cr(III) by *Agave lechuguilla* biomass. Thermodynamic parameters (ΔG°, ΔH°, and ΔS°) for Cr(VI) adsorption, determined 283–313 K, suggested that a portion of Cr(VI) became bound to surface functional groups on the adsorbent and then reduced to Cr(III). Further, the Dubinin–Radushkevick equation parameters indicated that chromium species sorption onto lechuguilla biomass mainly proceeds through binding surface functional groups, in agreement with the Romero-González et al. [253] paper.

Sawalha et al. [255] studied chromium adsorption by native, esterified, and hydrolyzed saltbush (*Atriplex canescens*) biomass. X-ray absorption spectroscopy studies determined the Cr oxidation state when bound to the biomass. The amounts of Cr adsorbed by saltbush biomass were determined by inductively coupled plasma-optical emission spectroscopy. The percentages of Cr(III) bound by native stems, leaves, and flowers at pH 4.0 were 98%, 97%, and 91%, respectively. On the other hand, the Cr(VI) binding by the native stems, leaves, and flowers of the native and hydrolyzed saltbush biomass decreased as pH increased. At pH 2.0 the stems, leaves, and flowers of native biomass bound 31%, 49%, and 46%, of Cr(VI), respectively. XAS experiments showed that Cr(VI) was reduced to Cr(III) to some extent by saltbush biomass at both pH 2.0 and 5.0. XANES analysis of the Cr(III) reaction with the saltbush biomass demonstrated an octahedral arrangement of oxygen atoms existed around the Cr(III) atom. EXAFS studies of saltbush plant samples confirmed these results. The sorption capacities for Cr(III) and Cr(VI) are presented in Table 7.

Oguz [256] investigated the use of Thuja oriantalis cones, a readily available waste, for Cr(VI) removal. Sorption data were analyzed by Langmuir, Freundlich, Radke-Prausnitz, Brunauer, Emmett and Teller (BET) and Dubinin–Radushkevick (D–R) sorption models. The maximum removal was achieved at pH 1.5. No Cr(VI) adsorption mechanism was discussed.

The aqueous Cr(III) sorption capacities of *Salvinia herzogii* and *Pistia stratiotes* were also reported [260]. Among the free-floating species, *Salvinia herzogii* and *Pistia stratiotes* are the most easily spread plants in Argentina. Cr(III) distribution in the aerial parts and roots versus time and the possible Cr(III) uptake mechanisms were investigated. Both macrophytes efficiently removed Cr from water at concentrations of 1, 2, 4 and 6 mg Cr/L. *S. herzogii* was the best-adapted species. Cr(III) uptake through direct contact between the leaves and the solution is the main route by which chromium uptake into the aerial parts occurs because Cr(III) is poorly translocated away from the roots. Both mechanisms were fast processes. The Cr uptake mechanism involves both a fast component and a slow one. Fast adsorption occurs due to mainly direct adsorption by the roots and leaves. This behavior is similar for both species. The slow component is different for each species probably because Cr(III) precipitation occurs in *P. stratiotes* induced by the roots.

Aoyama [261] studied aqueous Cr(VI) removal by London plane leaves. Aoyama reported that Cr(VI) did not reduce to Cr(III) and the dominating removal mechanism is adsorption. The total chromium removal by London leaves is almost equal to

Table 10
Removal of Cr(VI) from solutions[a] by London leaves [261]

Initial [Cr(VI)] (mg/L)	Removal (mg/g)	
	[Cr(VI)]	Total [Cr]
52.82	26.22 ± 0.10	26.09 ± 0.10
104.48	41.91 ± 0.23	41.80 ± 0.24
157.30	52.72 ± 0.45	52.54 ± 0.45
211.14	60.13 ± 0.45	59.82 ± 0.28
262.38	64.89 ± 0.15	64.56 ± 0.16
315.58	69.47 ± 0.14	69.02 ± 0.16

[a] The adsorbent (0.1 g) was shaken with $50\,cm^3$ of $K_2Cr_2O_7$ solutions (pH 3.0) at $30\,°C$ for 72 h.

the amount of Cr(VI) adsorbed (Table 10). Aoyama et al. [262] had previously explored coniferous leaves for the adsorption of hexavalent chromium from dilute aqueous solution. Several experiments were conducted and the amounts of Cr(VI), and total chromium after adsorption were compared to see if any to reduction occurred to Cr(III). Cr(VI) removal by leaves was mainly governed by the physicochemical adsorption since chemical reduction of Cr(VI) occurred to a lesser extent. Aoyama et al. [263] later tested the ability of Japanese ceder (*Cryptomeria japonica*) bark to remove aqueous Cr(VI). Dependence of the removal of Cr(VI) as well as total chromium was investigated. The initial pH of the solution was varied from 1.0 to 5.0. Cr(VI) removal was 100% at pH ≤ 2.0 but 39% of Cr was still Cr(III) at pH > 2.0. Larch bark [264] and black locust leaves [265] were also utilized for Cr(VI) remediation.

5.14.5. Wood, grasses, compost, peat moss

Peat is a natural humic substance with recognized potential for wastewater treatment due to its ability to sequester metals. Peat's hydroxyl, carboxyl and phenol functional groups play important roles in complexation and ion exchange during metal ions fixation. Peat is also relatively inexpensive. Depending on the type of peat used, mechanisms of cation uptake vary greatly [147,151,266].

Ma and Tobin [267] reported Cr^{3+}, Cu^{2+} and Cd^{2+} biosorption onto peat in batch experiments. The order of maximum uptake was Cr > Cu > Cd. Both H^+ ion competition and pH-dependent speciation affected uptake levels. The optimum pH for Cr(III) was 4.0. An extended Langmuir model, based on the direct competition of metal ions and protons for biosorbent sites, exhibited the best fit. Chromium biosorption by milled peat were reported between pH 2.0 and 7.0 [268]. Peat was chosen as an inexpensive and readily available biomass. Sorption of both cationic Cr(III) and anionic Cr(VI) species was studied. Maximum uptake of Cr(III) occurred at pH 4.0. At this pH, approximately 50% of the Cr(III) present was in the form of Cr^{3+} and 50% was in the form of $Cr(OH)^{2+}$ as predicted by MINEQL, a chemical speciation prediction program. The maximum Cr(III) uptake was 0.27 mmol/g which occurred at a final concentration of approximately 3 mmol/L. In contrast, maximum Cr(VI) uptake of 0.59 mmol/g occurred at pH 2.0, for a 3-mmol/L final concentration. The predominant species at this pH was $HCrO_4^-$.

Sharma and Forster [269] reported that peat moss could be a useful biosorbent for treating metal contaminated wastewaters. Cr(VI) adsorption at both pH 2.0 and 2.5 was examined in columns at two flow-rates for each pH value. Both adsorption and reduction occurred in the columns. The maximum Cr(VI) adsorption capacity (65.9 mg/g) was obtained at pH 2.0 and a flow-rate of 80 mL/min. Sharma and Forster [270] also employed Irish sphagnum peat for continuous Cr(VI) adsorption from acidic solutions. At an initial pH of 2.0, appreciable reduction to trivalent chromium occurred. Cr(III) was not adsorbed as readily as the hexavalent form. This reduction did not occur when the initial pH was 2.5. The adsorption capacities depended on both the pH and the forms of chromium present. The exhausted peat was regenerated *in situ* with 1% sodium hydroxide but the regeneration efficiencies were low (<40%).

Carrillo-Morales et al. [271] utilized the pulp of cactus (CACMM2) for the adsorption of aqueous Cd^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+} and Zn^{2+}. The adsorption capacities decreased in the order Cd(II) > Ni(II) > Cr(III) > Pb(II) > Cu(II) > Fe(II) > Zn(II).

The ability of four common plant-derived products—wood, grass, compost, and peat moss to remove cadmium, chromium and lead from dilute aqueous solutions was investigated [272]. These products were dried and ground. Then they were immobilized in polysulfone or poly(bisphenyl A) carbonate to form spherical beads through a phase inversion process. The dried and ground vegetation product (−80 mesh) was added to N-methylpyrrolidone solution of the polymer in a 1:1 mass ratio with the polymer, generating beads that were approximately 50% vegetation and 50% polymer matrix. This slurry added dropwise into a beaker containing clean water. Upon contact with the water, the water-miscible NMP separated from the polymer/vegetation mixture, resulting in the formation of spherical beads. These beads were transferred to a fresh water bath and agitated gently on a shaker table until the wash bath remained clear and did not smell of NMP solvent. After washing, the beads were dried at room temperature and screened for odd-shaped and oversized beads using a 1/4 in. mesh screen. This method resulted in a consistent ~3.5 mm diameter bead size. Dry beads were than placed in deionized water and agitated until they were clearly saturated with water. The soaked beads were then prepared for metal uptake by 0.1 M nitric acid extraction, under agitation, to remove acid-soluble contaminants, rinsing with deionized water, and then washing in 0.1 M sodium hydroxide to exchange active protons with Na^+.

Deepa et al. [273] reported batch sorption of aqueous Cr(VI) using live and pretreated *Aspergillus flavus* biomass. The autoclaved *Aspergillus flavus* biomass that showed maximum adsorption capacity (0.335 mg/g) was used as an adsorbent in column studies. The *adsorption capacities* for autoclaved adsorbent calculated from BDST model were (4.56, 7.28, 6.89, 3.07, 2.80) × 10^{-5} mg/g for 4, 8, 12, 16 and 20 mg/L of Cr(VI), respectively.

5.14.6. Chitin and chitosan

Braconnot first described chitin in 1811; upon isolating a substance he called "fungine" from fungi. The first scientific

reference to chitin was taken from the Greek word "chiton", meaning a "oat of mail", for the material obtained from the elytra of May beetles [199]. Chitin, the most widely occurring natural carbohydrate polymer next to cellulose, is a long, unbranched polysaccharide derivative of cellulose, where the C_2 hydroxyl group has been replaced by the acetyl amino group –NHCOCH$_3$. 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 is a product of deacetylation of chitin using concentrated alkali at high temperature. Chitosan is derived from the chitin found in the exoskeletons of Crustacea shellfish, shrimp, crabs, insects, etc. Chitin is prepared from shells of Crustacea at low cost by removing other components, such as calcium, and proteins, by treatment with acids and alkalines. Recently Crini [32] reviewed the developments in the synthesis of polysaccharide-containing adsorbents, in particular modified biopolymers derived from chitin, chitosan, starch and cyclodextrin. The important features of these polymeric materials were discussed to demonstrate the advantages gained using these adsorbents for wastewater treatment. Chitin and chitosan are excellent natural adsorbents [32,274] with high selectivities because:

(1) large numbers of hydroxyl and amino groups give chitosan high hydrophilicity;
(2) primary amino groups provide high reactivity;
(3) the chitosan polymer chains provide suitable configurations for efficient metal ion complexation.

The structures of chitin and chitosan are presented (Fig. 16).

Chromium adsorption of onto cross-linked chitosan was investigated by Rojas et al. [275]. Effect of pH, particle size, adsorbent weight, concentration and chromium oxidation state on adsorption was studied. The optimum adsorption pH was
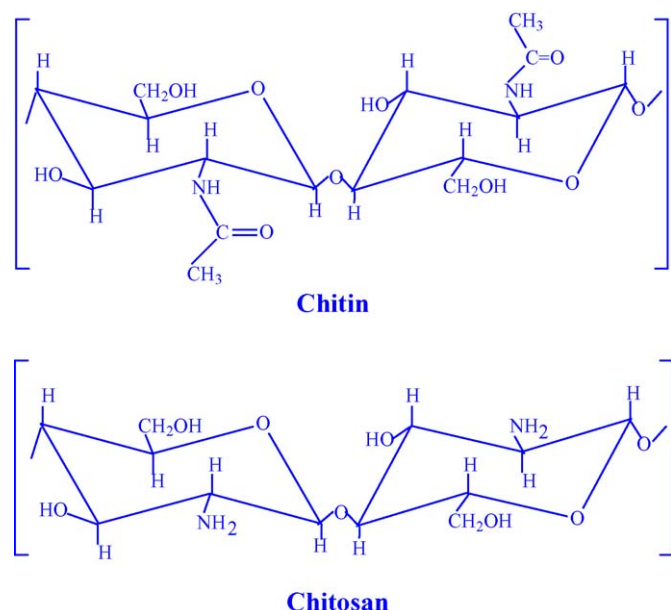
Fig. 16. Chemical structures of chitin and chitosan.

4.0, while chromium(VI) is partially reduced in the range pH ≤ 3.0. The lower chitosan affinity for chromium(III) (6 mg/g) differs with chitosan's very high capacity for chromium(VI) (215 mg/g). This high capacity is due to the large stoichiometry of protonated amine sites in the acidic range of pH. Equilibrium data fitted to both Langmuir and Freundlich isotherms.

Spinelli et al. [276] synthesized the quaternary ammonium salt of chitosan (QCS) (Fig. 17) via reaction of a quaternary trimethyl ammonium, glycidyl chloride. The resulting product was utilized for aqueous Cr(VI) removal. This polymer was characterized by IR, ^{1}H NMR, TGA and quantitation of the quaternary ammonium groups. The Langmuir isotherm model fitted the sorption data and the capacity was pH dependent. The Cr(VI) adsorption capacity at pH 9.0 was 30.2 mg/g, while at pH 4.5 the capacity was 68.3 mg/g (Table 1). Cr(VI) ions were eluted from cross-linked QCS by treatment with a 1 mol/L solution of NaCl/NaOH to give a chromium efficiency of more than 95%.

Castro Dantas et al. [277] examined the Cr(III) removal from aqueous solutions by chitosan impregnated with a microemulsion composed of 10 wt.% surfactant (saponified coconut oil); 25 wt.% aqueous phase (distilled water); 40 wt.% co-surfactant (isoamyl alcohol, 99% PA) and 25 wt.% oil phase (kerosene). The modified chitosan exhibited a remarkable increase in Cr(III) sorption capacity over the untreated sample. Dynamic column experiments were performed to study the influence of pH, concentration, and the presence of other metal ions (copper and nickel) in the chromium solutions. The nature of Cr(III) sorption equilibrium at different temperatures (30, 40, and 50 °C) was also investigated. The Langmuir isotherm model fitted the sorption data.

Boddu et al. [278] prepared a composite chitosan biosorbent by coating chitosan, onto nonporous ceramic alumina. This composite bioadsorbent was characterized by high temperature pyrolysis, porosimetry, scanning electron microscopy, and X-ray photoelectron spectroscopy. The oxalated dianion was used to form a bridge between alumina and chitosan (Fig. 18). One carboxylate group forms a relatively strong surface chelate via ester linkage with the alumina while the other one forms an ionic bond with a –NH$_3^+$ group present on chitosan. The oxalic acid could also form hydrogen bonds with –OH, –CH$_2$OH, or –NH$_2$ groups on the biopolymer. The micropore area of the biosorbent is only 3.3 m^2/g compared to the total surface area (105.2 m^2/g). This indicates that the sorbent is relatively nonporous. Batch and continuous column sorption experiments with this sorbent were carried out at 25 °C to evaluate Cr(VI) adsorption from synthetic and actual chrome plating wastewater samples. Experimental equilibrium data were fitted to Langmuir and Freundlich models. The ultimate capacity obtained from the Langmuir model was 154-mg/g chitosan (Table 7). Cr(VI) sorption occurred on protonated amine functional groups of the biopolymer as shown in Fig. 19.

Dambies et al. [279] employed X-ray photoelectron spectroscopy (XPS) to study chemical interactions between Cr(VI) and chitosan from crab shells. Three forms of chitosan were used—flakes, beads, and modified beads obtained by glutaraldehyde cross-linking. XPS identified the sorption sites involved in the accumulation of Cr(VI), as well as sorbed species.
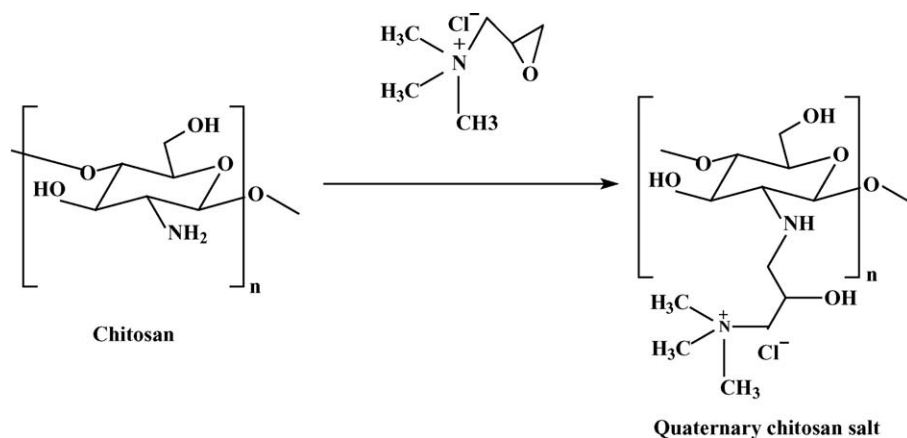
Fig. 17. Reaction scheme of quaternary chitosan salt (QCS). *Source*: Spinelli et al. [276].
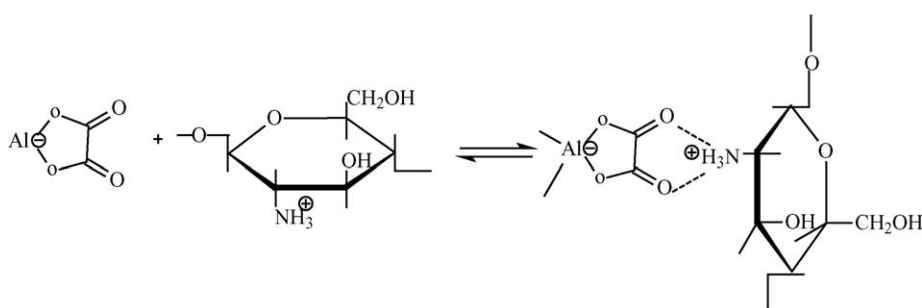

Fig. 18. Oxalated dianion used to form a bridge between alumina and chitosan. *Source*: Ref. [278].

Chromium was not detected by XPS measurements restricted to the first external layers of the sorbent. However, significant bands appeared at binding energies of 577.3 and 579.8 eV after grinding the sample. The disappearance of chromium from the external layers cannot be interpreted based on experimental artifacts, mass transfer mechanisms, or analysis criteria. The chromium element appeared in cross-linked chitosan beads and even with native beads. Unlike raw sorbents, only the 577.0 eV band appeared in cross-linked chitosan. The bands at 577.3 and 579.8 eV can be attributed to Cr(III) and Cr(VI), respectively, by analogy with other chromium compounds. Specifically the Cr $2p_{3/2}$ orbitals are assigned at 577.2 eV ($CrCl_3$) and 576.2–576.5 eV (Cr_2O_3) for Cr(III) compounds, while Cr(VI) forms are characterized by higher binding energies [e.g. 578.1 eV (CrO_3) or 579.2 eV ($K_2Cr_2O_7$)]. Thus, on cross-linked beads, chromate was entirely reduced to Cr(III), while on uncrosslinked chitosan only 60% of the chromium is found in its reduced Cr(III) form.

Hasan et al. [280] investigated Cr(VI) remediation using chitosan-coated perlite beads. Chitosan-coated perlite beads were prepared by addition of chitosan and perlite liquid slurry to an alkaline bath. The beads were characterized by SEM and EDS X-ray microanalysis. The chitosan content of the beads was 23%. The chitosan-coated perlite adsorption capacity was 104 mg/g using a batch determination method. The Cr(VI) capacity was 452 mg/g of chitosan. This large capacity was considerably higher than that of natural and modified chitosan, which ranged from 11.3 to 78 mg/g of chitosan. The beads loaded with chromium were regenerated with sodium hydroxide solution.

Tan et al. [281] reported the preparation of nickel imprinted chitosan resin, which can considerably enhance the adsorption capacity and selectivity of the metal ions including Cr(VI). Conditions influencing the preparation of chitosan-imprinted resin were optimized. These included the cross-linking agent, epichlororohydrin and ethylene glycol diglycidyl ether, and Ni(II) concentration. The chemical and physical stability were also discussed and the imprinted chitosan resin was used several times without losing adsorption capacity. The adsorption mechanism is illustrated in Fig. 20.

6. Chromium sorption mechanisms

Cr(VI) adsorption from aqueous solutions by activated carbon/low cost adsorbents/biosorbents consists mainly of two modes of uptake:

1. Hexavalent chromium species are removed by adsorption onto the interior surface of the adsorbent (carbon/biosorbent/adsorbent).
2. Chromium(VI) is reduced into Cr(III) and this trivalent state adsorbs at the external carbon surface.

The major parameters which governed the adsorption mechanism of Cr(VI)/Cr(III) are: pH, degree of mixing or velocity gradient, carbon/adsorbent dose, total chromium concentration
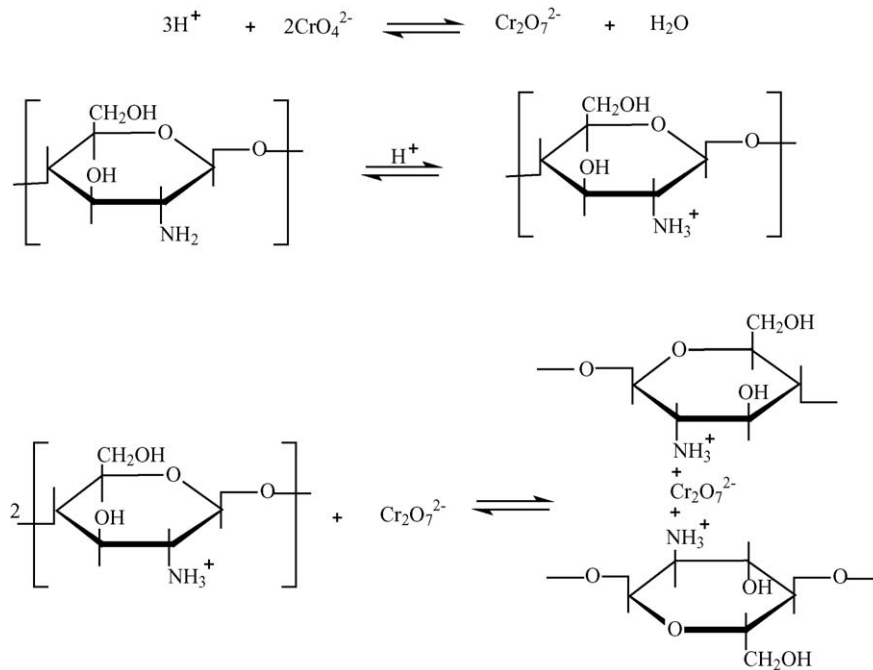
$$3H^+ + 2CrO_4^{2-} \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Fig. 19. Sorption of Cr(VI) on amine functional groups of the biopolymer. *Source*: Ref. [278].

(both Cr(III) and Cr(VI)), temperature, particle size, and type of adsorbents. The majority of the sorbents reviewed herein are activated carbons, biosorbents, clays or industrial/agricultural by-products. A number of equations have been used to describe kinetic reactions in these sorbents. These include first-, second-order and two constant rate equations [282,283]. In most of the papers discussed above the rate of the reaction was either governed by first- or second-order rate equations.

Further, the adsorption of Cr(VI) and Cr(III) is governed by the four consecutive steps [199]:

1. transport in the bulk solution;
2. diffusion across the liquid film boundary surrounding the sorbent particles;
3. intraparticle diffusion in the liquid contained in the pores and in the sorbate along the pore walls;

4. sorption and desorption within the particle and on the external surface.

Any of the above steps or combinations of them may control the rate [199]. To determine the exact mechanism it is necessary to carry out experiments to investigate such variables as initial concentration, sorbent particle size, solution temperature, pH, agitation time and then analyze the data for different kinetic orders or for pore/solid phase diffusion mechanisms.

The mathematical treatment of Boyd et al. [284] and Reichenberg [285] distinguishes between diffusion in the particle, film diffusion and a mass action-controlled exchange mechanism. This treatment laid the foundations of sorption/ion exchange kinetics.

Three steps which occur in the adsorption of an adsorbate by a porous adsorbent are:
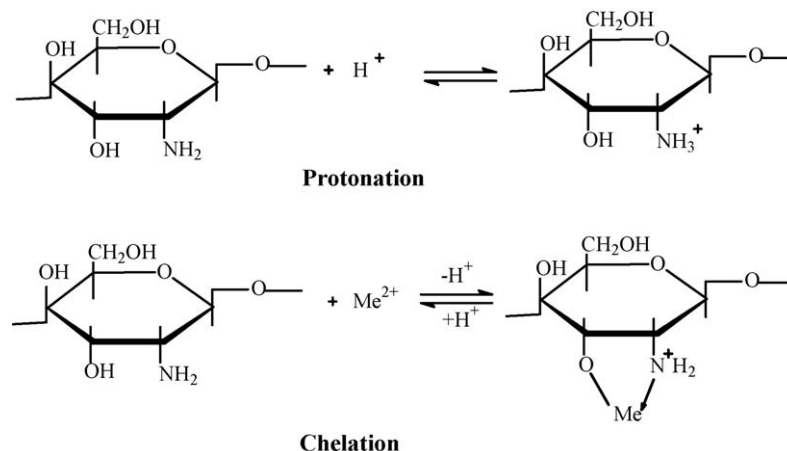

Fig. 20. Cr(VI) sorption on the chitosan resin. *Source*: Tan et al. [281].

(i) transport of the adsorbate to the external surface of the adsorbent (film diffusion);

(ii) transport of the adsorbate within the pores of the adsorbent (intraparticle diffusion);

(iii) adsorption of the adsorbate on the exterior surface of the adsorbent.

Process (i) is rapid and does not represent the rate-determining step in the uptake of adsorbate (1). Three distinct cases occur for the remaining two steps in the overall transport:

- case I: external transport > internal transport;
- case II: external transport < internal transport;
- case III: external transport ≈ internal transport.

In cases I and II, the rate is governed by diffusion in the film and in the particle, respectively. In case III, the transport rate of adsorbate to the boundary is not significant. This leads to liquid film formation with a concentration gradient surrounding the sorbent particles.

External transport is usually rate limiting in systems, which have: (a) poor mixing, (b) dilute adsorbate concentration, (c) small particle size and (d) high adsorbate affinity for adsorbent.

In contrast, intra-particle transport limits the overall transfer for those systems that have: (a) high adsorbate concentration, (b) good mixing, (c) large adsorbent particle size, and (d) low adsorbate/adsorbent affinity.

Kinetic data can easily be analyzed by applying the Reichenberg [285] and Helffrich [286] mathematical models using Eqs. (33)–(36):

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[\frac{-D_i t \pi^2 n^2}{r_0^2}\right] \tag{33}$$

or

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp[-n^2 Bt] \tag{34}$$

F is the fractional equilibrium that is reached at time t, obtained by the expression:

$$F = \frac{Q_t}{Q^0} \tag{35}$$

where Q_t is the amount of adsorbate taken up at time t. Q^0 is the maximum equilibrium uptake. B is given by the following equation:

$$B = \frac{\pi^2 D_i}{r_0^2} = \text{time constant} \tag{36}$$

where D_i is the effective diffusion coefficient of ions in the adsorbent phase and r_0 is the radius of spherical adsorbent particles. The term n is an integer that defines the infinite series solution. Bt values (the product of multiplying B by time t) were obtained for each observed value of F from Reichenberg's table [285] at different temperatures. The linearity test of Bt versus time plots was employed to distinguish between adsorption controlled by film versus particle diffusion. If a Bt versus time plot (slope = B) is linear and passes through the origin, then the adsorption rate is governed by diffusion in the particle. Otherwise, it is governed by film diffusion [2,3]. In most of adsorption studies reported in this review article, rate is controlled either by film diffusion or particle diffusion.

7. Comparative evaluation of sorbents

The adsorption capacities of various Cr(III) and Cr(VI) adsorbents are summarized in Table 7. It is very difficult to directly compare adsorption capacities due to a lack of consistency in the literature data. Sorption capacities were evaluated at different pHs (and not necessarily at the optimum pH values), temperatures, Chromium concentration ranges, adsorbent doses and various Cr(III)/Cr(VI) ratios. The adsorbents were used for treating ground water, drinking water, synthetic industrial wastewater, and actual wastewater and so on so fourth. So the types and concentrations of interfering ions are different and seldom documented. Some adsorption capacities were reported in batch experiments and others in continuous column modes. These certainly cannot be readily compared with each other. In batch sorption experiments, the sorption capacities were computed by the Langmuir isotherm or the Freundlich isotherm or experimentally. This makes comparisons more complicated to pursue. In other words rigorous direct comparisons of the tested adsorbents are largely impossible. Keeping these caveats in mind, some (Table 7) some adsorbents with very high capacities were chosen and compared using a 3D bar diagram (Fig. 21).

Obviously, some low cost adsorbents developed from agricultural wastes or industrial wastes have outstanding capacities. These include treated slags, carbons developed from agricultural waste (char carbons and coconut husk carbons), biosorbents (immobilized biomass, orange juice residue), goethite, etc. (Fig. 21). Some commercial adsorbents, which include resins, gels, silica, treated silica tested for chromium removal also performed well. Comparing sorbents by surface area alone is difficult. Adsorption of organics is usually dependent on adsorbents' surface area. The higher the surface area the greater is the adsorption. But this is often not true for the adsorption of metal ions or inorganics. Factors such as exchange and precipitation may contribute or dominate.

Out of the many sorbents compared in this review dried anaerobic activated sludge offered outstanding performances for hexavalent chromium remediation. In case of Cr(III), Amberlite IR-120 resin and dithizone-anchored poly(EGDMA-HEMA) were the best (Fig. 21). The conditions employed in those studies can be simulated for such large-scale applications as drinking water purification.

8. Cost estimation

The cost of chromium adsorbents developed from waste materials seldom appears in the literature. The cost of individual adsorbents depends on local availability, processing required, treatment conditions and both recycle and lifetime issues. These

(a)

(b)
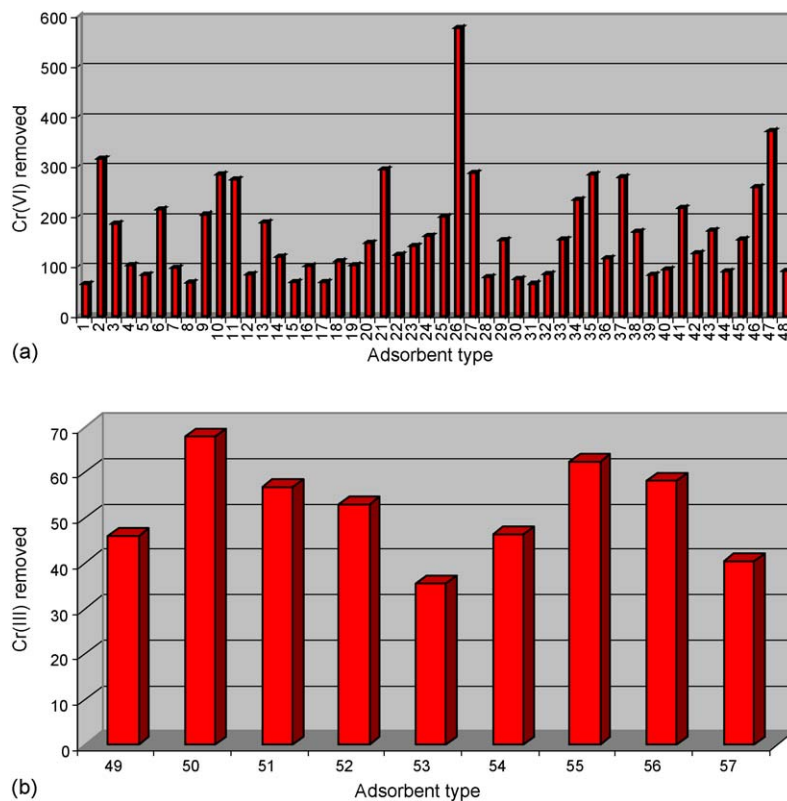
No.	Adsorbents	Reference
1	Sawdust activated carbon	[82]
2	Activated carbon (CKW)	[80]
3	Activated carbon (Acticarbone CXV)	[80]
4	Sugarcane bagasse	[136]
5	Corn stover	[136]
6	Cross-linked (glutaraldehyde)	[275]
7	*Tamarindus indica* seed (TS)	[115]
8	Quaternary chitosan salt (QCS)	[276]
9	*Pantoea* sp. TEM18	[248]
10	*Aeromonas caviae*, a gram-negative bacteria	[245]
11	Persimmon tannin (PT) gel	[17]
12	Ion exchange resin 1200H	[12]
13	Ion exchange resin 1500H	[12]
14	Hydrotalcite	[158]
15	Activated carbon, FS-100	[63]
16	Activated carbon, GA-3	[63]
17	Activated carbon, SHT	[63]
18	*Dunaliella* alga (sp. 1)	[213]
19	*Dunaliella* alga (sp. 2)	[213]
20	Granular activated carbon	[197]
21	Activated sludge	[197]
22	Untreated *Rhizopus nigricans*	[232]
23	CTAB-treated *R. nigricans*	[232]
24	PET-treated *R. nigricans*	[232]
25	APTS-treated *R. nigricans*	[232]
26	Dried anaerobic activated sludge	[198]
27	Tannin gel (77% water content)	[173]
28	Algae, *C. vulgaris*	[215]
29	Algae, *Synechocystis* sp.	[215]
30	Activated carbon	[107]
31	Peat moss	[269]
32	Chitosan impregnated with a microemulsion	[277]

Fig. 21. Comparative evaluation of the best adsorbents for (a) hexavalent chromium and (b) trivalent chromium.

No.	Adsorbents	Reference
33	Chitosan	[278]
34	Protonated brown seaweed *Ecklonia* sp.	[221]
35	*Aeromonas caviae* biomass	[245]
36	Activated carbon fabric cloth	[2]
37	PEI-modified biomass of *P. chrysogenum*	[228]
38	Hazelnut shell activated carbon	[90]
39	London leaves	[261]
40	Cationic surfactant-modified yeast	[244]
41	Kendu fruit gum dust (KGD)	[110]
42	Amine-modified polyacrylamide-grafted coconut coir pith	[104]
43	Sawdust (SD) of rubber wood (*Hevea brasiliensis*) grafted with polyacrylamide	[99]
44	Japanese ceder (*Cryptomeria japonica*)	[263]
45	Chitosan coated on perlite	[288]
46	Bagasse fly ash	[27]
47	Activated carbon developed from fertilizer waste slurry	[78]
48	Activated carbon obtained from black liquor lignin	[66]
49	Carrot residues	[116]
50	Amberlite IR-120 resin	[129]
51	Activated carbon from co-mingled natural organic wastes	[95]
52	Norit carbon (oxidized)	[95]
53	IRN77 resin	[10]
54	SKN1 resin	[10]
55	Dithizone-anchored poly(EGDMA-HEMA)	[171]
56	*R. arrhizus*	[227]
57	Activated carbon fabric cloth	[3]

Fig. 21. (*Continued*)

are not discussed in any paper. Cost will vary when the adsorbents are made in (and for) developed countries, developing countries or underdeveloped countries. Numerous commercially available activated carbons have been used for chromium adsorption, both as-received and after chemical modifications. However, chemical modification costs are seldom mentioned in the research reports. Furthermore, no consistency exists in the data presented. Most papers describe only batch experiments and no consideration was given to fixed-bed studies. Batch equilibrium adsorption isotherms cannot simulate or predict dynamic performances directly due to the following limitations:

1. Isotherms are equilibrium tests so the time restrictions are not considered.
2. Isotherms are based on carbon exhaustion–granular systems.
3. Long-term chemical and biological effects are not evident.

Ease and completeness of regression and the number of recycles over which adsorbent can be used are not elucidated. Most research reviewed herein has been limited to initial laboratory evaluations of solution adsorptive capacity and the uptake mechanism. Pilot-plant scale studies and cost evaluation remain to be explored. In the growing literature on natural adsorbents for chromium uptake, little literature exists containing full cost and application comparisons of various sorbents. In addition, different sorbents are difficult to compare because of inconsistencies in the data presentation. Thus, much work is necessary to demonstrate application costs at the sale of a single home, a village, a municipal region or an industrial process.

9. Conclusions

The chemical contamination of water from a wide range of toxic derivatives, in particular heavy metals, aromatic molecules and dyes, is a serious environmental problem owing to their potential human toxicity. The heavy metals, especially hexavalent chromium, appear to be the major pollutants globally in this century. Heavy metals, derived from industrial wastewater discharge, present an ongoing and serious threat to human health and to natural water. There are a number of treatment technologies available for chromium remediation but none of them is found to be applicable to all situations. A successful separation process should have two main products:

1. Low volume stream containing the contaminant(s) in a concentrated form.
2. A high volume stream containing the decontaminated matrix.

Adsorption is relatively new practice for the removal of metal ions/chromium. It has been a useful tool for controlling the extent of metal pollution. Activated carbon's role for the removal of chromium from water and wastewater was discussed. However, it is only able to remove few milligrams of metal ions per gram of activated carbon and there are still some problems encountered in the regeneration process. This makes activated carbon an expensive adsorbent for wastewater treatment. The use of activated carbon in developing countries is more problematic as they cannot afford the cost and demands of activated carbons. Therefore, low cost materials are sorely needed, which are comparable to activated carbon in terms of adsorption capacity and

should be locally available. The present discussion shows that some such materials have equal or more adsorption capacity than activated carbon.

On the other hand, solid waste has become one of the society's most vexing problems. This problem is compounded when the waste is contaminated with hazardous chemicals. One solution is recycling where a portion of the remediation cost is recaptured by sale of the recovered substance. No doubt it is a positive answer to solid waste disposal. However, the quality of recycled product is always in question. If the solid waste can be converted into a low cost adsorbent for the treatment of discharged wastewater, the cost of remediating metal ions from water might decrease. A perusal of Table 7 indicates that some of the activated carbons made from waste materials have higher adsorption capacities than commercially available carbons.

These can also be regenerated chemically and recycled which further lowers the treatment cost. Preliminary investigations reveal the applicability of the substances such as clay minerals, fly ash, fertilizer wastes, different types of coal, slags, zeolites, and so on as scavengers of heavy metal ions. As mention earlier by Pollard et al. [33], most of the studies are limited only to an initial evaluation of solution adsorptive capacity and there is a need to continue future studies at the pilot-plant scale.

Despite the large number of papers published on natural adsorbents for chromium uptake, few reports exist of full comparative studies of various sorbents. As already noted, comparisons of different sorbents are difficult because of inconsistencies in the data presentation. Thus, much work is necessary to better understand adsorption phenomenon and to demonstrate possible useful technology at a variety of scales for applications at various locations and scales worldwide.

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References

[1] L.R. Radovic, C. Moreno-Castilla, J. Rivera-Utrilla, Carbon materials as adsorbents in aqueous solutions, in: L.R. Radovic (Ed.), Chemistry and Physics of Carbon, vol. 27, Marcel Dekker, Inc., New York, 2000.

[2] D. Mohan, K.P. Singh, V.K. Singh, Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth, Ind. Eng. Chem. Res. 44 (2005) 1027–1042.

[3] D. Mohan, K.P. Singh, V.K. Singh, Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth, J. Hazard. Mater. 135 (2006) 280–295.

[4] R.J. Irwin, M.V.N. Mouwerik, L. Stevens, M.D. Seese, W. Basham, Environmental Contaminants Encyclopedia Chromium(VI) (Hexavalent Chromium) Entry, National Park Service Water Resources Divisions, Fort Collins, CO, 1971.

[5] US EPA/625/R-00/005, In-situ treatment of soil and groundwater contaminated with chromium, Technical Resources Guide, United States Environmental Protection Agency.

[6] Dionex, Determination of Cr(VI) in water, wastewater and solid waste extracts, Technical Note 26 LPN 34398-01 1M 7/96, Dionex Corporation, 1996. http://www1.dionex.com/en-us/webdocs/4428_tn26.pdf.

[7] D.E. Kimbrough, Y. Cohen, A.M. Winer, L. Creelman, C.A. Mabuni, Critical assessment of chromium in the environment, Crit. Rev. Environ. Sci. Technol. 29 (1) (1999) 1–46.

[8] J.W. Paterson, Wastewater Treatment Technology, Ann Arbour Science, Michigan, 1975, pp. 43–58.

[9] G. Tiravanti, D. Petruzzelli, R. Passino, Pretreatment of tannery wastewaters by an ion exchange process for Cr(III) removal and recovery, Water Sci. Technol. 36 (1997) 197–207.

[10] S. Rengaraj, K.-H. Yeon, S.-H. Moon, Removal of chromium from water and wastewater by ion exchange resins, J. Hazard. Mater. 87 (1–3) (2001) 273–287.

[11] S. Rengaraj, K.-H. Yeon, S.-Y. Kang, J.-U. Lee, K.-W. Kim, S.-H. Moon, Studies on adsorptive removal of Co(II), Cr(III) and Ni(II) by IRN77 cation-exchange resin, J. Hazard. Mater. 92 (2) (2002) 185–198.

[12] S. Rengaraj, C.K. Joo, Y. Kim, J. Yi, Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H, J. Hazard. Mater. 102 (2/3) (2003) 257–275.

[13] D. Petruzzelli, R. Passino, G. Tiravanti, Ion exchange process for chromium removal and recovery from tannery wastes, Ind. Eng. Chem. Res. 34 (1995) 2612–2617.

[14] F. Gode, E. Pehlivan, Sorption of Cr(III) onto chelating b-DAEG–sporopollenin and CEP–sporopollenin resins. Bioresour. Technol., in press.

[15] C.A. Kozlowski, W. Walkowiak, Removal of chromium(VI) from aqueous solutions by polymer inclusion membranes, Water Res. 36 (2002) 4870–4876.

[16] H. Shaalan, M. Sorour, S. Tewfik, Simulation and optimization of a membrane system for chromium recovery from tanning wastes, Desalination 14 (2001) 315–324.

[17] G. Ghosh, P.K. Bhattacharya, Hexavalent chromium ion removal through micellar enhanced ultrafiltration, Chem. Eng. J. 119 (1) (2006) 45–53.

[18] K.A. Matis, P. Mavros, Recovery of metals by ion flotation from dilute aqueous solutions, Sep. Purif. Meth. 20 (1991) 1–48.

[19] J.R. Parga, D.L. Cocke, V. Valverde, J.A.G. Gomes, M. Kesmez, H. Moreno, M. Weir, D. Mencer, Characterization of electrocoagulation for removal of chromium and arsenic, Chem. Eng. Technol. 28 (5) (2005) 605–612.

[20] E. Salazar, M.I. Ortiz, A.M. Urtiaga, Equilibrium, Kinetics of Cr(V1) extraction with Aliquat 336, Ind. Eng. Chem. Res. 31 (1992) 1516–1522.

[21] Z. Song, C.J. Williams, R.G.J. Edyvean, Sedimentation of tannery wastewater, Water Res. 34 (7) (2000) 2171–2176.

[22] D.M. Roundhill, H.F. Koch, Methods and techniques for the selective extraction and recovery of oxoanions, Chem. Soc. Rev. 31 (2002) 60–67.

[23] J.M.N. Chen, O.J.N. Hao, Microbial chromium(VI) reduction, Crit. Rev. Environ. Sci. Technol. 28 (3) (1998) 219–251.

[24] H. Ozaki, K. Sharma, W. Saktaywin, Performance of an ultra-low-pressure reverse osmosis membrane (ULPROM) for separating heavy metal: effects of interference parameters, Desalination 144 (2002) 287–294.

[25] T. Mohammadi, A. Moheb, M. Sadrzadeh, A. Razmi, Modeling of metal ion removal from wastewater by electrodialysis, Sep. Purif. Technol. 41 (1) (2005) 73–82.

[26] V.K. Gupta, I. Ali, in: Somasundaran (Ed.), Adsorbents for water treatment: development of low cost alternatives to carbon for the updated 'Encyclopedia of Surface and Colloid science', Marcel Dekker, 2003, pp. 1–34.

[27] V.K. Gupta, K.T. Park, S. Sharma, D. Mohan, Removal of chromium(VI) from electroplating industry wastewater using bagasse flyash—a sugar industry waste material, Environmentalist 19 (1999) 129–136.

[28] V.K. Gupta, S.K. Srivastava, D. Mohan, Design parameters for fixed bed reactors of activated carbon developed from fertilizer waste for the removal of some heavy metal ions, Waste Manage. 17 (8) (1997) 517–522.

[29] V.K. Gupta, M. Gupta, S. Sharma, Process development for the removal of lead and chromium from aqueous solutions using red mud—an aluminium industry waste, Water Res. 35 (5) (2001) 1125–1134.

[30] S. Babel, T.A. Kurniawan, Low cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater. B 97 (2003) 219–243.

[31] M. Tels, Advances in treating heavy metals containing wastes, Resour. Conserv. 14 (1987) 71–92.

[32] G. Crini, Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, Prog. Polym. Sci. 30 (1) (2005) 38–70.

[33] S.J.T. Pollard, G.D. Fowler, C.J. Sollars, R. Perry, Low cost adsorbents for waste and wastewater treatment: a review, Sci. Tot. Environ. 116 (1992) 31–52.

[34] S.J. Allen, L. Whitten, G. McKay, The production and characterization of activated carbons: a review, Dev. Chem. Eng. Min. Process. 6 (5) (1998) 231–262.

[35] D. Mohan, K.P. Singh, Granular activated carbon, in: J. Lehr, J. Keeley, J. Lehr (Eds.), Water Encyclopedia: Domestic, Municipal, and Industrial Water Supply and Waste Disposal, Wiley/Interscience, New York, 2005.

[36] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (11) (1999) 2469–2479.

[37] T.A. Davis, B. Volesky, A. Mucci, A review of the biochemistry of heavy metal biosorption by brown algae, Water Res. 37 (18) (2003) 4311–4330.

[38] A. Kapoor, T. Viraraghavan, Fungal biosorption—an alternative treatment option for heavy metal bearing wastewaters: a review, Bioresour. Technol. 53 (1995) 195–206.

[39] Y. Sag, Biosorption of heavy metals by fungal biomass and modeling of fungal biosorption: a review, Sep. Sci. Technol. 30 (1) (2001) 1–48.

[40] P.N. Cheremisinoff, C.M. Angelo, Carbon adsorption applications, in: Carbon Adsorption Handbook, Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1980, pp. 1–54.

[41] M. Gavrilescu, Removal of heavy metals from the environment by biosorption, Eng. Life Sci. 4 (3) (2004) 219–232.

[42] E.L.K. Mui, D.C.K. Ko, G. McKay, Production of active carbons from waste tyres—a review, Carbon 42 (2004) 2789–2805.

[43] R.P. Bansal, J.-P. Donnet, F. Stoeckli, Active Carbon, Marcel Dekker, New York, 1988.

[44] C.L. Mantell, Carbon and Graphite Handbook, Interscience, New York, 1968.

[45] Y. Hamerlinck, D.H. Mertens, in: E.F. Vansant (Ed.), Activated Carbon Principles in Separation Technology, Elsevier, New York, 1994.

[46] R.C. Bansal, M. Goyal, Activated Carbon Adsorption, CRC Press, 2005.

[47] R.F. Rodriguez-Reinoso, A.L. Solano, Microporous structure of activated carbons as revealed by adsorption methods, in: P.A. Thrower (Ed.), Chemistry and Physics of Carbon, vol. 12, Marcel Dekker, New York, 1989.

[48] J.W. Hassler, Active Carbon, Chemical Publishing Company, New York, 1963.

[49] T. Otowa, Y. Nojima, T. Miyazaki, Development of KOH activated high surface area carbon and its application to drinking water purification, Carbon 35 (9) (1997) 1315–1339.

[50] J.S. Mattson, H.B. Mark Jr., Activated Carbon, Marcel Dekker, New York, 1971.

[51] M.O. Corapcioglu, C.P. Huang, The adsorption of heavy metals onto hydrous activated carbon, Water Res. 21 (9) (1987) 1031–1044.

[52] J.R. Perrich, Activated Carbon Adsorption for Wastewater Treatment, CRC Press, 1981.

[53] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Reporting physisorption data for gas/solid systems, Pure Appl. Chem. 57 (1985) 603–619.

[54] H. Freundlich, Uber die adsorption n losungen, Z. Phys. Chem. 57 (1906) 385–470.

[55] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1367.

[56] W.J. Weber Jr., Physicochemical Processes for Water Quality Control, Wiley/Interscience, New York, 1972.

[57] S. Brunauer, S.P.H. Emmett, E. Teller, Adsorption of gases in multi-molecular layers, J. Am. Chem. Soc. 60 (1972) 309–319.

[58] C.P. Huang, M.H. Wu, Chromium removal by carbon adsorption, J. Water Pollut. Contr. Fed. 47 (10) (1975) 2437–2446.

[59] C.P. Huang, M.H. Wu, The removal of chromium(VI) from dilute aqueous solution by activated carbon, Water Res. 11 (8) (1977) 673–679.

[60] C.P. Huang, A.R. Bowers, The use of activated carbon for chromium(VI) removal, Prog. Water Technol. 10 (5/6) (1978) 45–65.

[61] C.P. Huang, Activated carbon process for treatment of wastewaters containing hexavalent chromium, EPA-600/2-79-130, 1979.

[62] M. Schlautman, B. Batchelor, I. Han, Removal of chromium from pan-tex ground water by granular activated carbon. A Report to the Amarillao National Resource Center for Plutonium (ANRCP) for the Project Chemical Models and Redox Chemistry of Chromium, Department of Energy, Amarillo Area Office, Amarillo, TX, submitted for publication.

[63] Z. Hu, L. Lei, Y. Li, Y. Ni, Chromium adsorption on high-performance activated carbons from aqueous solution, Sep. Purif. Technol. 31 (1) (2003) 13–18.

[64] S.-J. Park, Y.-S. Jang, Pore structure and surface properties of chemically modified activated carbons for adsorption mechanism and rate of Cr(VI), J. Colloid Interface Sci. 249 (2) (2002) 458–463.

[65] D. Aggarwal, M. Goyal, R.C. Bansal, Adsorption of chromium by activated carbon from aqueous solution, Carbon 37 (12) (1999) 1989–1997.

[66] E. Gonzalez-Serrano, T. Cordero, J. Rodriguez-Mirasol, L. Cotoruelo, J.J. Rodriguez, Removal of water pollutants with activated carbons prepared from H_3PO_4 activation of lignin from kraft black liquors, Water Res. 38 (2004) 3043–3050.

[67] J. Rivera-Utrilla, M. Sanchez-Polo, Adsorption of Cr(III) on ozonised activate carbon. Importance of $C\pi$–cation interactions, Water Res. 37 (2003) 3335–3340.

[68] L. Monser, N. Adhoum, Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater, Sep. Purif. Technol. 26 (2/3) (2002) 137–146.

[69] R. Dobrowolski, E. Stefaniak, Study of chromium(VI) adsorption from aqueous solution on to activated carbon, Adsorp. Sci. Technol. 18 (2) (2000) 97–106.

[70] R. Leyva-Ramos, L. Fuentes-Rubio, R.M. Guerrero-Coronado, J. Mendoza-Barron, Adsorption of trivalent chromium from aqueous solutions onto activated carbon, J. Chem. Technol. Biotechnol. 62 (1) (1995) 64–67.

[71] R. Leyva-Ramos, J. Martinez, R. Guerrero-Coronado, Adsorption of Cr(IV) from aqueous solutions onto activated carbon, Water Sci. Technol. 30 (1994) 191–197.

[72] I. Han, M.A. Schlautman, B. Batchelor, Removal of hexavalent chromium from groundwater by granular activated carbon, Water Environ. Res. 72 (1) (2000) 29–39.

[73] S. Babel, T.A. Kurniawan, Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan, Chemosphere 54 (2004) 951.

[74] S. Mor, K. Ravindra, N.R. Bishnoi, Adsorption of chromium from aqueous solution by activated alumina and activated charcoal, Bioresour. Technol., in press.

[75] S.-J. Park, J.-S. Kim, Anodic surface treatment on activated carbons for removal of chromium(VI), J. Colloid Interface Sci. 239 (2) (2001) 380–384.

[76] I. Bautista-Toledo, J. Rivera-Utrilla, M.A. Ferro-García, C. Moreno-Castilla, Influence of the oxygen surface complexes of activated carbons on the adsorption of chromium ions from aqueous solutions: effect of sodium chloride and humic acid, Carbon 32 (1) (1994) 93–100.

[77] C. Selomulya, V. Meeyoo, R. Amal, Mechanisms of Cr(VI) removal from water by various types of activated carbons, J. Chem. Technol. Biotechnol. 74 (2) (1999) 111–122.

[78] S.K. Srivastava, R. Tyagi, N. Pant, Adsorption of heavy melt ions on carbonaceous material developed from the waste slurry generated in local fertilizer plants, Water Res. 23 (9) (1989) 1161–1165.

[79] S.K. Srivastava, V.K. Gupta, D. Mohan, Kinetic parameters for the removal of lead and chromium from wastewater using activated carbon developed from fertilizer waste material, Environ. Model. Assess. 1 (4) (1996) 281–290.

[80] L. Khezami, R. Capart, Removal of chromium(VI) from aqueous solution by activated carbons: kinetic and equilibrium studies, J. Hazard. Mater. 123 (1–3) (2005) 223–231.

[81] K. Mohanty, M. Jha, B.C. Meikap, M.N. Biswas, Removal of chromium(VI) from dilute aqueous solutions by activated carbon developed from *Terminalia arjuna* nuts activated with zinc chloride, Chem. Eng. Sci. 11 (11) (2005) 3049–3059.

[82] T. Karthikeyan, S. Rajgopal, L.R. Miranda, Chromium(VI) adsorption from aqueous solution by *Hevea brasiliensis* sawdust activated carbon, J. Hazard. Mater. 124 (1–3) (2005) 192–199.

[83] N.R. Bishnoi, M. Bajaj, N. Sharma, A. Gupta, Adsorption of Cr(VI) on activated rice husk carbon and activated alumina, Bioresour. Technol. 91 (3) (2004) 305–307.

[84] T. Cordero, J. Rodriguez-Mirasol, N. Tancredi, J. Piriz, G. Vivo, J.J. Rodriguez, Influence of surface composition and pore structure on Cr(III) adsorption onto activated carbons, Ind. Eng. Chem. Res. 41 (24) (2002) 6042–6048.

[85] N.K. Hamadi, X.D. Chen, M.M. Farid, M.G.Q. Lu, Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tyres and sawdust, Chem. Eng. J. 84 (2) (2001) 95–105.

[86] D.D. Das, R. Mahapatra, J. Pradhan, S.N. Das, R.S. Thakur, Removal of Cr(VI) from aqueous solution using activated cow dung carbon, J. Colloid Interface Sci. 232 (2) (2000) 235–240.

[87] K.S. Kim, H.C. Choi, Characteristics of adsorption of rice-hull activated carbon, Water Sci. Technol. 38 (4/5) (1998) 95–101.

[88] M. Valix, W.H. Cheung, K. Zhang, Role of heteroatoms in activated carbon for removal of hexavalent chromium from wastewaters, J. Hazard. Mater. 135 (1–3) (2006) 395–405.

[89] C. Namasivayam, D. Sangeetha, Recycling of agricultural solid waste, coir pith: removal of anions, heavy metals, organics and dyes from water by adsorption onto ZnCl$_2$ activated coir pith carbon, J. Hazard. Mater. 135 (1–3) (2006) 449–452.

[90] M. Kobya, Adsorption kinetics and equilibrium studies of Cr(VI) by hazelnut shell activated carbon, Adsorp. Sci. Technol. 22 (1) (2004) 51–64.

[91] E. Demirbas, M. Kobya, E. Senturk, T. Ozkan, Adsorption kinetics for removal of chromium(VI) from aqueous solutions on the activated carbons prepared from agricultural wastes, Water SA 30 (4) (2004) 533–539.

[92] K. Ranganathan, Chromium removal by activated carbons prepared from *Casurina equisetifolia* leaves, Bioresour. Technol. 73 (2) (2000) 99–103.

[93] Y. Guo, J. Qi, S. Yang, K. Yu, Z. Wang, H. Xu, Adsorption of Cr(VI) on micro- and mesoporous rice husk-based active carbon, Mater. Chem. Phys. 78 (1) (2003) 132–137.

[94] M. Pérez-Candela, J. Martín-Martínez, R. Torregrosa-Maciá, Chromium(VI) removal with activated carbons, Water Res. 29 (9) (1995) 2174–2180.

[95] S.I. Lyubchik, A.I. Lyubchik, O.L. Galushko, L.P. Tikhonova, J. Vital, I.M. Onseca, S.B. Lyubchik, Kinetics and thermodynamics of the Cr(III) adsorption on the activated carbon from co-mingled wastes, Colloids Surf. A: Physicochem. Eng. Aspects 242 (1–3) (2004) 151–158.

[96] S.B. Lalvani, A. Hübner, A.A. Weston, N. Mandich, Removal of hexavalent chromium and metal cations by a selective and novel carbon adsorbent, Carbon 36 (7/8) (1998) 1219–1226.

[97] C. Raji, T.S. Anirudhan, Batch Cr(VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics, Water Res. 32 (12) (1998) 3772–3780.

[98] M. Ajmal, R.A.K. Rao, B.A. Siddiqui, Studies on removal and recovery of Cr(VI) from electroplating wastes, Water Res. 30 (6) (1996) 1478–1482.

[99] M.R. Unnithan, T.S. Anirudhan, The kinetics and thermodynamics of sorption of chromium(VI) onto the iron(III) complex of a carboxylated polyacrylamide-grafted sawdust, Ind. Eng. Chem. Res. 40 (12) (2001) 2693–2701.

[100] M. Dakiky, M. Khamis, A. Manassra, M. Mer'eb, Selective adsorption of chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents, Adv. Environ. Res. 6 (4) (2002) 533–540.

[101] L.J. Yu, S.S. Shukla, K.L. Dorris, A. Shukla, J.L. Margrave, Adsorption of chromium from aqueous solutions by maple sawdust, J. Hazard. Mater. 100 (1–3) (2003) 53–63.

[102] K.M.S.S. Sumathi, R.M. Naidu, Use of low-cost biological wastes and vermiculite for removal of chromium from tannery effluent, Bioresour. Technol. 96 (3) (2005) 309–316.

[103] H. Parab, S. Joshi, N. Shenoy, A. Lali, U.S. Sarma, M. Sudersanan, Determination of kinetic and equilibrium parameters of the batch adsorption of Co(II), Cr(III) and Ni(II) onto coir pith, Process Biochem. 41 (3) (2006) 609–615.

[104] M.R. Unnithan, V.P. Vinod, T.S. Anirudhan, Synthesis, characterization, and application as a chromium(VI) adsorbent of amino-modified polyacrylamide-grafted coconut coir pith, Ind. Eng. Chem. Res. 43 (2004) 2247.

[105] L. Chun, C. Hongzhang, L. Zuohu, Adsorptive removal of Cr(VI) by Fe-modified steam exploded wheat straw, Process Biochem. 39 (5) (2004) 541–545.

[106] I.C. Eromosele, C.O. Eromosele, J.O. Orisakiya, S. Okufi, Binding of chromium and copper ions from aqueous solutions by shea butter (*Butyrospermum parkii*) seed husks, Bioresour. Technol. 58 (1) (1996) 25–29.

[107] D.C. Sharma, C.F. Forster, A comparison of the sorptive characteristics of leaf mould and activated carbon columns for the removal of hexavalent chromium, Process Biochem. 31 (3) (1996) 213–218.

[108] L. Dupont, E. Guillon, Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran, Environ. Sci. Technol. 37 (18) (2003) 4235–4241.

[109] R. Machado, J.R.M. Carvalho, J.N. Correia, Removal of trivalent chromium(III) from solution by biosorption in cork powder, J. Chem. Technol. Biotechnol. 77 (12) (2002) 1340–1348.

[110] S. Samantaroy, A.K. Mohanty, M. Misra, Removal of hexavalent chromium by Kendu fruit gum dust, J. Appl. Polym. Sci. 66 (8) (1997) 1485–1494.

[111] H.S. Altundogan, Cr(VI) removal from aqueous solution by iron(III) hydroxide-loaded sugar beet pulp, Process Biochem. 40 (3/4) (2005) 1443–1452.

[112] E.A. Oliveira, S.F. Montanher, A.D. Andrade, J.A. Nóbrega, M.C. Rollemberg, Equilibrium studies for the sorption of chromium and nickel from aqueous solutions using raw rice bran, Process Biochem. 40 (11) (2005) 3485–3490.

[113] W.E. Marshall, L.H. Wartelle, An anion exchange resin from soybean hulls, J. Chem. Technol. Biotechnol. 79 (2004) 1286.

[114] V. Sarin, K.K. Pant, Removal of chromium from industrial waste by using eucalyptus bark, Bioresour. Technol. 97 (1) (2006) 15–20.

[115] G.S. Agarwal, H.K. Bhuptawat, S. Chaudhari, Biosorption of aqueous chromium(VI) by *Tamarindus indica* seeds, Bioresour. Technol. 97 (7) (2006) 949–956.

[116] B. Nasernejad, T.E. Zadeh, B.B. Pour, M.E. Bygi, A. Zamani, Comparison for biosorption modeling of heavy metals (Cr(III), Cu(II), Zn(II)) adsorption from wastewater by carrot residues, Process Biochem. 40 (3/4) (2005) 1319–1322.

[117] V.K. Garg, R. Gupta, R. Kumar, R.K. Gupta, Adsorption of chromium from aqueous solution on treated sawdust, Bioresour. Technol. 92 (1) (2004) 79–81.

[118] A. Kumar, N.N. Rao, S.N. Kaul, Alkali-treated straw and insoluble straw xanthate as low cost Adsorbents for heavy metal removal—preparation, characterization and application, Bioresour. Technol. 71 (2) (2000) 133–142.

[119] J.S. Melo, S.F. D'Souza, Removal of chromium by mucilaginous seeds of *Ocimum basilicum*, Bioresour. Technol. 92 (2) (2004) 151–155.

[120] N. Daneshvar, D. Salari, S. Aber, Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake, J. Hazard. Mater. 94 (1) (2002) 49–61.

[121] F.A. Mampton, Mineralogy and Geology of Natural Zeolites, Southern Printing Company, Blacksburg, VA, 1997.

[122] R.P. Townsend, in: H. Van Bekkum, E.M. Flannigen, J.C. Janmsen (Eds.), Ion Exchange in Zeolites, Introduction to Zeolite Science and Practice, Elsevier, Amsterdam, 1991, pp. 359–390.

[123] S. Kesraoui-Ouki, C.R. Cheeseman, R. Perry, Natural zeolite utilization in pollution control: a review of application to metal's effluents, J. Chem. Technol. Biotechnol. 59 (1994) 121–126.

[124] C. Covarrubias, R. Arriagada, J. Yáñez, R. García, M. Angélica, S.D. Barros, P. Arroyo, E.F. Sousa-Aguiar, Removal of chromium(III) from tannery effluents, using a system of packed columns of zeolite and activated carbon, J. Chem. Technol. Biotechnol. 80 (8) (2005) 899–908.

[125] G.Q. Lu, X.S. Zhao, in: G.Q. Lu, X.S. Zhao (Eds.), Nanoporous Materials—An Overview in Nanoporous Materials: Science and Engineering, Series on Chemical Engineering, vol. 4, World Scientific Publishing Company, 2004.

[126] J. Hu, G. Chen, I.M.C. Lo, Removal and recovery of Cr(VI) from wastewater by maghemite nanoparticles, Water Res. 39 (18) (2005) 4528–4536.

[127] J. Hu, I.M.C. Lo, G. Chen, Fast removal and recovery of Cr(VI) using surface-modified jacobsite (MnFe$_2$O$_4$) nanoparticles, Langmuir 21 (24) (2005) 11173–11179.

[128] Y.S. Kang, S. Rishud, J.F. Rabolt, P. Stroeve, Synthesis and characterization of nanoparticle-size Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ particles, Chem. Mater. 8 (1996) 2209–2211.

[129] F.J. Alguacil, M. Alonso, L.J. Lozano, Chromium(III) recovery from waste acid solution by ion exchange processing using Amberlite IR-120 resin: batch and continuous ion exchange modeling, Chemosphere 57 (8) (2004) 789–793.

[130] F. Gode, E. Pehlivan, A comparative study of two chelating ion-exchange resins for the removal of chromium(III) from aqueous solution, J. Hazard. Mater. 100 (1–3) (2003) 231–243.

[131] F. Gode, E. Pehlivan, Removal of Cr(VI) from aqueous solution by two Lewatit-anion exchange resins, J. Hazard. Mater. 119 (1–3) (2005) 175–182.

[132] F. Gode, E. Pehlivan, Removal of chromium(III) from aqueous solutions using Lewatit S 100: the effect of pH, time, metal concentration and temperature, J. Hazard. Mater. 136 (2) (2006) 330–337.

[133] N. Kabay, M. Arda, B. Saha, M. Streat, Removal of Cr(VI) by solvent impregnated resins (SIR) containing Aliquat 336, React. Funct. Polym. 54 (1–3) (2003) 103–115.

[134] B.R. Saha, J. Gill, D.G. Bailey, N. Kabay, M. Arda, Sorption of Cr(VI) from aqueous solution by Amberlite XAD-7 resin impregnated with Aliquat 336, React. Funct. Polym. 60 (2004) 223–244.

[135] P.A. Terry, Characterization of Cr ion exchange with hydrotalcite, Chemosphere 57 (7) (2004) 541–546.

[136] L.H. Wartelle, W.E. Marshall, Chromate ion adsorption by agricultural by-products modified with dimethyloldihydroxyethylene urea and choline chloride, Water Res. 39 (13) (2005) 2869–2876.

[137] S. Denga, R. Bai, Removal of trivalent and hexavalent chromium with aminated polyacrylonitrile fibers: performance and mechanisms, Water Res. 38 (9) (2004) 2424–2432.

[138] S.-J. Park, Y.-S. Jang, J.-W. Shim, S.-K. Ryu, Studies on pore structures and surface functional groups of pitch-based activated carbon fibers, J. Colloid Interface Sci. 260 (2) (2003) 259–264.

[139] S.-J. Park, W.-Y. Jung, Adsorption behaviors of chromium(III) and (VI) on electroless Cu-plated activated carbon fibers, J. Colloid Interface Sci. 243 (2) (2001) 316–320.

[140] V. Campos, P.M. Bucher, Removal of chromate from drinking water using powder carbon steel, Environ. Geol. 47 (2005) 926–930.

[141] S.J. Allen, P. Brown, Isotherm analysis for single component and multicomponent metal sorption onto lignite, J. Chem. Technol. Biotechnol. 62 (1995) 17–24.

[142] S.J. Allen, L.J. Whitten, M. Murray, O. Duggan, The adsorption of pollutants by peat, lignite and activated chars, J. Chem. Technol. Biotechnol. 68 (1997) 442–452.

[143] G.G. Pope, Pore structure and size for lignites, Fuel 63 (1984) 1681–1685.

[144] H. Gan, S.P. Nardi, P.L. Walker, Nature of the porosity in American coals, Fuel 51 (1972) 272–275.

[145] D. Mohan, S. Chander, Single, binary, and multicomponent sorption of iron and manganese on lignite, J. Colloid Interface Sci. 299 (1) (2006) 76–87.

[146] D. Mohan, S. Chander, Removal and recovery of metal ions from acid mine drainage using lignite—a low cost sorbent. J. Hazard. Mater., doi:10.1016/j.jhazmat.2006.04.053, in press.

[147] P.A. Brown, S.A. Gill, S.J. Allen, Metal removal from wastewater using peat, Water Res. 34 (2000) 3907–3916.

[148] D. Couillard, Appropriate wastewater management technologies using peat, J. Environ. Syst. 21 (1992) 1–19.

[149] D. Couillard, The use of peat in wastewater treatment, Water Res. 28 (1994) 1261–1274.

[150] J.K. McLellan, C.A. Rock, The application of peat in environmental pollution control: a review, Int. Peat. J. 1 (1986) 1–14.

[151] T. Viraragharan, A. Ayyaswami, Use of peat in water pollution control: a review, Can. J. Civil Eng. 14 (1987) 230–232.

[152] F. Gode, E. Pehlivan, Adsorption of Cr(III) ions by Turkish brown coals, Fuel Process. Technol. 86 (8) (2005) 875–884.

[153] F. Gode, E. Pehlivan, Chromium(VI) adsorption by brown coals, Energy Sources A 28 (5) (2006) 447–457.

[154] T. Kwon, G.A. Tsigdinos, T.J. Pinnavaia, Pillaring of layered double hydroxides (LDHs) by polyoxometalate anions, J. Am. Soc. 110 (11) (1988) 36.

[155] N.N. Das, J. Konar, M.K. Mohanta, S.C. Srivastava, Adsorption of Cr(VI) and Se(IV) from their aqueous solutions onto Zr^{4+}-substituted ZnAl/MgAl-layered double hydroxides: effect of Zr^{4+} substitution in the layer, J. Colloid Interface Sci. 270 (1) (2004) 1–8.

[156] R.F. de Farias, A.G. de Souza, L.M. Nunes, V.A. de Cardoso, Adsorption of Cr(III) and Fe(III) on an inorganic–organic silicon hybrid surface, Colloids Surf. A: Physicochem. Eng. Aspects 211 (2/3) (2002) 295–298.

[157] R.L. Goswamee, P. Sengupta, K.G. Bhattacharyya, D.K. Dutta, Adsorption of Cr(VI) in layered double hydroxides, Appl. Clay Sci. 13 (1) (1998) 21–34.

[158] N.K. Lazaridis, D.D. Asouhidou, Kinetics of sorptive removal of chromium(VI) from aqueous solutions by calcined Mg–Al–CO$_3$ hydrotalcite, Water Res. 37 (12) (2003) 2875–2882.

[159] A. Benhammou, A. Yaacoubi, L. Nibou, B. Tanouti, Study of the removal of mercury(II) and chromium(VI) from aqueous solutions by Moroccan stevensite, J. Hazard. Mater. 17 (2/3) (2005) 243–249.

[160] K. Csobán, P. Joó, Sorption of Cr(III) on silica and aluminium oxide: experiments and modeling, Colloids Surf. A: Physicochem. Eng. Aspects 15 (1/2) (1999) 97–112.

[161] M. Erdem, H.S. Altundogan, M.D. Turan, F. Tümen, Hexavalent chromium removal by ferrochromium slag, J. Hazard. Mater. B 126 (2005) 176–182.

[162] S.A. Khan, R.U. Rehman, M.A. Khan, Adsorption of chromium(III), chromium(VI) and silver(I) on bentonite, Waste Manage. 15 (4) (1995) 271–282.

[163] M. Lehmann, A.I. Zouboulis, K.A. Matis, Modeling the sorption of metals from aqueous solutions on goethite fixed-beds, Environ. Pollut. 113 (2) (2001) 121–128.

[164] J.H. Potgieter, S.S. Potgieter-Vermaak, P.D. Kalibantonga, Heavy metals removal from solution by palygorskite clay, Min. Eng. 19 (5) (2006) 463–470.

[165] H. Tel, Y. Alta, M.S. Taner, Adsorption characteristics and separation of Cr(III) and Cr(VI) on hydrous titanium(IV) oxide, J. Hazard. Mater. 112 (3) (2004) 225–231.

[166] C.S. Uyguner, M. Bekbolet, Evaluation of humic acid, chromium(VI) and TiO$_2$ ternary system in relation to adsorptive interactions, Appl. Catal. B: Environ. 49 (4) (2004) 267–275.

[167] M. Erdem, H.S. Altundogan, F. Tümen, Removal of hexavalent chromium by using heat-activated bauxite, Min. Eng. 17 (9/10) (2004) 1045–1052.

[168] N.K. Lazaridis, C. Charalambous, Sorptive removal of trivalent and hexavalent chromium from binary aqueous solutions by composite alginate–goethite beads, Water Res. 39 (18) (2005) 4385–4396.

[169] J. Bajpai, R. Shrivastava, A.K. Bajpai, Dynamic and equilibrium studies on adsorption of Cr(VI) ions onto binary bio-polymeric beads of cross linked alginate and gelatin, Colloids Surf. A: Physicochem. Eng. Aspects 236 (1–3) (2004) 81–90.

[170] J.P. Ibáñez, Y. Umetsu, Uptake of trivalent chromium from aqueous solutions using protonated dry alginate beads, Hydrometallurgy 72 (3/4) (2004) 327–334.

[171] B. Salih, A. Denizli, C. Kavakl, R. Say, E.P. Kin, Adsorption of heavy metal ions onto dithizone-anchored poly(EGDMA-HEMA) microbeads, Talanta 46 (5) (1998) 1205–1213.

[172] A. Nakajima, Y. Baba, Mechanism of hexavalent chromium adsorption by persimmon tannin gel, Water Res. 38 (12) (2004) 2859–2864.

[173] Y. Nakano, K. Takeshita, T. Tsutsumi, Adsorption mechanism of hexavalent chromium by redox within condensed-tannin gel, Water Res. 35 (2) (2001) 496–500.

[174] C. Heitz, W. Binana-Limbele, J. François, C Biver, Absorption and desorption of chromium ions by poly(acrylic acid) gels, J. Appl. Polym. Sci. 72 (4) (1999) 455–466.

[175] I.C. Eromosele, S.S. Bayero, Adsorption of chromium and zinc ions from aqueous solutions by cellulosic graft copolymers, Bioresour. Technol. 71 (3) (2000) 279–281.

[176] V.K. Gupta, I. Ali, Removal of lead and chromium from wastewater using bagasse fly ash—a sugar industry waste, J. Colloid Interface Sci. 271 (2) (2004) 321–328.

[177] M. Rao, A.V. Parwate, A.G. Bhole, Removal of Cr^{6+} and Ni^{2+} from aqueous solution using bagasse and fly ash, Waste Manage. 22 (7) (2002) 821–830.

[178] B. Bayat, Comparative study of adsorption properties of Turkish fly ashes. II. The case of chromium(VI) and cadmium(II), J. Hazard. Mater. 95 (3) (2002) 275–290.

[179] S.S. Banarjee, M.V. Joshi, R.V. Jayaram, Removal of Cr(VI) and Hg(II) from aqueous solutions using fly ash and impregnated fly ash, Sep. Sci. Technol. 39 (7) (2004) 1611–1629.

[180] A. Demirbaş, G. Arslan, E. Pehlivan, Recent studies on activated carbons and fly ashes from Turkish resources, Energy Sources A 28 (2006) 627–638.

[181] S.K. Srivastava, V.K. Gupta, D. Mohan, Removal of lead and chromium by activated slag—a blast furnace waste, J. Environ. Eng. (ASCE) 123 (5) (1997) 461–468.

[182] E. Lopez, B. Soto, M. Asias, A. Nunez, D. Rubinos, M.T. Barral, Adsorbent properties of red mud and its use for wastewater treatment, Water Res. 32 (1998) 1314–1322.

[183] S.B. Lalvani, A. Hubner, T.S. Wiltowski, Metal removal from process water by lignin, Environ. Technol. 18 (1997) 1663–1668.

[184] S.B. Lalvani, A. Hubner, T.S. Wiltowski, Chromium adsorption by lignin, Energy Sources 22 (2000) 45–56.

[185] C. Ali, D. Kenan, S. Hasan, An investigation of Cr(VI) ion removal from wastewaters by adsorption on residual lignin, Fresenius Environ. Bull. 13 (2) (2004) 124–127.

[186] Y.-S. Li, C.-C. Liu, C.-S. Chiou, Adsorption of Cr(III) from wastewater by wine processing waste sludge, J. Colloid Interface Sci. 273 (1) (2004) 95–101.

[187] K. Selvaraj, S. Manonmani, S. Pattabhi, Removal of hexavalent chromium using distillery sludge, Bioresour. Technol. 89 (2) (2003) 207–211.

[188] Z. Aksu, U. Açıkel, E. Kabasakal, S. Tezer, Equilibrium modeling of individual and simultaneous biosorption of chromium(VI) and nickel(II) onto dried activated sludge, Water Res. 36 (12) (2002) 3063–3073.

[189] R.A. Shawabkeh, Adsorption of chromium ions from aqueous solution by using activated carbo-aluminosilicate material from oil shale, J. Colloid Interface Sci. 299 (2) (2006) 530–536.

[190] E. Malkoc, Y. Nuhoglu, Fixed bed studies for the sorption of chromium(VI) onto tea factory waste, Chem. Eng. Sci. 61 (13) (2006) 4363–4372.

[191] E. Malkoc, Y. Nuhoglu, M. Dundar, Adsorption of chromium(VI) on pomace—an olive oil industry waste: Batch and column studies, J. Hazard. Mater., doi:10.1016/j.jhazmat.2006.05.051, in press.

[192] M.H. Entezari, N. Ghows, M. Chamsaz, Combination of ultrasound and discarded tire rubber: removal of Cr(III) from aqueous solution, J. Phys. Chem. A 109 (20) (2005) 4638–4642.

[193] C. Namasivayam, R.T. Yamuna, Adsorption of chromium(VI) by a low-cost adsorbent: biogas residual slurry, Chemosphere 30 (3) (1995) 561–578.

[194] C. Namasivayam, R.T. Yamuna, Studies on chromium(III) removal from aqueous solution by adsorption onto biogas residual slurry and its application to tannery wastewater treatment, Water Air Soil Pollut. 113 (1999) 371–384.

[195] V.K. Singh, P.N. Tiwari, Removal recovery of chromium(VI) from industrial waste water, J. Chem. Technol. Biotechnol. 69 (3) (1997) 376–382.

[196] A.K. Bhattacharya, C. Venkobachar, Removal of cadmium(II) by low-cost adsorbents, J. Environ. Eng. ASCE 110 (1) (1984) 110–122.

[197] Z. Aksu, F. Gönen, Z. Demircan, Biosorption of chromium(VI) ions by Mowital®B30H resin immobilized activated sludge in a packed bed: comparison with granular activated carbon, Process Biochem. 38 (2) (2002) 175–186.

[198] Z. Aksu, D. Akpinar, Competitive biosorption of phenol and chromium(VI) from binary mixtures onto dried anaerobic activated sludge, Biochem. Eng. J. 7 (3) (2001) 183–193.

[199] G. McKay, Use of Adsorbents for the Removal of Pollutants from Wastewaters, CRC Press, Boca Raton, NY, 1995.

[200] D. Mohan, C.U. Pittman Jr., P. Steele, Pyrolysis of wood/biomass for bio-oil: a critical review, Energy Fuels 20 (2006) 848–889.

[201] H.H. Nimz, Tappi J. 56 (1973) 124.

[202] N.N. Fathima, R. Aravindhan, J.R. Rao, B.U. Nair, Solid waste removes toxic liquid waste: adsorption of Cr(VI) by iron complexed protein waste, Environ. Sci. Technol. 39 (8) (2005) 2804–2810.

[203] A.I. Zouboulis, K.A. Kydros, K.A. Matis, Removal of hexavalent chromium anions from solutions by pyrite fines, Water Res. 29 (7) (1995) 1755–1760.

[204] O.A. Fadali, Y.H. Magdy, A.A.M. Daifullah, E.E. Ebrahiem, M.M. Nassar, Removal of chromium from tannery effluents by adsorption, J. Environ. Sci. Health 239 (2) (2004) 465–472.

[205] G.M. Gadd, Accumulation of metal by microorganisms and algae, in: H. Rehm (Ed.), Biotechnology: A Complete Treatise, vol. 6B: Special Microbial Processes, vol. 4, VCH, Verlagsgesellschaft, Weinheim, 1988, pp. 401–430.

[206] C.L. Brierley, Bioremediation of metal-contaminated surface and groundwater, Geomicrobiol. J. 8 (1990) 201–223.

[207] B. Volesky, Sorption and Biosorption, BVSorbex, Inc., Canada, 2003.

[208] B. Volesky, Z.R. Holan, Biosorption of heavy metals, Biotechnol. Prog. 11 (1995) 235–250.

[209] S. Schiewer, B. Volesky, Biosorption by marine algae, in: J.J. Valdes (Ed.), Remediation, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2000, pp. 139–169.

[210] D. Kratochvil, B. Volesky, Advances in the biosorption of heavy metals, Trends Biotechnol. 16 (1998) 291–300.

[211] V.K. Gupta, A.K. Shrivastava, N. Jain, Biosorption of chromium(VI) from aqueous solutions by green algae spirogyra species, Water Res. 35 (17) (2001) 4079–4085.

[212] M.Y. Arıca, G. Bayramoğlu, Cr(VI) biosorption from aqueous solutions using free and immobilized biomass of *Lentinus sajor-caju*: preparation and kinetic characterization, Colloids Surf. A: Physicochem. Eng. Aspects 253 (1–3) (2005) 203–221.

[213] G. Dönmez, Z. Aksu, Removal of chromium(VI) from saline wastewaters by *Dunaliella* species, Process Biochem. 38 (5) (2002) 751–762.

[214] Z. Aksu, U. Açikel, Modelling of a single-staged bioseparation process for simultaneous removal of iron(III) and chromium(VI) by using *Chlorella vulgaris*, Biochem. Eng. J. 4 (3) (2000) 229–238.

[215] G.Ç. Dönmez, Z. Aksu, A. Öztürk, T. Kutsal, A comparative study on heavy metal biosorption characteristics of some algae, Process Biochem. 34 (9) (1999) 885–892.

[216] Z. Aksu, Ü. Açikel, T. Kutsal, Investigation of simultaneous biosorption of copper(II) and chromium(VI) on dried *Chlorella vulgaris* from binary metal mixtures: application of multicomponent adsorption isotherms, Sep. Sci. Technol. 34 (3) (1999) 501–552.

[217] Z. Aksu, U. Açikel, A single-staged bioseparation process for simultaneous removal of copper(II) and chromium(VI) by using *C. vulgaris*, Process Biochem. 34 (6/7) (1999) 589–599.

[218] M. Nourbakhsh, Y. Sag, D. Özer, Z. Aksu, T. Kutsal, A. Çaglar, A comparative study of various biosorbents for removal of chromium(VI) ions from industrial waste waters, Process Biochem. 29 (1) (1994) 1–5.

[219] M.N. Nourbakhsh, S. Kiliçarslan, S. Ilhan, H. Ozdag, Biosorption of Cr^{6+} Pb^{2+} and Cu^{2+} ions in industrial waste water on *Bacillus* sp., Chem. Eng. J. 85 (2/3) (2002) 351–355.

[220] R. Aravindhan, B. Madhan, J.R. Rao, B.U. Nair, T. Ramasami, Bioaccumulation of chromium from tannery wastewater: an approach for chrome recovery and reuse, Environ. Sci. Technol. 38 (1) (2004) 300–306.

[221] D. Park, Y.-S. Yun, H.Y. Cho, J.M. Park, Chromium biosorption by thermally treated biomass of the brown seaweed, *Ecklonia* sp., Ind. Eng. Chem. Res. 43 (2004) 8226.

[222] Y.-S. Yun, D. Park, J.M. Park, B. Volesky, Biosorption of trivalent chromium on the brown seaweed biomass, Environ. Sci. Technol. 35 (21) (2001) 4353–4358.

[223] R. Aravindhan, B. Madhan, J.R. Rao, B.U. Nair, Recovery and reuse of chromium from tannery wastewaters using *Turbinaria ornata* seaweed, J. Chem. Technol. Biotechnol. 79 (11) (2004) 1251–1258.

[224] M.E.R. Carmona, M.A.P. da Silva, S.G.F. Leite, Biosorption of chromium using factorial experimental design, Process Biochem. 40 (2005) 779.

[225] H. Seki, A. Suzuki, H. Maruyama, Biosorption of chromium(VI) and arsenic(V) onto methylated yeast biomass, J. Colloid Interface Sci. 281 (2) (2005) 261–266.

[226] R.S. Prakasham, J.S. Merrie, R. Sheela, N. Saswathi, S.V. Ramakrishna, Biosorption of chromium(VI) by free and immobilized *Rhizopus arrhizus*, Environ. Pollut. 104 (3) (1999) 421–427.

[227] Y. Sag, T. Kutsal, Fully competitive biosorption of Cr(VI) and Fe(III) ions from binary metal mixtures by *R. arrhizus*: use of the competitive Langmuir model, Process Biochem. 31 (6) (1996) 573–585.

[228] S. Deng, Y.P. Ting, Polyethylenimine-modified fungal biomass as a high-capacity biosorbent for Cr(VI) anions: sorption capacity and uptake mechanisms, Environ. Sci. Technol. 39 (21) (2005) 8490–8496.

[229] K.C. Sekhar, S. Subramanian, J.M. Modak, K.A. Natarajan, Removal of metal ions using an industrial biomass with reference to environmental control, Int. J. Min. Process. 53 (1/2) (1998) 107–120.

[230] G. Bayramoğlu, G. Çelik, E. Yalçın, M. Yılmaz, M.Y. Arıca, Modification of surface properties of *Lentinus sajor-caju* mycelia by physical and chemical methods: evaluation of their Cr^{6+} removal efficiencies from aqueous medium, J. Hazard. Mater. 119 (1–3) (2005) 219–229.

[231] R.S. Bai, T.E. Abraham, Studies on chromium(VI) adsorption–desorption using immobilized fungal biomass, Bioresour. Technol. 87 (1) (2003) 17–26.

[232] R.S. Bai, T.E. Abraham, Studies on enhancement of Cr(VI) biosorption by chemically modified biomass of *Rhizopus nigricans*, Water Res. 36 (5) (2002) 1224–1236.

[233] R.S. Bai, T.E. Abraham, Biosorption of Cr(VI) from aqueous solution by *Rhizopus nigricans*, Bioresour. Technol. 79 (1) (2001) 73–81.

[234] S. Tunali, I. Kiran, T. Akar, Chromium(VI) biosorption characteristics of *Neurospora crassa* fungal biomass, Min. Eng. 18 (7) (2005) 681–689.

[235] N. Tewari, P. Vasudevan, B.K. Guha, Study on biosorption of Cr(VI) by *Mucor hiemalis*, Biochem. Eng. J. 23 (2) (2005) 185–192.

[236] J.S. Merrin, R. Sheela, N. Saswathi, R.S. Prakasham, S.V. Ramakrishna, Biosorption of chromium(VI) using *Rhizopus arrhizus*, Ind. J. Exp. Biol. 36 (1998) 1052–1055.

[237] R. Say, N. Yilmaz, A. Denizli, Removal of chromium(VI) ions from synthetic solutions by the fungus *Penicillium purpurogenum*, Eng. Life Sci. 4 (3) (2004) 276–280.

[238] M. Zhao, J.R. Duncan, Column sorption of Cr(VI) from electroplating effluent using formaldehyde cross-linked *Saccharomyces cerevisiae*, Biotechnol. Lett. 20 (6) (1998) 603–606.

[239] D. Park, Y.-S. Yun, J.H. Jo, J.M. Park, Mechanism of hexavalent chromium removal by dead fungal biomass of *Aspergillus niger*, Water Res. 39 (2005) 533.

[240] A. Baral, R.D. Engelken, Chromium-based regulations and greening in metal finishing industries in the USA, Environ. Sci. Policy 5 (2) (2002) 121–133.

[241] D. Park, Y.-S. Yun, J.M. Park, Use of dead fungal biomass for the detoxification of hexavalent chromium: screening and kinetics, Process Biochem. 40 (2005) 2559.

[242] D. Park, Y.-S. Yun, J.M. Park, Studies on hexavalent chromium biosorption by chemically-treated biomass of *Ecklonia* sp., Chemosphere 60 (10) (2005) 1356–1364.

[243] D. Park, Y.-S. Yun, J.H. Jo, J.M. Park, Effects of ionic strength, background electrolytes, heavy metals and redox-active species on the reduction of hexavalent chromium by *Ecklonia* biomass, J. Microbiol. Biotechnol. 15 (4) (2005) 780–786.

[244] A. Bingol, H. Ucun, Y.K. Bayhan, A. Karagunduz, A. Cakici, B. Keskinler, Removal of chromate anions from aqueous stream by a cationic surfactant-modified yeast, Bioresour. Technol. 94 (2004) 245.

[245] M.X. Loukidou, A.I. Zouboulis, T.D. Karapantsios, K.A. Matis, Equilibrium and kinetic modeling of chromium(VI) biosorption by *Aeromonas caviae*, Colloids Surf. A: Physicochem. Eng. Aspects 242 (1–3) (2004) 93–104.

[246] M.X. Loukidou, T.D. Karapantsios, A.I. Zouboulis, K.A. Matis, Diffusion kinetic study of chromium(VI) biosorption by *Aeromonas caviae*, Ind. Eng. Chem. Res. 43 (7) (2004) 1748–1755.

[247] Y. Şahin, A. Öztürk, Biosorption of chromium(VI) ions from aqueous solution by the bacterium *Bacillus thuringiensis*, Process Biochem. 40 (5) (2005) 1895–1901.

[248] G. Ozdemir, N. Ceyhan, T. Ozturk, F. Akirmak, T. Cosar, Biosorption of chromium(VI), cadmium(II) and copper(II) by *Pantoea* sp. TEM18, Chem. Eng. J. 102 (3) (2004) 249–253.

[249] G. Ozdemir, S.H. Baysal, Chromium and aluminum biosorption on *Chryseomonas luteola* TEM05, Appl. Microbiol. Biotechnol. 64 (2004) 599.

[250] M. Rabbani, H. Ghafourian, S. Sadeghi, Y. Nazeri, Biosorption of chromium(III) by new bacterial strain (NRC-BT-2), Int. Congr. Ser. 1276 (2005) 268–269.

[251] K.H. Cheung, J.D. Gu, Reduction of chromate (CrO_4^{2-}) by an enrichment consortium and an isolate of marine sulfate-reducing bacteria, Chemosphere 52 (2003) 1523–1529.

[252] F.N. Acar, E. Malkoc, The removal of chromium(VI) from aqueous solutions by *Fagus orientalis* L., Bioresour. Technol. 94 (1) (2004) 13–15.

[253] J. Romero-González, J.R. Peralta-Videa, E. Rodríguez, S.L. Ramirez, J.L. Gardea-Torresdey, Determination of thermodynamic parameters of Cr(VI) adsorption from aqueous solution onto *Agave lechuguilla* biomass, J. Chem. Thermodyn. 37 (4) (2005) 343–347.

[254] J. Romero-González, J.R. Peralta-Videa, E. Rodríguez, M. Delgado, J.L. Gardea-Torresdey, Potential of *Agave lechuguilla* biomass for Cr(III) removal from aqueous solutions: thermodynamic studies, Bioresour. Technol. 97 (1) (2006) 178–182.

[255] M.F. Sawalha, J.L. Gardea-Torresdey, J.G. Parsons, G. Saupe, J.R. Peralta-Videa, Determination of adsorption and speciation of chromium species by saltbush (*Atriplex canescens*) biomass using a combination of XAS and ICP–OES, Microchem. J. 81 (1) (2005) 122–132.

[256] E. Oguz, Adsorption characteristics and the kinetics of the Cr(VI) on the *Thuja oriantalis*, Colloids Surf. A: Physicochem. Eng. Aspects 252 (2/3) (2005) 121–128.

[257] J.L. Gardea-Torresdey, A. Hernandez, K.J. Tiemann, J. Bibb, O. Rodriguez, Adsorption of toxic metal ions from solution by inactivated cells of larrea tridentate (creosote bush), J. Hazard. Subst. Res. 1 (1998) 3–16.

[258] H. Ucun, Y.K. Bayhan, Y. Kaya, A. Cakici, O.F. Algur, Biosorption of chromium(VI) from aqueous solution by cone biomass of *Pinus sylvestris*, Bioresour. Technol. 85 (2) (2002) 155–158.

[259] J.L. Gardea-Torresdey, K.J. Tiemann, V. Armendariz, L. Bess-Oberto, R.R. Chianelli, J. Rios, J.G. Parsons, G. Gamez, Characterization of Cr(VI) binding and reduction to Cr(III) by the agricultural byproducts of *Avena monida* (oat) biomass, J. Hazard. Mater. 80 (2000) 175.

[260] M.A. Maine, N.L. Suñé, S.C. Lagger, Chromium bioaccumulation: comparison of the capacity of two floating aquatic macrophytes, Water Res. 38 (6) (2004) 1494–1501.

[261] M. Aoyama, Removal of Cr(VI) from aqueous solution by London plane leaves, J. Chem. Technol. Biotechnol. 78 (2003) 601–604.

[262] M. Aoyama, T. Sugiyama, S. Doi, N.-S. Cho, H.-E. Kim, Removal of hexavalent chromium from dilute aqueous solution by coniferous leaves, Holzforschung 53 (1999) 365–368.

[263] M. Aoyama, M. Kishino, T.-S. Jo, Biosorption of Cr(VI) on Japanese ceder bark, Sep. Sci. Technol. 39 (5) (2004) 1149–1162.

[264] M. Aoyama, M. Tsuda, Removal of Cr(VI) from aqueous solutions by larch bark, Wood Sci. Technol. 35 (5) (2001) 425–432.

[265] M. Aoyama, M. Tsuda, K. Seki, S. Doi, Y. Kurimoto, Y. Tamura, Adsorption of Cr(VI) from dichromate solutions onto black locust leaves, Holzforschung 54 (2000) 340–342.

[266] D.A.J. Wase, C. Forster, Biosorbents for Metal Ions, Taylor and Francis, 1997.

[267] W. Ma, J.M. Tobin, Determination and modelling of effects of pH on peat biosorption of chromium, copper and cadmium, Biochem. Eng. J. 18 (1) (2004) 33–40.

[268] S.A. Dean, J.M. Tobin, Uptake of chromium cations and anions by milled peat, Resour. Conserv. Recycl. 27 (1/2) (1999) 151–156.

[269] D.C. Sharma, C.F. Forster, Column studies into the adsorption of chromium(VI) using sphagnum moss peat, Bioresour. Technol. 52 (3) (1995) 261–267.

[270] S.D.C. Sharma, C.F. Forster, Continuous adsorption and desorption of chromium ions by sphagnum moss peat, Process Biochem. 30 (4) (1995) 293–298.

[271] G. Carrillo-Morales, M.M. Dávila-Jiménez, M.P. Elizalde-González, A.A. Peláez-Cid, Removal of metal ions from aqueous solution by adsorption on the natural adsorbent CACMM2, J. Chromatogr. A 938 (1/2) (2001) 237–242.

[272] A. Hardin, W. Admassu, Kinetics of heavy metal uptake by vegetation immobilized in a polysulfone or polycarbonate polymeric matrix, J. Hazard. Mater. 126 (1–3) (2005) 40–53.

[273] K.K. Deepa, S.M. Kumar, A.R. Binupriya, G.S. Murugesan, K. Swaminathan, S.E. Yun, Sorption of Cr(VI) from dilute solutions and wastewater by live and pretreated biomass of *Aspergillus flavus*, Chemosphere 62 (5) (2006) 833–840.

[274] B.J. Mcafee, W.D. Gould, J.C. Nedeau, A.C.A. da Costa, Biosorption of metal ions using chitosan, chitin, and biomass of *Rhizopus oryzae*, Sep. Sci. Technol. 36 (14) (2001) 3207–3222.

[275] G. Rojas, J. Silva, J.A. Flores, A. Rodriguez, M. Ly, H. Maldonado, Adsorption of chromium onto cross-linked chitosan, Sep. Purif. Technol. 44 (1) (2005) 31–36.

[276] V.A. Spinelli, M.C.M. Laranjeira, V.T. Fávere, Preparation and characterization of quaternary chitosan salt: adsorption equilibrium of chromium(VI) ion, React. Funct. Polym. 61 (3) (2004) 347–352.

[277] T.N. Castro Dantas de, A.A. Dantas Neto, M.C.P. de, A. Moura, E.L. Barros Neto, E. de Paiva Telemaco, Chromium adsorption by chitosan impregnated with microemulsion, Langmuir 17 (14) (2001) 4256–4260.

[278] V.M. Boddu, K. Abburi, J.L. Talbott, E.D. Smith, Removal of hexavalent chromium from wastewater using a new composite chitosan biosorbent, Environ. Sci. Technol. 37 (19) (2003) 4449–4456.

[279] L. Dambies, C. Guimon, S. Yiacoumi, E. Guibal, Characterization of metal ion interactions with chitosan by X-ray photoelectron spectroscopy, Colloid Surf. A 177 (2000) 203–214.

[280] S. Hasan, A. Krishnaiah, T.K. Gosh, D.S. Viswanath, V.M. Boddu, E.D. Smith, Adsorption of chromium(VI) on chitosan-coated perlite, Sep. Sci. Technol. 38 (15) (2003) 3775–3793.

[281] T. Tan, X. He, W. Du, Adsorption behavior of metal ions on imprinted chitosan resins, J. Chem. Technol. Biotechnol. 76 (2001) 191–195.

[282] S. Lagergren, Kungliga Svenska Vetenskapsakademiens, Handlinger 24 (1898) 1.

[283] Y.S. Ho, J.C.Y. Ng, G. McKay, Kinetics of pollutant sorption by biosorbents: review, Sep. Purif. Meth. 29 (2) (2000) 189–232.

[284] G.E. Boyd, A.W. Adamson, L.S. Mayers, The exchange adsorption of ions from aqueous solution by organic zeolites. II. Kinetics, J. Am. Chem. Soc. 69 (1947) 2836.

[285] D. Reichenberg, Properties of ion-exchange resin in relation to their structure. III. Kinetics of exchange, J. Am. Chem. Soc. 75 (1953) 589.

[286] F. Helffrich, Ion-Exchange, McGraw-Hill, New York, 1962.

[287] J.O. Nriagu, J.M. Pacyna, Quantitative assessment of worldwide contamination of air, water and soils by trace metals, Nature 333 (xf) (1988) 134–139.

[288] M.Y. Arıca, İ. Tüzün, E. Yalçın, Ö. İnce, G. Bayramoğlu, Utilisation of native, heat and acid-treated microalgae *Chlamydomonas reinhardtii* preparations for biosorption of Cr(VI) ions, Process Biochem. 40 (7) (2005) 2351–2358.

[289] H.S. Altundogan, Cr(VI) removal from aqueous solution by iron(III) hydroxide-loaded sugar beet pulp, Process Biochem. 40 (2005) 1443–1452.

[290] V.K. Singh, P.N. Tiwari, Removal and recovery of chromium(VI) from industrial wastewater, J. Chem. Technol. Biotechnol. 69 (1997) 376–382.

[291] K.K. Panday, G. Prasad, V.N. Singh, Removal of Cr(VI) from aqueous solutions by adsorption on fly ash-wollastonite, J. Chem. Technol. Bioechnol. A 34 (1984) 367–374.

[292] D.C. Sharma, C.F. Forster, A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents, Bioresour. Technol. 47 (3) (1994) 257–264.

[293] S. Qian, G. Huang, J. Jiang, F. He, Y. Wang, Studies of adsorption behavior of cross-linked chitosan for Cr(VI), Se(VI), J. Appl. Polym. Sci. 77 (2000) 3216–3219.

[294] D. Park, Y.-S. Yun, J.M. Park, Reduction of hexavalent chromium with the brown seaweed *Ecklonia* biomass, Environ. Sci. Technol. 38 (18) (2004) 4860–4864.

Further readings

[295] L.R. Radovic, C. Moreno-Castilla, J. Rivera-Utrilla, Carbon materials as adsorbents in aqueous solutions, in: L.R. Radovic (Ed.), Chemistry and Physics of Carbon, vol. 27, Marcel Dekker, Inc., New York, 2000.

[296] G. McKay (Ed.), Use of Adsorbents for the Removal of Pollutants from Wastewaters, CRC Press, Boca Raton, NY, 1995, ISBN 0849369207.

[297] W.J. Thomas, B.D. Crittenden (Eds.), Adsorption Technology and Design, Butterworth-Heinemann, 1998, ISBN 0750619597.

[298] J. Jozsef Toth (Ed.), Adsorption, Marcel Dekker, 2002, ISBN 0824707478.

[299] D.A. John Wase, C. Forster (Eds.), Biosorbents for Metal Ions, Taylor and Francis, 1997, ISBN 0748404317.

[300] J. Tascon (Ed.), Adsorption by Carbons, Elsevier, 2005, ISBN 0-08-044464-4.

[301] Y.-S. Wong, N.F.Y. Tam (Eds.), Wastewater Treatment with Algae, Springer, 1998, ISBN 3-540-63363-4.

[302] R.Y. Yang (Ed.), Adsorbents: Fundamentals and Applications, Wiley/Interscience, 2003, ISBN 0-471-29741-0.

[303] D.C. Cooney (Ed.), Adsorption Design for Wastewater Treatment, Lewis Publishers, 1998, ISBN 0-56670-336-6.

[304] K.E. Noll (Ed.), Adsorption Technology for Air and Water Pollution Control, Lewis Publishers, 1991, ISBN 0-87371-340-0.

[305] D.D. Do (Ed.), Adsorption Analysis: Equilibria an Kinetics, vol. 2, Imperial College Press, 1998, ISBN 1-86094-130-3.

[306] D. Basmadjian (Ed.), The Little Adsorption Book : A Practical Guide for Engineers and Scientists, CRC Press, 1996, ISBN 0-8493-2692-3.

[307] T.J. Bandosz, Activated Carbon Surfaces in Environmental Remediation, Academic Press, 2006, ISBN 0-12-370536-3.

[308] J.M.D. Tascon (Ed.), Adsorption by Carbons, Elsevier Science, 2006, ISBN 0080444644.

[309] C. Palmer, R. Puls, 1994. Natural attenuation of hexavalent chromium in ground water and soils, EPA/540/S-94/505. U.S. Environmental Protection Agency Ground Water Issue. October 1994.