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Review

Biosorbents for hexavalent chromium elimination from industrial and municipal effluents

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ABSTRACT

The presence of hexavalent chromium in wastewater is a potential hazard to aquatic animals and humans. There are various mechanisms proposed, kinetic models used and adsorption isotherms employed for the efficient removal of hexavalent chromium from industrial and municipal wastewaters using biosorbents. Biosorption of heavy metals is a most promising technology involved in the removal of toxic metals from industrial waste streams and natural waters. Metal removal treatment systems

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using microorganisms are cheap because of the low cost of sorbent materials used and may represent a practical replacement to conventional processes. The present review discusses hexavalent chromium biosorption properties of algae, bacteria, fungi, and agricultural products, as well as adsorption properties of non-living substances. Cell walls are responsible for biosorption of dead biomaterial; compositions of cell walls are discussed. Chemical modification of biosorbents, optimization of biosorption parameters, mixtures of different biosorbents and the study of biosorption mechanisms are the main keys to transfer the biosorption process from lab to industry.

1. Introduction

Heavy metal contamination is one of the most noteworthy environmental problems of this century [1–5]; chromium is the seventh most abundant element on earth [6]. In the last few decades, the amount of chromium in aquatic and terrestrial ecosystems has increased as a consequence of different human activities. Chromium is the new entry, after lead, cadmium and mercury in the major toxic metal series. The toxicity of chromium(VI) is the central theme of the Hollywood blockbuster movie "Erin Brockovitch".

In the case of Hinkley (a small desert town in San Bernardino Country, USA) hexavalent chromium was used by Pacific Gas and Electric Company (PG & E) in cooling systems to prevent pipes from rusting. The runoff of hexavalent chromium contaminated water on the PG & E property, seeped into the ground and contaminated local water supplies. PG & E was required to compensate the plaintiffs $333 million, clean up the hexavalent chromium contamination, and stop using hexavalent chromium in their operations. This is the highest compensation award in metal toxicity history. A similar case occurred in 2007 in the Asopos River, near Oinofyta, Greece. In June 2009, the ground water in Midland, Texas (USA) was found to be contaminated with chromium. In 2005, the Indian Supreme court fined Hema chemicals for illegal chromium dumping. Clearly this is a continuing problem of ecology and coordination chemistry.

The world production of chromite ore is several millions of tons per year. Ferrochromite is obtained by direct reduction of the ore while chromium metal is produced either by chemical reduction (the aluminothermic process) or by electrolysis of either CrO_3 or chrome alum solutions. Chromium and its compounds are extensively used in industry with the most common and important sources coming from the electroplating, tanning, water cooling, pulp production, dyes and pigments, film and photography, wood preservation and alloy manufacture industries. Petroleum refining processes have resulted in introduction into soil, air and water [7–9].

Tanning is a process of converting raw hides or skins into leather. The conversion of animal hides and skins into useful artifacts may be man's oldest technology [10]. Tanning is defined as a process by which unstable biological material is transformed into a stable material which resists microbial attack and has enhanced resistance to wet and heat [10]. A considerable quantity of basic chrome sulfate (known as tanning powder, which is manufactured from the simple reduction of Cr(VI) to Cr(III) by sulfur dioxide) is used in chrome tanning to convert polypeptide collagen strands in the hide to a cross-linked helix [10], obviating penetration of water into leather pores [11] and supplying thermal stability. The options for cross-linking are threefold: they are intra single helix, intra triple helix and inter triple helix [10,11]. The Cr(III) fixation (cross-linking) can occur in two ways, either a covalent reaction between one chromium ion and two carboxyl groups of collagen, or hydrogen bonding between chromium species (monomer, dimer, etc.) and the protein, particularly along the polypeptide backbone. About 40% of used chromium is discharged in the effluent as Cr(VI) and Cr(III). The Cr(III) in soil may be oxidized to Cr(VI) in presence of manganese [12]. Cr(VI) is produced in leather during photoaging [13].

Chrome plating, the result of which is often referred to simply as chrome, is a technique of electroplating a thin layer of chromium onto a metal [14]. The chromed layer is attractive and provides corrosion resistance, easy cleaning and surface hardness. There are two types of chrome plating baths: hexavalent and trivalent, although the latter are not common. Hexavalent chromium baths are widely used. A typical bath composition of a hexavalent chromium bath [14] is as follows: (i) electrolytic solution: chromic acid; (ii) anode: lead with tin up to 7%; (iii) operating temperature: 45–60 °C; (iv) plating current: 1.5–3.0 kA/m^2. About 35% of used chromium is discharged in the effluent as trivalent and hexavalent chromium [14].

Chromium compounds are used in paint pigments [12]. Chromates of barium, lead and zinc provide the pigments of lemon chromium, chromium yellow, chromium red, chromium orange, zinc yellow and zinc green. Chromium green is used in the making of green glass [14]. Chromium chemicals enhance the colors of fabrics and are used to achieve the brightly colored Cr-based paints for automobiles and buildings. The chromates of Ba, Pb and Zn ($MCrO_4$) are toxic and these compounds are discharged in the wastewater [14]. Potassium dichromate is used in the manufacture of waterproof glues and photography [12]. Almost all chemical laboratories (academic, research and industry) discharge considerable amounts of chromium, both trivalent and hexavalent, to the environment [12].

Chromium(VI) is used widely in the laboratory as an oxidant. Dichrometry (potassium dichromate is a primary standard, its solution is used to standardize secondary standards and quantitative estimation of metal ions) is a significant analytical tool. Chromium compounds have been used in the formulation of wood preservatives for about a century [15]. These are "Wolman" compounds (based on sodium fluoride and dinitrophenol with sodium dichromate or potassium dichromate), copper-chromate (CC) (mixture of potassium dichromate and copper sulfate), copper–chromium–arsenic (CCA) (mixture of copper sulfate, sodium dichromate and arsenic trioxide), copper–chromium–boron (CCB), copper–chromium–fluoride (CCF) and copper–chromium–phosphate (CCP) but the most extensive and commercially leading system has been CCA [15]. Chromium compounds fulfill two principal functions in wood preservatives, as a chemical fixative to prevent or reduce loss by leaching of other components of the preservative, and as an anti-corrosion agent [15].

Though chromium can exist in eleven valence states ranging from −IV to +VI [16], Cr(III) and Cr(VI) have major environmental significance because of their stability in the natural environment. Cr(VI) is known to have 100-fold more toxicity than Cr(III) because of its high water solubility and mobility, as well as easy reduction [17]. Thus, the United States Environmental Protection Agency (USEPA) has laid down the maximum contaminant level (MCL) for Cr(VI) in domestic water supplies to be 0.05 mg/L, while total Cr containing Cr(III), Cr(VI) and other species of chromium is regulated to be discharged below 2 mg/L [18]. The toxicological effect of Cr(VI) originates from the action of this form itself as an oxidizing agent, as well as the formation of free radicals during the reduction of Cr(VI) to Cr(III) occurring inside the cell [19]. Research on the

carcinogenicity of Cr(VI) has focused on the fact that chromate ions (CrO_4^{2-}) quickly pass through cellular and nuclear membranes, often via anion transporter routes (e.g. for sulfate), while the trivalent species are slower [20]. In fact Cr(III) hydrolyses smoothly at physiological pH to give insoluble hydroxide. Cr(III) is kinetically inert due to its d^3 electronic configuration; concomitant ligand exchange processes at Cr(III) are very slow. After entry into the cytoplasm, chromate ions can either pass the nuclear membrane and be reduced to Cr(III), or be reduced in the cytoplasm. Cr(VI) not Cr(III) reacts strongly with DNA, it is thought the reduction of Cr(VI) to Cr(III), either in the cytoplasm, nucleus or blood, produces free radicals which in turn can bind to DNA [21]. Breathing and holding of Cr(VI) containing material can cause perforation of the nasal septum, asthma, bronchitis, pneumonitis, inflammation of larynx and liver and increased incidence of bronchogenic carcinoma [22]. Skin contact with Cr(VI) compounds can produce skin allergies, dermatitis, dermal necrosis and dermal corrosion [23,24].

Hexavalent chromium shows adverse effects on growth parameters and also causes accumulation of chromium in plants [25–28]; via plants, it enters the food chain. Chromium also shows toxicity towards different animals. Studies have shown the toxicity of chromium picolinate in renal impairment, skin blisters and pustules, anemia, hemolysis, tissue edema, liver dysfunction, neuronal cell injury, impaired cognitive, perceptual and motor activity, enhanced production of hydroxyl radicals, chromosomal aberration, depletion of antioxidant enzymes and DNA damage in mice [29].

Protozoa, fungi, algae, bacteria and cyanobacteria are able to gather chromium [27,30]. Cr(VI) is the cause of the reduction in cell size and the redox reaction when cultures of *Chlorella pyrenoidosa*, *Spirulina maxima*, *Spirulina platennis*, *Selenastrum capriornutum* and *Scenedesmus quadricauda* are grown in chromium solutions [31].

Several methods are utilized to remove chromium from the industrial wastewater. These include reduction followed by chemical precipitation [32], ion exchange [33], reduction [34], electrochemical precipitation [35], solvent extraction [36], membrane separation [37], cementation (as one of the techniques for recovering toxic and or valuable metals from industrial waste solutions, it is also used in purifying leach liquor prior to electrowinning of metals, and consists of displacing the metal from its solution by a less noble metal, which is usually cheap and nontoxic) [38], evaporation [39] and foam separation [40]. The chemical precipitation method involves a two-step process. The first step is the reduction of Cr(VI) under acidic conditions, followed by the precipitation of Cr(III) hydroxide. Commonly used reducing agents are sulfur dioxide, sodium sulfite, sodium bisulfite and ferrous sulfate. The process requires addition of other chemicals, which finally leads to the generation of a high water content sludge, the disposal of which is cost intensive. An ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The anion exchange sorption process is used for the removal of hexavalent chromium from the wastewater. The strongly basic commercial anion exchangers AV-17(Cl) (containing $-N^+(CH_3)_3$ groups) and Varion AD (containing $-N^+(CH_3)_2C_2H_4OH$ group) were reported as excellent exchangers [41]. Chromium removal efficiencies by electrochemical precipitation are greater than 99% and the residual chromium concentration is <0.5 mg dm^{-3} [42]. Electrochemical precipitation consumes huge amounts of power. In solvent extraction of chromium, several ion-association systems have been used such as triphenylsulfonium, ammonium, triphenylphosphonium, tetraphenylstibonium and triphenylselenium cations [43]. The solvents used for the extraction of Cr(VI) are diethylether, isobutyl ketone, ethyl acetate, hexane, tri-*n*-butylphosphate and chloroform [43]. Different strippants are used for the stripping of extracted Cr(VI) such as sodium hydroxide (NaOH), sodium chloride (NaCl), sodium nitrate ($NaNO_3$) and sodium sulfite (Na_2SO_3) [43]. The major drawbacks of solvent extraction are the loss of solvent and the release of the hexavalent chromium-containing waste solution. Membrane separations are of three types: bulk liquid membrane (BLM), emulsion liquid membrane (ELM) and supported liquid membrane (SLM). BLM is practically a liquid–liquid extraction, while ELM is based on water immiscible emulsions dispersed in an organic phase. In ELM extraction studies, extractant, surfactant, organic diluent and strippant are used in emulsion preparations. The extraction and stripping are governed by Eqs. (1) and (2) [44].

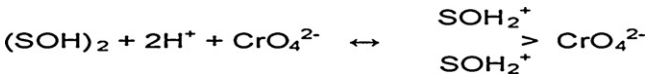


Fig. 1. Surface complexation model [85] (SOH stands for surface functional group).

$$Cr_2O_7^{2-} + 2[R_3NR'\text{-}Cl]_{org} \rightleftharpoons [(R_3NR')_2Cr_2O_7]_{org} + 2Cl^- \quad (1)$$

Stripping in caustic solution occurs as in Eq. (2).

$$[(R_3NR')_2Cr_2O_7]_{org} + 2NaOH \rightleftharpoons 2[R_3NR'OH]_{org} + 2Na^+ + Cr_2O_7^{2-} \quad (2)$$

Foam separation is based on surface adsorption. It is a process in which solute substances adsorb at the gas–liquid interface between a dispersed phase and a liquid phase. This method can remove surface-active agents or non surface-active materials which can adsorb or combine with surfactants. The foam is collected and collapsed in the bubble collector, and the collapsed formate solution containing chromium is much more concentrated in the surfactant than in the initial solution [45].

The cited conventional chromium elimination processes are costly or ineffective at small concentrations and may also lead to environmental problems from waste disposal. In recent years biosorption research has focused on using readily available biomass that can accumulate heavy metals [46]. This approach involves the use of biological materials that form complexes with metal ions using their ligands or functional groups. It is particularly the cell wall structure of certain algae, fungi, bacteria and plants that is responsible for this phenomenon. This process can be applied as a cost-effective way of purifying industrial wastewater whereby drinking water quality can be attained. Thus, much research has focused on identifying biological materials that can capably remove heavy metals from aqueous environments. These materials are recognized as biosorbents and the binding of metals by biomass is referred to as biosorption.

There are two schools of thought regarding the nature of biomass; according to one biomass may be living or dead [2,46–48], and the other is that it is non-living [49–52]. We subscribe to the first opinion. The major advantages of biosorption over conventional treatment methods include: low price, high effectiveness, minimization of chemical and/or biological mud, restoration of biosorbent and possibility of metal recovery. On this basis we review the literature of the collection and analysis of data on hexavalent chromium biosorption.

2. Aqueous chemistry of chromium

Chromium remains mainly as +III and +VI oxidation states in aqueous solution. Chromium(III) remains as hexa aqua ion $[Cr(H_2O)_6]^{3+}$ in aqueous solution [53]. The aqua ion is acidic ($pK_a = 4$), and the hydroxo ion condenses to give a dimeric hydroxo bridged species. The process of condensation through the formation

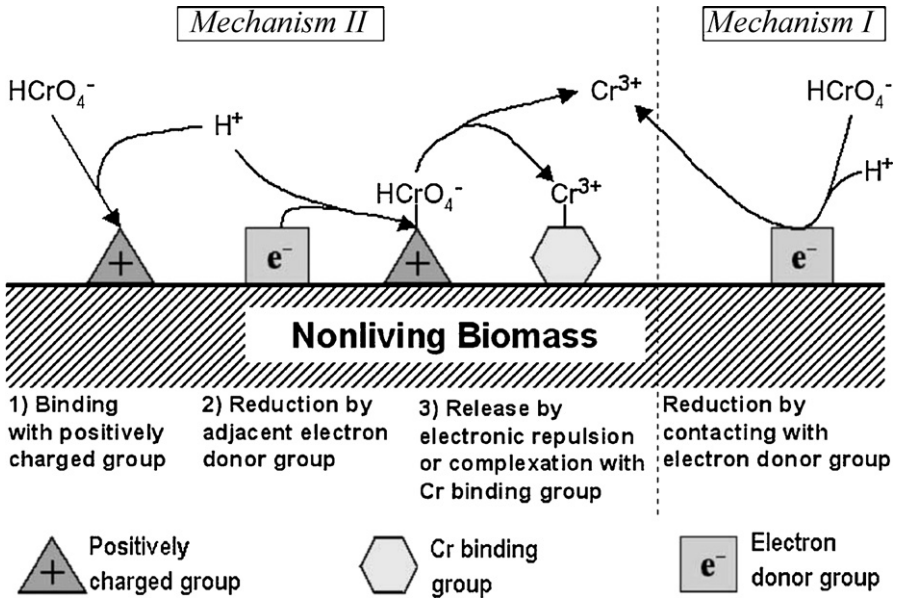
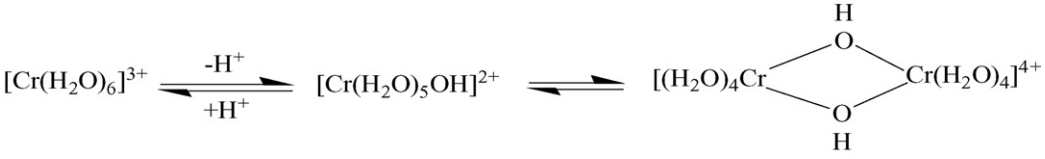


Fig. 2. Proposed mechanism of Cr(VI) biosorption by non-living biomass [115] reproduced with permission.

of hydroxo-bridges is known as "olation" (Eq. (3)).



(3)

In aqueous solution above pH 6, Cr(VI) forms tetrahedral yellow chromate ion CrO_4^{2-}; between pH 2 and 6, $HCrO_4^-$ and the orange red dichromate ion $Cr_2O_7^{2-}$ are in equilibrium [53]. At pH < 1 the main species is H_2CrO_4 [53]. The following pH-dependent equilibria exist in aqueous solution (Eqs. (4)–(6)).

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+, \quad K = 10^{-5.9} \tag{4}$$

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+, \quad K = 4.1 \tag{5}$$

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^-, \quad K = 10^{-2.2} \tag{6}$$

Acidic solutions of dichromate are strong oxidants [53]. During oxidation Cr(VI) is reduced to Cr(III) through the formation of intermediates Cr(V), Cr(IV) and Cr(II); however, basic solutions of chromate are less oxidizing [53] as evident from E^0 values (Eqs. (7) and (8)).

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O, \quad E^0 = 1.33\,V \tag{7}$$

$$CrO_4^{2-} + 4H_2O + 3e \rightleftharpoons Cr(OH)_3(s) + 5OH^-, \quad E^0 = -0.13\,V \tag{8}$$

Cr(VI) does not give rise to an extensive complex series of polyacids and polyanions [53,54] characteristics of somewhat less acidic oxides, such as those of V(V), Mo(VI) or W(VI). The reason for this is perhaps the greater extent of multiple bonding (Cr=O) for the smaller chromium. Polymerization beyond dichromate is apparently limited to formation of tri ($Cr_3O_{10}^{2-}$) and tetra ($Cr_4O_{13}^{2-}$) chromate [54].

3. Biosorption mechanisms

There are four models for Cr(VI) biosorption: anionic adsorption [9,55–103,104,105], adsorption-coupled reduction [3,5,8,64,106–119], anionic and cationic adsorption [120–122] and reduction and anionic adsorption [123–129].

3.1. Anionic adsorption [9,55–103,104,105]

Negatively charged chromium species (chromate (CrO_4^{2-})/dichromate ($Cr_2O_7^{2-}$) in the medium) bind through electrostatic attraction to positively charged functional groups on the surface of biosorbents. This mechanism is based on the observation that at low pH Cr(VI) adsorption increases and at high pH Cr(VI) adsorption decreases. At low pH functional groups of the biosorbent become protonated, and easily attract negatively charged chromium, but at high pH deprotonation occurs, functional groups become negatively charged repelling negatively charged chromium. In addition to Coulombic force of electrostatic attraction, surface complexation has important roles in the elimination of Cr(VI) from aqueous media [85,91,93] (Fig. 1).

3.2. Adsorption-coupled reduction [3,5,8,64,106–119]

Reduction followed by cationic adsorption was first proposed by Volesky for algae sargassum biomass [106]. This mechanism is popularized by Park on the basis of experiments [8]. According to this mechanism Cr(VI) is totally reduced to Cr(III) by biomass in the presence of acid. Then part of Cr(III) is adsorbed to biomass. The amount of adsorption depends on the nature of the biomass (Fig. 2).

3.3. Anionic and cationic adsorption [120–122]

According to this mechanism a part of hexavalent chromium is reduced to trivalent chromium. The hexavalent chromium (anionic) and trivalent chromium (cationic) are adsorbed to biomass.

3.4. Reduction and anionic adsorption mechanism [123–129]

According to this mechanism a part of the hexavalent chromium is reduced to Cr(III) by biosorbent and mainly Cr(VI) is adsorbed to the biomass while Cr(III) remains in the solution.

4. Modeling biosorption

Mathematical models can describe the behavior of the biosorption processes operating under different experimental conditions. They are very useful for scaleup studies or process optimization. A number of models with varying degrees of complexity have been developed to describe the metal biosorption systems. These are of two types: kinetic models and equilibrium models.

4.1. Kinetic models

The study of adsorption dynamics describes the solute uptake rate, and this rate controls the habitation time of adsorbate uptake at the solid–solution interface. Chemical kinetics gives information about reaction pathways and times to reach equilibrium. Sorption kinetics show a large dependence on the physical and/or chemical characteristics of the sorbent material. Different models have been used to investigate the mechanism of sorption. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (r^2 values close or equal to 1). A relatively high r^2 value indicates that the model successfully describes the kinetics of Cr(VI) adsorption.

4.1.1. Pseudo-first-order or Lagergen kinetic model

It is the first equation for sorption [130,131] of liquid/solid system based on solid capacity [120]. The pseudo-first-order equation is generally expressed as in Eq. (9).

$$\frac{d_q}{d_t} = k_1(q_e - q_t) \tag{9}$$

Here q_e and q_t are the adsorption capacities at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). Eq. (9) can be rearranged to obtain the more useful form Eq. (10).

$$\log(q_e - q_t) = \log\ q_e - \left(\frac{k_1}{2.303}\right) t \tag{10}$$

The values of $\log(q_e - q_t)$ were linearly correlated with t. The plot of $\log(q_e - q_t)$ vs. t should give a linear relationship from which k_1 can be determined from the slope. Eq. (10) differs from a true first-order equation in two ways: (i) the parameter $k_1(q_e - q_t)$ does not represent the number of available sites, and (ii) the parameter $\log q_e$ is an adjustable parameter and often it is found not equal to the intercept of the plot of $\log(q_e - q_t)$ vs. t, whereas in a true first-order $\log q_e$ should be equal to the intercept [132].

The above model is best fit for hexavalent chromium removal by *Azadirachta indica* [133], *Nostoc muscorum* [134], *Tamarindus indica* [95], tea fungal biomass [78], tea factory waste [135], rice husk [110] and wollastonite [93].

4.1.2. Pseudo-second-order kinetic model

The pseudo-second-order adsorption kinetic rate equation is expressed in Eq. (11) [136–138]:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{11}$$

where k_2 is the rate constant of pseudo-second-order adsorption ($g^{-1}\ min^{-1}$). Eq. (11) can be rearranged to obtain more useful form Eq. (12).

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{12}$$

The linear form is Eq. (13)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{13}$$

and k_2 is obtained from the plot of t/q_t vs t.

The model is best fit for hexavalent chromium removal by many agents: *Salvinia cucullata* [139], tamarind seeds [100], hydrous titanium oxide [140], activated carbons prepared from agricultural wastes [104], humic acids [122], dead *Bacillus licheniformis* biomass [65], low cost adsorbents like rice husk ash, activated alumina, fuller's earth, fly ash, saw dust and neem bark [88], palm flower (*Borassus aethiopum*) [81], *Laminaria japonica* (brown macroalga), *P. yezoensis ueda* (red macroalga), rice bran and wheat bran [84], mangrove leaves and water lily [86], activated carbon derived from olive bagasse [87], fungi *Agaricus bisporus* [79], sulfuric acid carbonization products of sugar beet pulp [141], commercially available material puresorbe (an oil adsorbent) [22], seaweed *Hydrilla verticillata* [142], dried *Rhizopus arrhizus* [143], red algae *Ceramium virgatum* [89], *Mucor hiemalis* [62], fungus *Lentinus sajor-caju* [59], modified bauxite tailings [77], marine *Aspergillus niger* [97], *Cassia fistula* biomass [96], and agricultural waste maize bran [120].

4.1.3. First-order reversible kinetic model

The biosorption process may be regarded as a first-order reversible reaction, which can be expressed as Eq. (14) [120,139,140,142,144].

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \tag{14}$$

The rate equation for the reaction is expressed as Eq. (15):

$$\ln(1 - Ut) = -(k_1 + k_{-1})t \tag{15}$$

where Ut is the fractional attainment of equilibrium and is given by Eq. (16).

$$Ut = \frac{C_{Ao} - C_A}{C_{Ao} - C_{Ae}} \tag{16}$$

where C_A and C_B are the concentrations of the adsorbate in solution and adsorbent, respectively, at a given time t, C_{Ae} and C_{Be} are the equilibrium concentrations of adsorbate and adsorbent respectively, and k_1 and k_{-1} are the first-order rate constants. Under equilibrium condition, Eq. (17) obtains.

$$K_c = \frac{C_{Be}}{C_{Ae}} = \frac{k_1}{k_{-1}} \tag{17}$$

Hexavalent chromium removal by magnesia cement follows first-order reversible kinetics [145]. Hexavalent chromium removal by *Salvinia cucullata* [139], hydrous titanium oxide [140], seaweed *Hydrilla verticillata* [142] is better represented by the pseudo-second-order kinetic model.

4.1.4. Ritchie's second-order kinetic model

Ritchie's second-order equation can be represented as Eq. (18) [139,142]:

$$\frac{q_e}{q_e - q_t} = 1 + k_2 t \tag{18}$$

where q_t = uptake at time t, q_e = equilibrium uptake capacity and k_2 is the Ritchie's reaction rate constant.

4.1.5. Elovich kinetic equation

The Elovich equation (19) [100,104,146,147] incorporates α as the initial adsorption rate (mg g^{-1} min^{-1}), β (g mg^{-1}) is the desorption constant related to the extent of the surface coverage and

$$\frac{dq}{dt} = \alpha\, e_t^{-\beta q} \tag{19}$$

activation energy for chemisorption and $^{q}{}_{t}$ is the amount of gas chemisorbed at time t. Eq. (19) can be simplified to Eq. (20) by considering $\alpha\beta \gg t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ [146].

$$q_t = \frac{1}{\beta}\ \ln(\alpha\beta) + \frac{1}{\beta}\ \ln(t) \tag{20}$$

If hexavalent chromium adsorption fits the Elovich model, a plot of q_t vs ln(t) should give a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)\ln(\alpha\beta)$. Hexavalent chromium removal by waste tea fungus [78] followed the Elovich equation.

4.1.6. Intra-particle diffusion model

The adsorption of hexavalent chromium on a porous adsorbent is the combination of four consecutive steps [142]: diffusion in the bulk solution, then diffusion across the thin film surrounding the adsorbent particles, followed by intra-particle diffusion and adsorption within the particles [142]. According to Weber and Morris [148] if the rate limiting step is the intra-particle diffusion, then the amount adsorbed at any time t should be directly proportional to the square root of contact time t and shall pass through the origin which is defined mathematically in Eq. (21).

$$q_t = k_{id} t^{0.5} \tag{21}$$

A linearised form is Eq. (22) where q_t is the amount Cr(VI) adsorbed, t is the contact time, k_{id} is the intra-particle diffusion coefficient.

$$\log\ q_t = \log\ k_{id} + 0.5\ \ \log\ t \tag{22}$$

A plot of log q_t against 0.5 log t should give a straight line with a positive intercept for intra-particle diffusion controlled adsorption process. The value of k_{id} can be calculated from intercept of such plot. Higher values of k_{id} illustrate an enhancement in the rate of adsorption. Intra-particle diffusion coefficient values have been calculated by various workers to bring a better understanding of the process [104,120,139,140,142,149].

4.1.7. Park model

This is the latest kinetic model based on redox reaction for chromium biosorption [3,5,8,107–109].

$$\text{biomass} + \text{Cr(VI)} \xrightarrow{k} \text{biomass(oxidized)} + \text{Cr(III)} \tag{23}$$

The following assumptions are considered: (i) organic compounds in the biosorbent are responsible for reducing Cr(VI), (ii) only one kind of organic compound (OC) is capable of reducing Cr(VI), and (iii) the rate equation of Cr(VI) reduction is first-order (Eq. (24)) with respect to both Cr(VI) concentration and concentration of OC capable of reducing Cr(VI).

$$\frac{d[\text{Cr(VI)}]}{dt} = -k[\text{OC}][\text{Cr(VI)}] \tag{24}$$

The final kinetic Eq. (25) is expressed as:

$$[\text{Cr(VI)}] = \frac{C^*[B][\text{Cr(VI)}]_O - [\text{Cr(VI)}]_O{}^2}{C^*[B]\exp(k(C^*[B] - [\text{Cr(VI)}]_O)t) - [\text{Cr(VI)}]_O} \tag{25}$$

where C^*_{OC} indicates the content of equivalent organic compound per unit of biomass, B is the biomass concentration and k is the rate equation coefficient. In addition to Park et al., Balasubramanian et al. used this model [5] and found good results.

4.2. Equilibrium model

An adsorption isotherm is used to characterize the interaction of the metal ions with the adsorbents. This provides a relationship between the concentration of metal ions in the solution and the amount of metal ions adsorbed to the solid phase when the two phases are at equilibrium.

4.2.1. Langmuir model

The Langmuir isotherm [150] was derived originally from studies on gas adsorption to activated carbon. The Langmuir isotherm model [4,22,59–62,65,70–73,76,77,80,82,83,87–89,92,94–96,103,64,105,112,120,121,133–135,140–142,144,145,149,161–168,170–175] is used to estimate the adsorption capacity of adsorbent used and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The Langmuir adsorption isotherm is represented as Eq. (26).

$$q_e = \frac{q_{\max} b C_{eq}}{1 + bC_{eq}} \tag{26}$$

Here q_e is the metal concentration adsorbed in solid (biomass), C_{eq} is the metal residual concentration in solution, $q_{\max}$ is the maximum specific uptake corresponding to sites saturation, and b is the ratio of adsorption/desorption rates. Two derivatives of the Langmuir equation are Eqs. (27) and (28):

$$\frac{C_{eq}}{q_e} = \frac{1}{q_{\max} b} + \frac{C_{eq}}{q_{\max}} \tag{27}$$

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b}\frac{1}{C_{eq}} \tag{28}$$

4.2.2. Freundlich model

The Freundlich isotherm, first proposed in 1906, is based on multilayer adsorption with interaction between adsorbed molecules [151]. The model applies to adsorption onto heterogeneous surfaces with a uniform energy distribution and reversible adsorption. The Freundlich isotherm is the earliest known relationship describing the adsorption equation. The application of the Freundlich equation (29) suggests that adsorption energy exponentially decreases on completion of the adsorptional centers of an adsorbent. For adsorption from solution, the Freundlich isotherm is represented by Eq. (29).

$$q_e = K_f C_{eq}^{1/n} \tag{29}$$

Here K_f is the Freundlich constant and is also known as Freundlich capacity and n stands for adsorption intensity, q_e is the amount of chromium adsorbed at equilibrium and C_{eq} is the residual concentration of Cr(VI) in solution. The Freundlich equation is expressed linearly as Eq. (30):

$$\log\ q_e = \log\ K_f + \frac{1}{n}\ \log\ C_{eq} \tag{30}$$

The values of K_f and n can be obtained from the slope and intercept of a plot of log q_e versus log C_{eq}. Both the parameters K_f and n affect the adsorption isotherm. A large number of workers [9,22,59–61,63,70–72,74,75,77–80,84,87,88,90,92,94,95,64,112,118,121,122,133,134,145,163,166,169–172,175–178] have used the Freundlich model to study hexavalent chromium removal.

4.2.3. Langmuir–Freundlich model

In this model [143], the surface of the sorbent is considered to be homogeneous and sorption is a cooperative process due to

adsorbate–adsorbate interaction. The Langmuir–Freundlich model is represented as [152] in Eq. (31).

$$q_e = \frac{q_{max} b C_{eq}^{1/n}}{1 + b C_{eq}^{1/n}} \quad (31)$$

4.2.4. BET model

The Brunauer, Emmer and Teller (BET) model is an extension of the Langmuir model [153], and represents the isotherm with a multilayer adsorption at the adsorbent surface. It assumes that the Langmuir equation is applicable to each layer and a given layer may not be completely formed before the next layer forms (Eq. (32)).

$$q_e = \frac{q_{max} B C_{eq}}{C_s - C_{eq}} \left[1 + (B-1)\frac{C_{eq}}{C_s}\right] \quad (32)$$

where C_s is the saturation concentration of the solute, B is a constant relating to the energy of interaction with the surface and other symbols are as previously described. A large number of researchers have used BET to describe hexavalent chromium biosorption [60,78].

4.2.5. Redlich–Peterson model

The Redlich–Peterson isotherm contains three parameters which may be used to represent adsorption equilibrium over a wide concentration range, and can be applied either in homogeneous or heterogeneous systems due to its versatility [154]. Jossens et al. modified the model to incorporate features of both the Langmuir and Freundlich isotherms [155]. It is described in Eq. (33).

$$q_e = \frac{K_R C_{eq}}{1 + a_R C_{eq}^{bR}} \quad (33)$$

The linearized form is Eq. (34).

$$\ln \frac{K_R C_{eq}}{q_e - 1} = b_R \ln(C_{eq}) + \ln(a_R) \quad (34)$$

It has three isotherm constants K_R, a_R and b_R. The Redlich–Peterson isotherm constants [22,140] cannot be obtained using graphical methods because of the three unknown parameters. A professional graphics software package is ideal for this.

4.2.6. Tempkin model

The Tempkin isotherm model contains a factor that takes care of the adsorbent–adsorbate interactions [156]. Tempkin considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms. Tempkin noted experimentally that heats of adsorption would more often decrease than increase with increasing coverage. The nonlinear form of Tempkin equation is given by Eq. (35) and the linear form in Eq. (36).

$$q_e = \frac{RT}{b_T} \ln(A_T C_{eq}) \quad (35)$$

$$q_e = B_T \ln A_T + B_T \ln C_{eq} \quad (36)$$

Here $B_T = (RT/b_T)$, T is the absolute temperature, R is the universal gas constant, the constant b_T is related to the heat of adsorption, A_T is the equilibrium binding constant corresponding to the maximum binding energy. A plot of q_e versus $\ln C_{eq}$ at a fixed temperature will give Tempkin isotherm constants, A_T and b_T. The Tempkin isotherm constants are calculated by various groups [78,87,103], giving the value of heat of adsorption.

4.2.7. Koble–Corrigan isotherm

The Koble–Corrigan model is another three-parameter empirical model [157] for representing of equilibrium adsorption data. It is a combination of the Langmuir and Freundlich isotherm models. The Koble–Corrigan isotherm equation is highly nonlinear as compared to the Redlich–Peterson model and is expressed in Eq. (37).

$$q_e = \frac{A C_{eq}^n}{1 + B C_{eq}^n} \quad (37)$$

where A, B and n are the Koble–Corrigan parameters.

4.2.8. Toth isotherm

The Toth isotherm [158] has proven useful in describing biosorption [5,140,159]. It is derived from potential theory and is applicable to heterogeneous adsorption. It assumes an asymmetrical quasi-Gaussian energy distribution with a widened left hand side, i.e., most sites have sorption energy less than the mean value [160]. It can be represented as in Eq. (38).

$$q_e = \frac{q_{max} b_T C_{eq}}{[1 + (b_T C_{eq})_T^{1/n}]_T^n} \quad (38)$$

Here b_T is the Toth model constant and n_T is the Toth model exponent. It is obvious that for $n_T = 1$ this isotherm reduces to the Langmuir isotherm equation.

Table 1
The major classes of chemical components present in the walls and envelopes of Gram-positive and Gram-negative bacteria [179a].

Chemical component	Examples
Gram-positive cell walls	
Peptidoglycan	All species
Polysaccharides	*Streptococcus* group; A, B, C substances
Teichoic acids	
Ribitol	*S. aureus*, *B. subtilis*, *Lactobacillus* spp
Glycerol	*S. epidermidis*, *Lactobacillus* spp
Teichuronic acids (amino galacluronic or amino mannuronic acid polymers)	*B. licheniformis*, *M. lysodeikticus*
Peptidoglycolipids (muramylpeptide-polysaccharide-mycolates)	*Corynebacterium* spp, *Mycobacterium* spp, *Nocardia* spp
Glycolipids (waxes) (polysaccharide-mycolates)	
Gram-negative envelopes	All species
LPS (lipoteichoic acids)	*E. coli* and many enteric bacteria,
Lipoprotein	*Pseudomonas aeruginosa* *E. coli*, *Salmonella typhimurium*
Porins (major outer membrane proteins)	All species
Phospholipids and proteins	Almost all species
Peptidoglycan	

5. Biosorbent materials

A large number of materials have been investigated as biosorbents for hexavalent chromium removal. The tested biosorbents can be classified into the following categories (a) bacteria; (b) fungi; (c) algae; (d) yeast; (e) agricultural products and (f) others. Various functional groups present in the biosorbent material are responsible for hexavalent chromium biosorption. Examples are summarized in Tables 1–9 .

6. Instrumental tools and techniques used in chromium biosorption studies

The real challenge in the field of biosorption is to identify the mechanisms that govern metal uptake by biosorbents. Temperature could be a parameter that affects the sorption of metal ions; Romero-Gonzalez et al. [305] found that the sorption capacity of

Table 2
Bacterial biomass as biosorbent.

Name of bacteria	Sorption capacity (mg/g) (a) or removal efficiency(%) (b)	Refs.
Active sludge bacteria	3.2 mg g^{-1} min^{-1}	[179(b)]
Aeromonas caviae	284.44 (a)	[180]
Aeromonas caviae	124.46 (a)	[181]
Bacillus circulans	34.5 (a)	[182]
Bacillus megaterium (dead)	30.7 (a)	[182]
Bacillus coagulans (dead)	39.9 (a)	[182]
Bacillus coagulans (live)	23.8 (a)	[182]
Bacillus licheniformis	69.35 (a)	[65]
Bacillus thuringiensis (vegetative)	83.33 (a)	[61]
Bacillus thuringiensis (Spore–crystal mixture)	72.99 (a)	[61]
Biofilm of *E. coli* supported on carbon	97.70 (a)	[171]
Corynebacterium glutamicum	95 (b)	[8]
Chroococcus sp. HH-11	21.36 (a)	[183]
E. coli ASU 7	64.36 (a)	[171]
Nostoc muscorum	22.92 (a)	[134]
Nostoc calcicola HH-12	12.23 (a)	[183]
Ochrobactrum anthropi	86.20 (a)	[184]
Pseudomonas sp.	95 (a)	[70]
Phormidium sp.	24.3(a)	[185]
Pseudomonas aeruginosa and *Bacillus subtilis*	1.44 (a)	[186]
Staphylococcus xylosus	143 (a)	[70]
Zoogloea ramigera	3.4 mg g^{-1} min^{-1}	[55]

Agave lechuguilla leaves, a plant of the Chihuahuan desert, for hexavalent chromium increased on increasing the temperature in the 10–40 °C range. The authors justified the endothermicity of the process with the apparent binding and reduction of hexavalent chromium to trivalent chromium. Malkoc and Nuhoglu [135] also found that the process of hexavalent chromium sorption on tea factory waste is endothermic and metal uptake increases on increasing the temperature from 25 °C to 60 °C. The favourable effect of temperature on sorption may be a result of a swelling effect within the internal structure of the sorbent, enabling large metal ion hexavalent chromium to penetrate further.

Many analytical techniques have been used to study hexavalent chromium binding to biomaterials, including infrared spectroscopy or Fourier transformed infrared spectroscopy (IR or FTIR) [4,86,97,103,140,163,306], UV–vis spectroscopy [86–88,97,122,140,307], atomic adsorption spectrometry (AAS) [141], scanning electron microscopy (SEM) and transmission electron microscopy (TEM) [82,102,103,178,306], as well as X-ray diffraction (XRD) analysis [75,140] and X-ray photoelectron spectroscopy (XPS) [107,117,273,308]. The functional groups on the sorbent surface that may involve metal ion sorption are usually investigated by FTIR spectroscopy. The energy needed to excite the bonds in a compound, making them vibrate more energetically, occurs in the infrared region of the spectrum, rendering IR a most useful technique. IR and FTIR are used to characterize the functional groups present in the adsorbent. This sheds very important light for chemical modification of adsorbent for better performance. UV–vis spectroscopy is used for the detection of hexavalent chromium. The absorbance of pink colored 1,5-diphenyl carbazide complex of hexavalent chromium is measured at 540 nm. Atomic absorption spectroscopy (AAS) is used for the detection of total chromium (trivalent and hexavalent). Electronic microscope SEM and TEM are used to study the morphology of the adsorbent (before and after adsorption of chromium). Photoelectron spectroscopy (PES) is an excellent technique for probing atomic and molecular electronic energy levels. X-ray diffraction (XRD) analysis and X-ray photoelectron spectroscopy (XPS) are studied to understand the nature of adsorbed chromium. XPS was employed by Park et al. [107] to verify the oxidation state of the chromium bound to the biomaterials. Prior to mounting for XPS, biomaterials were washed with deionized–distilled water several times, and then freeze-dried in a vacuum freeze drier. The resulting biomaterials were transported to the spectrometer in a portable gas-tight chamber. Park et al. [107] collected high-resolution XPS spectra from the Cr2p core region of 16 biomaterials indicated that there were significant contributions of the chromium bound to the biomaterials. Hexavalent chromium can be characterized by higher binding energies than trivalent chromium since the hexavalent form is more electrophilic. The spectra of Cr-laden biomaterials can be compared with those of Cr(III); these results imply that the chromium bound to the surface of sixteen biomaterials were mostly or totally in trivalent form [107].

A colorimetric method has been used to measure the concentrations of the different chromium species present in aqueous

Table 3
The major classes of chemical components present in the cell walls of fungi [187].

Chemical category	Taxonomic group		Common name
Cellulose-glycogen (incompletely characterized)	Acrasiales		
	Oomycetes		Water molds
Cellulose-glucan (incompletely characterized)	Hyphochytridiomycetes		
Cellulose-chitin	Zygomycetes		Bread molds
Chitosan-chitin	Chytridiomycetes		
Chitin-glucan (incompletely characterized)	Ascomycetes		Sac fungi
	Basidiomycetes (except Sporobolomycetaceae)		Club fungi
	Deuteromycetes (except Cryptococcaceae and Rhodotorulaceae)		Fungi imperfecti
Mannan-glucan (incompletely characterized)	Saccharomycetaceae	Cryptococcaceae	
Mannan-chitin	Sporobolomycetaceae	Rhodotorulaceae	
Polygalactosamine-galactan	Trichomycetes		

Table 4
Fungal biomass as biosorbent.

Name of fungi	Sorption capacity (mg/g) (a) or removal efficiency (%) (b)	Refs.
Aspergillus niger	30.1 (a)	[188]
Aspergillus flavus	0.335 (a)	[189]
Aspergillus sydoni	9.07 (a)	[71]
Aspergillus niger	17.61 (a)	[71]
Aspergillus niger	117.33 (a)	[149]
Aspergillus niger	29.3 (b)	[109]
Aspergillus niger MTCC2594	3.0 (a)	[190]
Agaricus bisporus	8 (a)	[79]
Candida intermedia	0.021 (a)	[20]
Coriolus versicolor (HT)	62.89 (a)	[112]
Coriolus versicolor (UT)	44.25 (a)	[112]
Fusarium sp	50.25 (a)	[191]
Lentinus sajor-caju (untreated)	0.363 m mol g^{-1}	[192]
Lentinus sajor-caju (free)	23.32 (a)	[59]
Lentinus sajor-caju (immobilized)	39.57 (a)	[59]
Lentinus sajor-caju (heat treated)	0.613 m mol g^{-1}	[192]
Mucor hiemalis	53.5 (a)	[62]
Neurospora crassa (AcOH pretreated)	15.85 (a)	[63]
Penicillium janthinellum	9.35 (a)	[71]
Penicillium purpurogenum	40 (a)	[162]
Penicillium chrysogenum	40.3 (b)	[109]
Rhizopus arrhizus	23.92 (a)	[193]
Rhizopus arrhizus	8.40 mg g^{-1} min^{-1}	[55]
Rhizopus arrhizus	78 (a)	[143]
Rhizopus arrhizus	23.88 (a)	[194]
Rhizopus nigricans	49.81 (a)	[195]
Rhizopus nigricans (polyacrylamide)	21.22 (a)	[195]
Rhizopus oryzae	23.5 (b)	[109]
Saccharomyces cerevisiae	44.2 (b)	[109]
Saccharomyces cerevisiae	0.56 (a)	[196]
Saccharomyces cerevisiae	6.3 (a)	[197]
Saccharomyces cerevisiae	32.6 (a)	[198]
Saccharomyces cerevisiae	6.607 (a)	[199]
Surfactant-modified yeast	94.34 (a)	[200]
Tea fungal biomass (live)	30.8 (b)	[78]
Tea fungal biomass (dried)	74.15 (b)	[78]
Trametes versicolor	32.2 (b)	[201]
Yeast biomass (mycota)	86.95(a)	[202]
Yarrowia lipolytica (NCIM-3589)	63.73 (a)	[203]
Yarrowia lipolytica (NCIM-3590)	46.09 (a)	[203]

solution. The pink colored complex formed from 1,5-diphenyl carbazide and Cr(VI) in acidic solution, has been spectrophotometrically analyzed at 540 nm [107,113,120]. For the determination of Cr(III) concentration, Cr(III) (formed due to the reduction of Cr(VI) into Cr(III) during the sorption process) was again converted to Cr(VI) by the addition of excess potassium permanganate at high temperature (130–140 °C) there after 1,5-diphenylcarbazide was added. The pink colored complex formed gives the concentration of Cr(VI) and Cr(III) which is the total chromium. The Cr(III) concentration was then calculated by the difference of the total chromium and measured Cr(VI) concentration [107,113,120].

Table 5
The major classes of chemical components present in the walls of algae [204].

Common name	Cell wall component
Green algae	Cellulose, hydroxyproline glucosides, xylans (polysaccharides made from units of xylose) and mannan (polymer of the sugar mannose) or wall absent
Brown algae	Cellulose, alginic acid and sulfated mucopolysaccharides (fucoidan)
Red algae	Cellulose, xylans, several sulfated polysaccharides (galactans), calcification in some alginate in corallinaceae

Table 6
Algal biomass as biosorbent.

Name of algae	Sorption capacity [{(m mol/g) (a)} or {mg/g (c)}] or removal efficiency (%) (b)	Refs.
Chlorella vulgaris	27.77 (c)	[205]
Chlamydomonas reinhardetti	21.2 (c)	[206]
Chlorella vulgaris	79.3 (c)	[207]
Cystoseira indica	20.9–27.9 (a)	[208]
Cladophora albida	41.7 (a)	[209]
Fucus vesiculosus	0.82 (a)	[4]
Fucus spiralis	0.68 (a)	[4]
L. japonica	59.35 (c)	[84]
Oedogonium hatei	31.0 (c)	[210]
Padina (brown algae)	54.6 (c)	[211]
Pilayella littoralis	90 μmol g^{-1}	[212]
P. yezoensis Ueda	56.32 (c)	[84]
Palmaria palmata	0.65 (a)	[4]
Polysiphonia lanosa	0.88 (a)	[4]
Rhizoclonium heiroglyphicum	11.81 (c)	[163]
Sargassum sp.	68.94 (c)	[213]
Sargassum (brown algae)	31.7 (c)	[211]
Scenedesmus obliquus	58.8 (c)	[207]
Sargassum sp.	65 (b)	[214]
Sargassum siliquosum	66.4 (c)	[215]
Spirogyra condensata	14.82 (c)	[163]
Spirogyra sp.	14.7 (a)	[100]
Ulva lactuca	0.53 (a)	[4]
Ulva lactuca	92 (b)	[216]
Ulva sp.	0.58 (a)	[4]
Turbinaria ornate	65 (b)	[217]

7. Future directions

With only one exception [309] (a biosorption system consisting of a bacterial biofilm supported on synthetic zeolites in which the biofilm reduces hexavalent chromium to trivalent chromium and trivalent chromium is captured in the zeolite by ion exchange), hexavalent chromium biosorption today still is mainly confined to lab studies only. There are likely three reasons for this: the mechanism is not fully understood, shortcomings in biosorption technology, and limited research on chemically modified biosorbent and mixture of two different type biosorbent. In future work various aspects should be considered, as listed below:

(1) The biosorption mechanism should be further studied [46,310]. In this respect non-functional surfactants [311–315] may be useful. Non-functional surfactants will provide better insight into the reaction mechanism with preferential partitioning of the reactants in hydrophobic and hydrophilic layer. The electrostatic attraction between charged species and micellar head group is also important here and this depends on the pH of the solution. In addition, the proper choice of non-functional surfactant will speed up the relatively slow biosorption process [311–315]. The rate of biosorption can be increased by the proper choice of adsorbent; in this respect ascorbic acid containing biomaterial may be a good choice.

Table 7
Chemical components responsible for adsorption present in agricultural product.

Material	Chemical component
Bark	Tannin
Saw dust	Tannin, lignin
Brazilian pine fruit coat	Polyphenols
Bagasse	Lignocellulose
Hardwood	Xylan, lignin (is covalently linked with xylan)
Softwood	Xylan, lignin (is covalently linked with galactoglucomannans)

Table 8
Agricultural products as biosorbents.

Agricultural product	Sorption capacity [{(mg/g) (a)} or {(m mole/g) (c)}] or removal efficiency (%) (b)	Refs.
Almond shell	22.22 (a)	[218]
Alternanthera philoxeroides (Alligator weed)	20.45 (a)	[219]
Acid treated palm flower	7.13 (a)	[81]
Acid treated tamarind fruit nut shell	77.5 (a)	[95]
Almond shell	19.98 (a)	[104]
Apricot stone	20.98 (a)	[104]
Almond shell activated carbon	190.3 (a)	[90]
Ac from Hazelnut shell	170.00 (a)	[220]
Ac made from *Hevea brasilinesis* (rubber wood) saw dust	65.78 (a)	[221]
Ac from Coconut tree saw dust	3.46 (a)	[222]
Ac from fir wood slabs	315.6 (a)	[223]
Ac from *Terminalia arjuna* (medicinal plant) nut	28.43 (a)	[224]
Ac from olive bagasse	109.89 (a)	[87]
Activated Tamarind seeds	29.7 (a)	[100]
Banana skin	25.5 (b)	[107]
Bagasse fly ash	260 (a)	[225]
Brazilian pine fruit wastes	240.0(a)	[226]
Bael fruit (Aegle *marmelos correa*) shell	17.27 (a)	[227]
Chemically modified chicken feather	14.47 (a)	[9]
Coconut shell based activated carbon	20 (a)	[228]
Commercial activated carbon	11.1 (c)	[128]
Coir pith	317.65 (a)	[229]
Coir pith	11.56 (a)	[230]
Cornelian cherry	20.98 (a)	[104]
Coniferous leaves	6.3 (a)	[125]
Carbonized sugar beet pulp	24.15 (a)	[141]
Coffe dusts	39.0 (a)	[5]
Depectinated sugar beet pulp	0.40 (a)	[231]
Ethylene-modified rice hull	0.45 (c)	[232]
Green tarto	5.747 (a)	[86]
Groundnut shell	5.88 (a)	[218]
Groundnut husk carbon	7.0 (a)	[178]
Grape waste	1.91mol/kg	[233]
Hazelnut shell	17.7 (a)	[234]
Hydrilla verticillata (flora of North America)	247 (a)	[142]
Iron III hydroxide loaded sugar beet pulp	5.12 (a)	[235]
Japanese cedar bark	71.94 (a)	[168]
Larch bark	31.3 (a)	[124]
Leaf mould	25.9 (a)	[236]
Leaf mould	43.1(a)	[237]
London plane leaves	83.33 (a)	[238]
Mangrove leaves	11.377(a)	[86]
Maple saw dust	80 (b)	[239]
Maize cob	13.8 (a)	[240]
Maize bran	312.52 (a)	[120]
Mucilaginous seed	205 (a)	[241]
Neem bark	19.60 (a)	[88]
Neem leaf powder	87 (b)	[133]
Nitric-oxidized coconut shell	10.88 (a)	[242]
Oak leaf	48.7(b)	[107]
Orange peel	49.9(b)	[107]
Ocimum americanum L. seed pods	83.33 (a)	[243]
Polyacrylamide grafted saw dust	91 (b)	[244]
Pine bark	85(b)	[107]
Pine needle	38(b)	[107]
Pine needles	21.5 (a)	[245]
Pine cone	71.8(b)	[107]
Palm pressed-fibers	14.0 (a)	[246]
Pinnus sylvestris (Scots Pine) bark	86.9 (b)	[247]
Pomegranate husk carbon	35.2(a)	[248]
Quercus ilex L (Holly Oak)	0.09 (a)	[249]
Rice bran	58.89 (a)	[84]
Rice bran	312.50 (a)	[250]
Raw rice bran	40 (b)	[251]
Rice husk ash	25.64 (a)	[88]
Rice husks	0.6 (a)	[252]
Rice husk (boiled)	8.5 (a)	[253]
Rice husk (formaldehyde treated)	10.4 (a)	[253]
Rice husk	25.2(b)	[107]
Rice husk carbon	48.31 (a)	[103]
Rice straw	26.3(b)	[107]
Rice husk carbon	45.6 (a)	[254]
Reed mat (*Cannomois vvirgata*)	3.393 (a)	[86]
Reed biomass (*Phragmites australis*)	58(a)	[76]
Raw palm flower	4.9(a)	[81]
Saw dust carbon	53.48 (a)	[103]
Sugarcane bagasse	92.23 (b)	[255]
Sugarcane bagasse	0.63 (a)	[256]
Saw dust	1.482 (a)	[252]
Saw dust	19.9 (b)	[107]
Saw dust	20.70 (a)	[88]
Saw dust	39.7 (a)	[240]
Saw dust (Brazilian)	168.57 (a)	[257]
Slurry (converted into carbonaceous material)	55(b)	[258]
Saw dust	16.5 (a)	[259]
Sunflower stem	4.9 (a)	[260]
Sugarcane bagasse	1.04 (c)	[261]
Sugar beet pulp	17.42 (a)	[240]
Sphagnum moss peat	119 (a)	[262]
Soya cake	0.28 (a)	[263]
Solid waste from leather industry	133.33 (a)	[164]
Sulfuric acid treated waste activated carbon	7.485 (a)	[264]
Silver impregnated groundnut	11.34 (a)	[178]
Solanum elaeagnifolium (weed of western North America)	2.2(a)	[265]
Salvinia cucullata (weed)	159.2 (a)	[266]
Treated saw dust (Sal tree, *Shorea robusta*)	9.55 (a)	[267]
Tea factory waste	54.65 (a)	[135]
Tea dust	44.9 (a)	[5]
Tamarind fruit nut shell	44.8 (a)	[95]
Tamarind wood activated carbon	89.94 (b)	[268]
Thuja oriantalis (Asiatic shrub)	48.8 (a)	[60]
Tamarind hull	81.0 (a)	[269]
Treated pine saw dust	121.95 (a)	[144]
Water lily	7.559(a)	[86]
Water hyacinth	6.378 (a)	[86]

Table 8 (*Continued*)

Agricultural product	Sorption capacity [{(mg/g) (a)} or {(m mole/g) (c)}] or removal efficiency (%) (b)	Refs.
Walnut shell	18.51 (a)	[218]
Wheat bran	40.80 (a)	[84]
Waste tea	1.55 (a)	[270]
Waste pomace of olive oil factory	18.69 (a)	[271]
Yohimbe bark waste	42.5 (a)	[105]

Table 9
Other (non-living) biosorbents.

Name of product	Sorption capacity [{(mg/g) (a)} or {(mmole/g) (c)}] or removal efficiency (%) (b)	Refs.
Activated alumina	25.57 (a)	[88]
Aniline–formaldehyde condensate coated silica gel	65.0 (a)	[272]
Aminated polyacrylonitrile fibers	20.7 (a)	[273]
Anion exchange resins	1.31 (c)	[274]
Anion exchange resin	94.34 (a)	[275]
Activated bentonite	91.7 (a)	[276]
Acid activated clay	83 (a)	[172]
Acid activated pillared clay	16.9 (a)	[172]
Bentonite (clay)	0.572 (a)	[277]
Brown coal	0.98 (c)	[278]
Biogas residual slurry	5.87 (a)	[99]
Clarified sludge	26.31 (a)	[88]
Calcinied bauxite	2.021 (a)	[279]
Crystalline hydrous titanium oxide	20.00 (a)	[140]
Coal (oxihumolite)	0.151 (c)	[280]
Coal	6.78 (a)	[245]
Chitosan beads	76.92 (a)	[281]
Clay crude	113 (a)	[172]
Clay purified	109 (a)	[172]
Cationic starch	98 (b)	[282]
Clinoptilolite (natural zeolite)	2.40 (a)	[283]
Chitosan	153.850 (a)	[284]
Cationic surfactant-modified lichen	61 (b)	[285]
Ceria nanoparticles	31.55 (a)	[286]
Fuller's earth	23.58 (a)	[88]
Fly ash	23.86 (a)	[88]
Fly ash	0.0005 (a)	[287]
Imidazol grafted silica	113.0 (a)	[288]
Hydrotalcite like compound (HLC)	25.7 (a)	[289]
Lewatit MP 64 (anion exchange resin)	0.40 (c)	[290]
Lewatit MP 500 (anion exchange resin)	0.41 (c)	[290]
Humic acid	2.75 (a)	[122]
Modified chitosan beads	256.4 (a)	[291]
Modified jacobsite magnetic nanoparticles	31.55 (a)	[292]
Modified hectorite clays	14.01 (c)	[293]

Table 9 (*Continued*)

Name of product	Sorption capacity [{(mg/g) (a)} or {(mmole/g) (c)}] or removal efficiency (%) (b)	Refs.
Nanocrystalline akaganeite (mineral)	80.0 (a)	[294]
PVP coated silica gel	100 (b)	[295]
PANI-jute	4.66 (a)	[296]
Red mud	0.436 (c)	[166]
Red mud	30.74 (c)	[297]
Riverbed sand	0.15 (a)	[298]
STAC-modified rectorite	21 (a)	[75]
Spent activated clay	1.42 (a)	[82]
Surfactant-modified kaolinite (clay)	0.68 (a)	[299]
Surfactant-modified montmorillonite (clay)	41.34 (a)	[300]
Turkish brown coal (BC_1)	11.2 (c)	[176]
Titanium dioxide (anatase)	14.56 (a)	[301]
Used tires	58.48 (a)	[302]
Waste crab shell	22.9 (a)	[303]
Yarikkaya (YK) brown coal	0.293 (c)	[304]

(2) Models play a key role in transferring technologies from the laboratory to a full-scale application. Development of dynamic models to simulate the biosorption process and contribute useful information for its practical application should receive more attention [46,316].
(3) Molecular biotechnology should be deployed to understand the biosorption mechanism at the molecular level. This will help to design modified organisms with better sorption capacity and specificity for target metal ions [317].

8. Conclusions

Biomass represents an efficient and potential class of biosorbents for the removal of hexavalent chromium from industrial and municipal wastewater. Although some attempts have been made to commercialize biosorption for wastewater treatment, progress has been very slow, especially considering that there has been more than three decades of fundamental research (reviewed herein). The important features required for the successful application of biosorption technology to real situations include, but are not limited to, (1) screening and selection of the most promising biomass, with sufficiently high biosorption capacity and selectivity, (2) using real wastewater, not synthetic wastewater, as synthetic waste water generally does not contain humic acid, other metal ions and various microorganisms, and (3) optimizing the different parameters for biosorption and recycling the biosorbents.

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