



Review

Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: A review

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ABSTRACT

In aqueous systems, chromium usually exists in both trivalent and hexavalent oxidation states, being Cr(VI) of particular importance and concern due to its great toxicity. Industrial sources of Cr(VI) are leather tanning, mining of chrome ore, production of steel and alloys, etc. The most common conventional method for Cr(VI) removal is reduction to Cr(III) at pH 2.0 and precipitation of Cr(OH)₃ with lime at pH 9–10. The disadvantage of precipitation is the disposal of the solid waste. Adsorption of Cr by different low cost materials seems to be a suitable choice for wastewater treatment. Many by-products of agriculture have proved to be suitable low cost adsorbents for Cr(VI) and Cr(III) removal from water. Lignocellulosic residues, which include both wood residues and agricultural residues, have adsorption capacity comparable to other natural sorbents, but they have the advantage of very low or no cost, great availability and simple operational process. This study is a review of the recent literature on the use of natural and modified lignocellulosic residues for Cr adsorption. The Cr maximum adsorption capacity and the adsorption mechanism under different experimental conditions are reported when possibly.

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1. Introduction

In natural waters, the range of chromium concentration is quite large, from 5.2 to 208,000 mg L⁻¹ [1]. Nevertheless, for most natural waters the Cr concentration is below the 50 µg L⁻¹ value recommended for drinking water by the World Health Organization or the US Environmental Protection Agency [2,3].

Cr can exist under six oxidation states like most transition metals, but in the Eh–pH range of natural waters the only important ones are trivalent Cr(III) and hexavalent Cr(VI). In low Eh environments, the main aqueous species are Cr³⁺, Cr(OH)²⁺, Cr(OH)₃⁰ and Cr(OH)₄⁻. At pH less than 3.6, Cr³⁺ is the prevalent species. Under oxidizing conditions, the principal species are HCrO₄⁻, CrO₄²⁻, Cr₂O₇²⁻ depending on the pH and on the Cr concentration [1,4].

Cr(VI) is the most toxic form, being carcinogenic and mutagenic to living organisms [5]. In addition, it leads to liver damage, pulmonary congestion and causes skin irritation resulting in ulcer formation [6]. Trivalent Cr(III) is about 300 times less toxic than Cr(VI) and due to the fact that has limited hydroxide solubility, it is less mobile and less bioavailable [7]. Cr(III) is essential to animals and plants and plays an important role in sugar and fat metabolism, although in excess can cause allergic skin reactions and cancer [8].

The use of Cr chemicals in several industrial processes (leather tanning, mining of chrome ore, production of steel and alloys, dyes and pigment manufacturing, glass industry, wood preservation, textile industry, film and photography, metal cleaning, plating and electroplating, etc.) leads to contamination of natural waters mainly due to improper disposal methods [9].

Because of its high toxicity, Cr(VI) must be substantially removed from the wastewater before being discharged into the aquatic system. Different technologies are available: chemical precipitation, coagulation, ion exchange, membrane technologies, adsorption, etc. The most common conventional method for Cr(VI) removal is reduction to Cr(III) at pH 2.0 and precipitation of Cr(OH)₃ by increasing pH to 9–10 using lime. The disadvantage of precipitation is the disposal of the solid waste. Nowadays, adsorption has become by far the most versatile and widely used technology, and activated carbon, the most commonly used sorbent. However, the use of activated carbon is expensive, so there has been increased interest in the last years in the use of other adsorbent materials. The removal of chromium from wastewaters using bacteria, fungi, algae and different plants has been reported, but although these material show good performance under laboratory conditions, their use for large scale effluent treatments may not be suitable due to their rel-

atively poor natural abundance [10]. The use of low cost adsorbents showed higher potential for Cr removal from wastewaters. There are excellent reviews on heavy metal removal from wastewaters by the use of low cost adsorbents [4,11,12], in particular, by chemically modified plant wastes [13], by agro-based waste materials [14], by plants and lignocellulosic agrowastes [7].

Many by-products of agriculture have proved to be good low cost adsorbents for the removal of both tri- and hexavalent chromium from water. Lignocellulosic residues include wood residues (sawdust and paper mill discards) and agricultural residues (sugarcane bagasse, wheat bran, wheat straw, corn stoves, etc.). Although lignocellulosic wastes have adsorption capacity comparable to other natural sorbents, they have the advantage of very low or no cost, great availability, simple operational process and the fact that through their use as biosorbents, added value is provided to products that otherwise would be considered as a waste [7].

The aim of this study is to review the recent literature (mainly last ten years) on the adsorption of Cr from solution using natural and modified lignocellulosic residues as adsorbent material. The Cr maximum adsorption capacity and the adsorption mechanism under different experimental conditions are reported when possible. It has to be mentioned that chemical modifications that lead to activated carbon as adsorbent are not considered in this review.

2. Chemical composition of lignocellulosic residues

Lignocellulosic wastes are composed mainly of cellulose, hemicelluloses and lignin [15]. Lignin is a three dimensional, highly branched polyphenolic polymer, most commonly derived from wood and an integral part of the secondary cell wall of plants that presents a three-dimensional structure. Lignin fills the spaces in the cell wall between cellulose, hemicellulose and pectin components, conferring mechanical strength to the cell wall. Lignin accounts for 23–33% of softwood mass, for 16–25% of hardwood mass and for 26–33% of plant biomass [16]. In plants, lignin is second in natural abundance, cellulose being the first. Lignin is an amorphous crosslinked resin which serves as main binder for the agglomeration of fibrous cellulosic components and also provides a shield against rapid microbial or fungal destruction of the cellulosic fibers [4]. Lignin macromolecule has a high surface area: 180 m² g⁻¹ and molecular weight from 2000 to 15,000 g mol⁻¹ [17].

Lignin is composed of three methoxylated monolignol monomers: p-coumaryl alcohol, coniferyl alcohol and sinapyl

Table 1
Percentage of major components in unmodified lignocellulosic wastes.

Agricultural by-products	Ash (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
<i>Agave lechuguilla</i> biomass		5	80	15	Vieira et al. [97]
Almond shells	2.9	40.5	19.7	27.2	Wartelle and Marshall [98]
Almond shells	0.8	29.0	35.2	30.0	Pehlivan et al. [94]
Apple pulp		16.0	16.0	21.0	Cagnon et al. [91]
Bagasse	1.5–5	32–48	19–24	23–32	Reddy and Yang [95]
Banana		60–65	6–8	5–10	Reddy and Yang [95]
Barley straw		31–45	27–38	14–19	Reddy and Yang [95]
Coconut husks (coir)	5.5	40.0	0.2	43.0	Reddy and Yang [95]
Coconut shell		14.0	32.0	46.0	Cagnon et al. [91]
Corn cob	1.3	38.4	40.7	9.1	Wartelle and Marshall [98]
Corn stover	6.7	39.2	29.6	8.2	Wartelle and Marshall [98]
Cotton seed hulls	1.1	48.7	18.5	22.3	Wartelle and Marshall [98]
Dende shells	1.1	24.9	27.0	45.4	Ouensanga et al. [93]
Ectodermis of <i>Opuntia</i>		28.2	14.4	14.5	Barrera et al. [73]
Guava seeds	16.8	28.0	15.5	41.7	Ouensanga et al. [93]
Hazelnut shells	1.5	18.2	28.9	48.6	Pehlivan et al. [94]
Jujube seeds	0.3	37.3	25.9	35.4	Ouensanga et al. [93]
Oak chips	1.8	49.7	19.1	5.4	Wartelle and Marshall [98]
Oat hulls	4.5	42.7	39.2	7.3	Wartelle and Marshall [98]
Olive stones		14.0	15.0	42.0	Cagnon et al. [91]
Peanut shells	2.3	45.3	8.1	32.8	Wartelle and Marshall [98]
Pecan shells	3.5	33.2	9.6	48.3	Wartelle and Marshall [98]
Pineapple leaf fiber	0.8	70–80	18.0	5–12	Reddy and Yang [95]
Plum pulp		6.5	14.5	39.0	Cagnon et al. [91]
Plum stones		23.0	20.0	49.0	Cagnon et al. [91]
Rice hulls	21.9	34.8	6.0	17.2	Wartelle and Marshall [98]
Rice husk	17.0	35.0	25.0	20.0	Krishnani et al. [49]
Rice straw	13.1	43.3	25.1	5.4	Wartelle and Marshall [98]
Sawdust from oak tree		41.5	32.7	22.8	Argun et al. [63]
Soft wood		36.0	18.5	30.5	Cagnon et al. [91]
Sorghum stalks		27.0	25.0	11.0	Reddy and Yang [95]
Soybean hulls	3.6	67.6	13.7	4.9	Wartelle and Marshall [98]
Sugarcane	0.4	58.2	9.2	13.4	Wartelle and Marshall [98]
Wheat straw		31.5	33.3	11.6	Chen et al. [92]

alcohol, incorporated into lignin in the form of phenylpropane units: p-hydroxyphenyl, guaiacyl and syringal, respectively [18]. There are many different types of lignin in different types of lignocellulosic materials, the lignin from grasses, softwoods and hardwoods differ in the methoxyl substitution and the degree of carbon-carbon linkage between phenyl groups [19]. Lignin is covalently linked with xylans in hardwoods and with galactoglucomannans in softwoods [20]. Lignin comprises a variety of functional groups such as aliphatic and phenolic hydroxyl groups (9–11%), methoxyl groups (13–26%) and carbonyl groups, which present the ability to bind heavy metals by donation of an oxygen electron pair from these groups to form complexes with metal ions in solution [14,21]. Physical and chemical properties of lignin may differ depending on the extraction technology employed to isolate it from the polysaccharide moieties [4].

Cellulose is a straight chain polymer of D-glucose bound together by β (1–4) glycosidic bonds. The hydroxyl groups of the glucose residues from one chain form hydrogen bonds with oxygen on another chain holding the chains firmly together. Cellulose from wood pulp has chain length between 300 and 1700 units, whereas cellulose from plants ranges from 800 to 10,000 units [22]. Cellulose molecules are aggregated together in the form of microfibrils in which highly ordered (crystalline) regions exist with less ordered (amorphous) regions [19].

Hemicellulose comprises 20% of most plants. It is a polymer of different monosaccharides units, mainly glucose and xylose, but also, mannose, galactose, rhamnose and arabinose, bond in branched short chains, of around 200 units.

The carbohydrate polymers, cellulose and hemicelluloses are bound to the lignin in lignocellulosic residues by hydrogen bond and covalent bonds. In general, raw lignocellulosic biosorbents are modified by various chemical methods to increase the metal sorption capacity as metal binding takes place mainly through

chemical functional groups such as carboxyl and hydroxyl. The hemicellulose, cellulose and lignin percentages of some unmodified lignocellulosic wastes are shown in Table 1.

3. Chromium determination in aqueous phase

3.1. Cr(VI) determination

The 1,5 diphenyl carbazide method followed by spectrophotometric determination at λ 540 nm [23] for the determination of Cr(VI) concentrations in aqueous phase was the method of choice of a great number of researchers [9,10,17,24–56]. The performance of this method has been compared with that of the iodometric method by Celik et al. [17].

Nevertheless, it is important to point out that several authors reported Cr(VI) concentration in the course of their investigations but they determined total Cr by flame atomic absorption spectrometry (AAS), inductively coupled plasma spectrometry (ICP-OES) or by inductively coupled plasma mass spectrometry (ICP-MS) without taking into account that Cr(VI) could be reduced to Cr(III) specially at low pH values, so their results may be wrong [21,57–70].

3.2. Cr(III) determination

Ahmad [71] and Malik et al. [72] used radiotracer ^{51}Cr to determine Cr(III) concentration in aqueous solution by gamma counts, but Cr(III) concentration was usually determined by most of the researchers as the difference between total Cr and Cr(VI) concentration [9,10,24,26–28,30,31,42,47–51,73].

3.3. Total Cr detection

Total Cr concentration was determined by potassium permanganate oxidation of Cr(III) to Cr(VI) at high temperature (130 °C) prior using the 1,5 diphenyl carbazide method [9,10,24,27,28,30,42,50–52,73,74], by ICP-AES [31,49], AAS [47,48] or ICP-MS [26].

4. Characterization of lignocellulosic materials

Characterization of lignocellulosic substrates has been performed by X-ray diffraction (XRD) [9,75], scanning electron microscopy (SEM) [9,40,43,49,103], scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) [44,73,75] and transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (TEM-EDX) [75,100].

5. Determination of the oxidation state of chromium bound to the lignocellulosic residue

The oxidation state of chromium bound on the biomaterial, the coordination geometry and the nature of the bond between the adsorbing atom and its ligands, was performed by X-ray photoelectron spectroscopy (XPS) [31,49–51], X-ray absorption near-edge structure (XANES) [44,75,76], extended X-ray absorption fine structure spectroscopy (EXAFS) [31,75,76], electronic paramagnetic resonance or electronic spin resonance (EPR or ESR) [45,75] and by energy electron loss spectroscopy (EELS) [100].

6. Determination of functional groups present in lignocellulosic residues

Determination of functional groups present in the biomass was usually performed by infrared spectroscopy (IR) [9,31,39,59,73], by Fourier transform infrared spectroscopy (FT-IR) [40,43,44,47–49,64,66,74,77–79] and by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FT-IR) [101]. Excellent reviews on description and discussion of the different techniques mentioned above can be seen elsewhere [109–117].

7. Cr adsorption mechanism

7.1. Cr(VI)

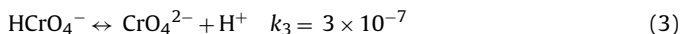
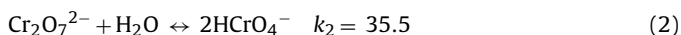
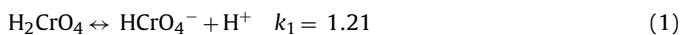
7.1.1. Mechanism I

The pH of the aqueous solution influences Cr speciation and the dissociation of active functional groups (–OH, –COOH, –NH₂). Therefore, Cr adsorption is critically associated with solution pH. The presence of hydroxyl groups has been confirmed in sawdust, pine leaves, *Eichornia crassipes* biomass, *Jatropha* oil cake [38,41,43]; hydroxyl and carboxyl groups, in the lignocellulosic moieties of the husk of Bengal gram, in pomace and in modified red pine sawdust [34,40,79]; carboxyl in lignocellulosic groups in the residues of wheat bran and rice straw [10,31], and amide groups in an herb biomass [70].

At low pH, the functional groups in the surface of the lignocellulosic material are protonated and restrict the approach of cationic species as the result of repulsive forces. As the pH increases, the degree of protonation decreases, and the functional groups become negatively charged (pH > pK_a). Aqueous Cr(VI) exists as five main species: H₂CrO₄; HCrO₄[–]; CrO₄^{2–}; HCr₂O₇[–]; Cr₂O₇^{2–} which distribution depends on pH and total Cr concentration [80]. At solution pH values between 2.0 and 6.0, Cr(VI) ions are probably in solution as HCrO₄[–] and Cr₂O₇^{2–} species, at lower pH (pH < 2.0) the principal species are Cr₄O₁₃^{2–}, Cr₃O₁₀^{2–}. These anionic species

can be adsorbed to the protonated active sites of the biosorbent [70].

The following equilibria may be written for the Cr(VI) anions present in aqueous solution [81]:



There is no significant adsorption of Cr(VI) at pH values higher than 6.0 due to competition of the anions HCrO₄[–], Cr₂O₇^{2–} and OH[–] for the adsorption sites.

Many studies reported that Cr(VI) was removed from aqueous solutions by biomaterials through an adsorption process between positive charged adsorption sites in the adsorbent and the anionic Cr(VI) species [9,17,21,25,27,29,30,34,35,37–39,41,42,46,53,54,56,58,59,62–65,67–70,79,82,83]. Nevertheless, Mohan and Pittman [4] reported that the removal of Cr(VI) by the electrostatic mechanism could be misinterpreted due to errors in measuring chromium species in aqueous phase, insufficient contact time required for equilibrium and the lack of information about the oxidation state of chromium bound on the biomaterials.

7.1.2. Mechanism II

Nowadays, the “adsorption-coupled reduction” reaction is widely accepted as the true mechanism of Cr(VI) adsorption by natural biomaterials under acidic conditions [10,24,28,31,36,40,43–45,47–52,55,61,66,73,74,76,84,85].

The reduction of Cr(VI) to Cr(III) occurs after Cr(VI) is adsorbed with living plants, wetland plants, bacteria, biomass, rice husk, dead fugal biomass, coir pith and oat by-products under acidic conditions because of its high redox potential value (above +1.3 V at standard condition). Park et al. [50–52] reported that Cr(VI) could be removed from solution by natural biomaterial through both direct and indirect reduction mechanisms:

- (i) *Direct reduction mechanism*: The reduction of Cr(VI) to Cr(III) occurs in the aqueous phase by contact with the electron-donor groups of the biomaterial that have lower reduction potential values than that of Cr(VI). Cr(III) ions remain in the aqueous solution or form complexes with the Cr-binding groups present in the biomaterial.
- (ii) *Indirect reduction mechanism consists in 3 steps*: (a) binding of anionic Cr(VI) to the positively charged groups in the biomaterial surface such as amino and carboxyl groups, (b) reduction of Cr(VI) to Cr(III) by adjacent electron-donor groups and (c) release of Cr(III) into aqueous phase due to repulsion between positively charged Cr(III) and positively charged groups in the biomaterial surface, or complexation of Cr(III) with adjacent groups. Amino and carboxyl groups take part in step (a) of indirect reduction.

Cr(VI) remains bound to the biomaterial surface if there is a small number of electron-donor groups in the biomaterial or protons in the aqueous phase. The removal rate of Cr(VI) increases when Cr(VI) concentration and biomaterial dose increases (first-order kinetics). An increase in temperature increases the Cr(VI) removal rate, owing to the endothermic nature of the redox reaction. The occurrence of direct or indirect mechanism depends on the biosorption system: pH, temperature, type of biomaterial and metal concentration.

The influence of pH is very important in both mechanisms since protons take part in the reaction. A low pH makes the biomaterial surface positively charged as amino and carboxyl groups become protonated, enhancing the rate of anionic Cr(VI) removal from aqueous phase.

Table 2
Cr(VI) adsorption by lignocellulosic wastes.

Adsorbent material	Q_{\max} (mg g ⁻¹)	pH optimal	Type of study	Isotherm	Kinetic model	Thermodynamics	Mechanism proposed	Adsorbent characterization, metal speciation, functional groups	Reference
<i>Bagasse</i> Sugarcane	13.40	2.0	E	L, F			Cr(VI) reduction to Cr(III)		Sharma and Forster [24]
Sugarcane			E				Cr(VI) reduction to Cr(III)		Krishnani et al. [85]
Sugarcane	23.00	1.9	E, D	L, D, S			Cr(VI) reduction to Cr(III)		Krishnani et al. [102]
Sugarcane	0.28	2.0	E	L, F			Cr(VI) reduction to Cr(III)	FT-IR, SEM	Garg et al. [43]
<i>Bark</i> Eucalyptus (pretreated)	45.00	2.0	E, K	L, F	Lagergren first order	Spontaneous	Electrostatic attraction	SEM, XRD, IR	Sarin and Pant [42]; Sarin et al. [9]
Japanese cedar	71.94	3.0	E, T	L		Spontaneous, endothermic	Cr(VI) reduction to Cr(III)	FT-IR	Aoyama et al. [74]
Larch (pretreated)	31.25	3.0	E, T	L, F		Endothermic	Physico-chemical adsorption		Aoyama and Tsuda [27]
<i>Biomass</i> Cone (<i>Pinus sylvestris</i>)		1.0	E	F			Electrostatic attraction		Ucun et al. [29]
Cone (<i>Thuja orientalis</i>)	48.80	1.5	E, K, T	L, F, B, D-R, R-P	Pseudo-second order	Spontaneous, endothermic	Electrostatic attraction		Oguz [35]
<i>Eichornia crassipes</i>		1.0	E, K	F	Pseudo-second-order, intraparticle diffusion		Electrostatic attraction	FT-IR	Mohanty et al. [41]
Oat (<i>Avena monida</i>)			E				Cr(VI) reduction to Cr(III)	XAS, XANES, EXAFS	Gardea-Torresdey et al. [76]
Reed	33.00	2.0	E, T	L		Spontaneous, endothermic	Electrostatic attraction		Rawajfih and Nsour [54]
Sunflower stem pretreated	5.37–4.81	2.0	E	L, F, D-R			Chemical complexation	FT-IR, SEM	Jain et al. [69]
<i>Bran</i> Rice	285.71	2.0	E, K, T	L, F	Pseudo-first order	Spontaneous, endothermic	Electrostatic attraction	IR	Singh et al. [83]
Wheat bran	35.00	2.1	E	L			Cr(VI) reduction to Cr(III)	EXAFS, IR, XPS. TEM-EDXS, EELS	Dupont and Guillon [31]; Dupont et al. [100]
<i>Cake</i> Oil cake from <i>Jatropha</i>	0.63	2.0	E	L, F			Cr(VI) reduction to Cr(III)	FT-IR, SEM	Garg et al. [43]
Olive cake	35.44	2.0	E, K	L, F	Lagergren first order	Spontaneous	Electrostatic attraction		Dakiky et al. [58]
Soya cake	0.28	<1.0	E	L, F			Cr(VI) reduction to Cr(III)		Daneshvar et al. [28]
<i>Coir</i> Coconut	6.30	2.0	E	L, F, R-P, T, etc.			Cr(VI) reduction to Cr(III)	FT-IR	Gonzalez et al. [66]

Table 2 (Continued)

Adsorbent material	Q_{\max} (mg g ⁻¹)	pH optimal	Type of study	Isotherm	Kinetic model	Thermodynamics	Mechanism proposed	Adsorbent characterization, metal speciation, functional groups	Reference
Pith	197.23 (30 °C)	2.0	E, K, T	L	Pseudo-second order	Endothermic	Cr(VI) reduction to Cr(III)	SEM-EDX, XANES, FT-IR, ESR	Suksabye et al. [44]; Suksabye et al. [45]
Pith	262.89 (45 °C)	3.0	E, D	F			Electrostatic attraction and or reduction Cr(VI) to Cr(III)		Sumathi et al. [36]
<i>Husk and hull</i> Bengal gram husk	91.64	2.0	E	L, F			Electrostatic attraction	FT-IR	Ahalya et al. [34]
Coconut husk Coconut husk	29.00	2.05	E, D E	L					Tan et al. [96] Parimala et al. [99]
Rice hull quaternized Rice husk		2.0	D E, K		Park's model		Cr(VI) reduction to Cr(III)	XPS	Low et al. [57] Park et al. [51]
Rice husk	52.1	2.0	E, D	L, F, D, S			Cr(VI) reduction to Cr(III)	SEM, FT-IR, XPS	Krishnani et al. [49]
Rice husk		3.0	E, D	F			Electrostatic attraction and or reduction Cr(VI) to Cr(III)		Sumathi et al. [36]
Walnut hull	98.13	1.0	E, K, T	L, F	First-order, modified Freundlich, intraparticle diffusion and Elovich		Electrostatic attraction		Wang et al. [56]
<i>Leaves</i> Cactus	7.08	2.0	E, K, T	L, F	Lagergren first order	Non-spontaneous	Electrostatic attraction		Dakiky et al. [58]
<i>Ficus religiosa</i>	26.25	1.0	E, K	L	Pseudo-second order		Ion exchange	FT-IR	Qaiser et al. [64]
London plane	68.03	3.0	E, K, T	L	Lagergren first order	Spontaneous, endothermic	Physico-chemical adsorption		Aoyama [30]
Oak Pine	0.47	2.0 2.0	E, K E	L, F	Park's model		Electrostatic attraction	XPS	Park et al. [51] Aliabadi et al. [38]
<i>Sawdust</i> <i>Acacia arabica</i> (pretreated)	111.61	6.0	E, K, T	L, F	Lagergren first order		Surface complexation-ion exchange		Meena et al. [67]
Beech	16.13	1.0	E	L, F			No mechanism proposed		Acar and Malkoc [32]
Indian Rosewood pretreated		3.0	E				Electrostatic attraction		Garg et al. [33]
Origin no reported	43.00	2.0	E	L, F			Cr(VI) reduction to Cr(III)		Sharma and Forster [24]
Origin no reported	0.20	2.0	E	L, F			Electrostatic attraction	FT-IR	Aliabadi et al. [38]
Origin no reported	15.82	2.0	E, K, T	L, F	Lagergren first order	Spontaneous	Electrostatic attraction		Dakiky et al. [58]

Origin no reported	41.52	1.0	E, K	L, F, D-R, R-P, T	Pseudo-second order		Electrostatic attraction and or reduction Cr(VI) to Cr(III)		Gupta and Babu [55]
Origin no reported	41.90	1.0	D	L			Electrostatic attraction and or reduction Cr(VI) to Cr(III)		Gupta and Babu [107]
Maple		5.0	E	L, F			Chelation ion exchange	IR	Yu et al. [59]
Oak tree (treated)	1.74	3.0	E, K, T	L, D-R	Pseudo-second-order: external mass transfer	Spontaneous, endothermic	Electrostatic attraction		Argun et al. [63]
Pine (modified)	30.49	2.0	E, K, T	L, F	Lagergren first order	Spontaneous, endothermic	Electrostatic attraction		Uysal and Ar [46]
Red pine	8.30	3.0	E	L, F			Chelation ion exchange	FT-IR	Gode et al. [79]
Red pine (modified)	15.2 (BESD)	3.0	E	L, F			Chelation ion exchange	FT-IR	Gode et al. [79]
Rubber wood (polyacrylamide grafted)	22.6 (TASD)	3.0	E, K, T	F	Lagergren first-order, intraparticle diffusion	Spontaneous, exothermic	Electrostatic attraction		Raji and Anirudhan [25]
<i>Shorea robusta</i> (treated)	9.55	3.5	E, K	L	Pseudo-second order		Electrostatic attraction		Baral et al. [39]
Teak (<i>Teclona grandis</i>)		3.0	E, D	F			Electrostatic attraction and or reduction Cr(VI) to Cr(III)		Sumathi et al. [36]
Shell									
Almond	22.20	4.0	E, K	L, F	Lagergren first order		Electrostatic attraction		Agarwal et al. [37]
Almond	10.61	2.0	E, K, T	L, F	Lagergren first order	Non-spontaneous	Electrostatic attraction		Dakiky et al. [58]
Almond	3.40	3.2	E	L, F			Electrostatic attraction		Pehlivan and Altun [53]
Coconut		4.0	E, K	L, F	Lagergren first order		Electrostatic attraction		Agarwal et al. [37]
Ground nut	5.88	4.0	E, K	L, F	Lagergren first order		Electrostatic attraction		Agarwal et al. [37]
Hazelnut	8.28	3.5	E	L, F			Electrostatic attraction		Pehlivan and Altun [53]
Peanut		2.0	E, K		Park's model		Cr(VI) reduction to Cr(III)	XPS	Park et al. [51]
Walnut	2.28	4.0	E, K	L, F	Lagergren first order		Electrostatic attraction		Agarwal et al. [37]
Walnut	8.01	3.5	E	L, F			Electrostatic attraction		Pehlivan and Altun [53]
Walnut		2.0	E, K		Park's model		Cr(VI) reduction to Cr(III)	XPS	Park et al. [51]
Various									
Banana skin		1.5-4.0	E, K		Park's model		Cr(VI) reduction to Cr(III)	XPS	Park et al. [51]
Lignin from paper industry	13.48	3.0	E	L			Electrostatic attraction		Celik et al. [17]
Maize cob	13.80	1.5	E	L, F			Cr(VI) reduction to Cr(III)		Sharma and Forster [24]
Maize corn cob	0.82	2.0	E	L, F			Cr(VI) reduction to Cr(III)	FT-IR, SEM	Garg et al. [43]

Table 2 (Continued)

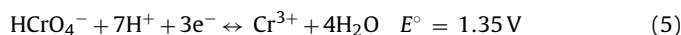
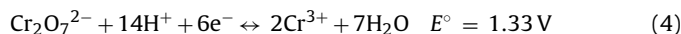
Adsorbent material	Q_{\max} (mg g ⁻¹)	pH optimal	Type of study	Isotherm	Kinetic model	Thermodynamics	Mechanism proposed	Adsorbent characterization, metal speciation, functional groups	Reference
Pine needles	21.50	2.0	E, K, T	L, F	Lagergren first order	Non-spontaneous	Electrostatic attraction	XPS	Daikiky et al. [58] Park et al. [50]
Pine needles		2.0–4.0	E, K		Par'k's first order		Cr(VI) reduction to Cr(III)		
Pomace	13.95	2.0	E, D, T	L, F		Spontaneous, endothermic	Cr(VI) reduction to Cr(III)	FT-IR, SEM	Malkoc et al. [40]
Rice straw	3.15	2.0	E	L, F			Cr(VI) reduction to Cr(III)		Gao et al. [10]
Paddy straw	21.50	2.0	E	L, D, S			Cr(VI) reduction to Cr(III)	SEM, XPS	Krishnani et al. [103]
<i>Tamarindus indica</i> seeds (TS)	55.30	4.0	E, K	L, F	Lagergren first order		Electrostatic attraction		Agarwal et al. [37]

E: equilibrium; K: kinetic; D: dynamic; T: thermodynamic.

L: Langmuir; F: Freundlich; T: Tempkin; R-P: Redlich–Peterson; D-R: Dubinin–Radushkevich; B: Brunauer, R-D: Radke–Prausnitz; D: Dahlquist, S: Scatchard isotherms.

X-ray diffraction (XRD); scanning electron microscopy (SEM); scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX); X-ray photoelectron spectroscopy (XPS); X-ray absorption near-edge structure (XANES); extended X-ray absorption fine structure spectroscopy (EXAFS); electronic paramagnetic resonance or electronic spin resonance (EPR or ESR); infrared spectroscopy (IR); Fourier transform infrared spectroscopy (FT-IR); energy electron loss spectroscopy (EELS); transmission electron microscopy (TEM) coupled with energy-dispersive X-ray spectroscopy (EDXS).

At pH: 2.0–4.0



The consumption of H^+ by Cr(VI) reduction leads to the rise of solution pH. Suksabye et al. [45] reported that the reduction of Cr(VI) to Cr(III) by living plant and bacteria occurred through an intermediate Cr(V) species.

It is important to point out that protons and electrons (supplied by the electron-donor groups in the biomaterial) are required for the reduction of Cr(VI) to Cr(III). The information is scarce on the electron-donor groups present in the biosorbents. The identification of these groups would be helpful in the selection of new biomaterials for Cr(VI) removal from contaminated waters [52]. Thiol, phenolic and carboxylic functional groups have been reported as electron-donor groups in biomaterials [31,47–49]. Dupont and Guillon [31] conducted studies on Cr adsorption with pure cellulose and pure lignin at acidic pH and observed no significant adsorption onto cellulose, whereas Cr(VI) reduction to Cr(III) was carried out on lignin. Therefore, the reduction of Cr(VI) into lignocellulosic substrate clearly involves lignin moieties, mainly through carboxyl groups [49] or methoxy and carbonyl groups as electron-donors [44,45].

7.2. Cr(III)

Cr(III) adsorption by lignocellulosic wastes is almost negligible at pH < 2.0 and above this value, increases with pH up to pH ~ 5.0. This behavior can be explained by the change in the ionic state of the acid functional groups in the biomaterial, mainly carboxyl groups [75–77,86,87]. At a pH higher than the pK_a (~3.5) these groups are negatively charged and Cr^{3+} ion (principal species at low pH) can be bound to negative charged groups by electrostatic attraction. At pH lower than pK_a , functional groups are protonated, and metal uptake decreases. Also, chromic ion species exist in acidic solution as bulky hydrated species ($\text{Cr}(\text{H}_2\text{O})_6^{3+}$), being this ion too large to enter in the microporous system of the adsorbent [74]. An increase in pH results in a decrease of Cr^{3+} concentration and other species become important such as CrOH^{2+} , also attracted to negatively charged functional groups [87].

7.3. Total Cr

Due to the fact that the removal efficiency for Cr(VI) increases with the decrease of pH, and that the removal efficiency for Cr(III) increases with the increase of pH, the removal efficiency of total Cr is maximum at pH 4–5, depending on the contact time [51].

8. Cr adsorption studies

Modeling aspects of adsorption is beyond the scope of this paper. Excellent reviews on the empirical and mechanistic modeling of both sorption isotherms and adsorption kinetics are those of Demirbas [14], Febrianto et al. [118], Limousin et al. [119], Volesky [120] and Kratochvil and Volesky [121].

8.1. Cr(VI)

Reported results on Cr(VI) adsorption onto different lignocellulosic wastes are shown in Table 2.

8.1.1. Bagasse

Sugarcane bagasse, sawdust, sugar beet pulp and maize cob, were used as biosorbent for Cr(VI) removal [24]. Batch experiences

showed that the percentage of Cr(VI) removal decreased as the initial Cr(VI) concentration increased, suggesting that the adsorbents had a limited number of sites which became saturated above a certain concentration. The removal efficiency improved decreasing the pH due to the reduction of Cr(VI) to Cr(III). The studies also showed that Cr(III) was not adsorbed onto these sorbents and remained in solution. The adsorption data followed Langmuir and Freundlich isotherms.

A lignocellulosic agricultural waste material (bagasse) for the removal of Cr(VI) from highly saline coastal water was investigated [85]. Different products were prepared from bagasse (filaments, powder, temperature charred bagasse powder, charred bagasse powder with sulphuric acid). The maximum removal capacity was found for bagasse charred with sulphuric acid being dried bagasse powder the second most effective.

Cr adsorption onto a lignocellulosic sorbent prepared from bagasse obtained from sugarcane agro-industry was performed by Krishnani et al. [102]. Previous studies [106] had showed that Cr(VI) removal was due to the reduction of Cr(VI) to Cr(III) and that carboxylic groups acted as electron-donors. The Cr(III) ions were adsorbed onto the biosorbent by exchange process with Ca^{2+} ions. However in this study, the concentration of Cr(III) ions adsorbed was $0.442 \text{ mmol g}^{-1}$ and the Ca^{2+} ions released $0.1676 \text{ mmol g}^{-1}$. It was concluded that acidification contributed to the release of Ca^{2+} ions, and Cr(III) removal could be possible due to adsorption in other ligands.

Garg et al. [43] studied the Cr(VI) adsorption from aqueous solution onto different agricultural wastes: sugarcane bagasse, maize corn cob and Jatropha oil cake under different experimental conditions (adsorbent dose, Cr(VI) initial concentration, pH, contact time). FT-IR spectra of the adsorbents were recorded before and after the adsorption process to explore number and position of the functional groups available for binding of chromium ions. SEM studies of the adsorbents were recorded to study their morphology. Adsorption data of each system fitted Langmuir and Freundlich isotherms.

8.1.2. Bark

Eucalyptus bark was used for Cr(VI) removal from industrial waste [9,42]. Formaldehyde pretreatment of eucalyptus bark led to crosslinking of compounds in the bark to form a phenol-formaldehyde copolymer that preserved high capacity towards adsorption. The influence of the chromium concentration, pH and contact time on removal of Cr(VI) from effluent was investigated. Adsorption data fitted Freundlich isotherm. The kinetic data followed first-order Lagergren kinetic model. Thermodynamic parameters were analyzed. The ΔG° value ($-1.879 \text{ kJ mol}^{-1}$) indicated the feasibility and spontaneous nature of the adsorption process. The adsorption mechanism proposed was electrostatic interaction between HCrO_4^- species and positively surface charged groups at pH 2.0.

The ability of larch (*Larix leptolepis*) bark to remove Cr(VI) from aqueous solutions was investigated by Aoyama and Tsuda [27]. The influence of experimental conditions (pH, temperature, contact time, initial Cr(VI) concentration) was determined. Adsorption data fitted Langmuir and Freundlich isotherms. The Cr(VI) removal was governed by physico-chemical adsorption although Cr(VI) reduction could not be ignored. The positive enthalpy change value indicated the endothermic nature of adsorption process. The irreversible nature of the adsorption and the heat adsorption value suggested its chemical nature. Also, biosorption of Cr(VI) on Japane cedar (*Cryptomeria japonica*) bark was studied by Aoyama et al. [74]. In this case, the authors postulated that reduction of Cr(VI) to Cr(III) occurred extensively at solution $\text{pH} \leq 2.0$. The equilibrium data fitted Langmuir isotherm. The nature of the adsorption process was endothermic and spontaneous.

8.1.3. Biomass

Biosorption of Cr(VI) on to cone biomass of *Pinus sylvestris* was studied at different experimental conditions (pH, initial Cr(VI) concentration, agitation speed) [29]. Experimental sorption data fitted Freundlich isotherm. The Cr(VI) adsorption increased as solution pH decreased from 7.0 to 1.0. The authors postulated that the principal adsorption mechanism was electronic attraction between positively charged sites on the surface and Cr(VI) anionic species.

Thermodynamic and kinetic studies of Cr(VI) adsorption on *Thuja orientalis* cone biomass were conducted by Oguz [35]. Various isotherms were fitted to experimental data, being Freundlich and Dubinin–Radushkevich the best. The adsorption process followed pseudo-second-order kinetics. Thermodynamic parameters, ΔG° , ΔH° , ΔS° were calculated. The nature of the adsorption process was spontaneous and endothermic.

The removal of Cr(VI) from solutions using the biomass (roots and stems) of non-living *E. crassipes* as biosorbent was studied [41]. The researchers found that the pseudo-second-order kinetic model was applicable to all data and that equilibrium data followed Freundlich isotherm model. FT-IR studies on the biomass showed that the hydroxyl group was the chromium-binding site within the pH range studied (pH 1–5).

The characterization of the binding of Cr(VI) to oat biomass and subsequent reduction to Cr(III) was studied by Gardea-Torresdey et al. [76]. Batch experiments on temperature and time-dependence were performed at pH 2.0. The reduction of Cr(VI) to Cr(III) by oat biomass was confirmed using X-ray absorption spectroscopy, X-ray absorption near-edge structure (XANES) and also extended X-ray absorption fine structure (EXAFS). The studies determined which functional groups were responsible for the binding and subsequently reducing the Cr(VI) to Cr(III). EXAFS studies demonstrated that the reduced Cr(III) was bound to oxygen containing ligands, possibly carboxyl groups.

Rawajfih and Nsour [54] used reed (*Phragmites australis*) as a biosorbent for Cr(VI) removal from aqueous solution. The removal of Cr(VI) ions decreased with an increase in pH and increased with an increase in temperature. The mechanism proposed was chemisorption. Experimental data fitted Langmuir isotherm. The negative value of $\Delta G_{\text{ads}}^\circ$ indicated spontaneous adsorption of Cr(VI) on reed biosorbent and the positive ΔH° value (822 kJ kg^{-1}) confirmed the endothermic nature of the adsorption process. ΔS° value was $2205 \text{ kJ kg}^{-1} \text{ K}^{-1}$.

The Cr(VI) removal efficiency of sunflower waste adsorbent under two different process conditions (i) boiled in water and (ii) treated with formaldehyde, was investigated by Jain et al. [69]. The Cr(VI) removal efficiencies were 81.7 and 76.5% for boiled and formaldehyde treated adsorbent, respectively (4.0 g L^{-1} adsorbent dose). The applicability of Langmuir, Freundlich and Dubinin–Radushkevich isotherms was also tested. FT-IR studies confirmed the complexation of Cr(VI) with functional groups present in the adsorbents.

8.1.4. Bran

Rice bran was used for the removal of Cr(VI) from wastewater [83]. The maximum removal was 99.4% at pH 2.0 and initial Cr(VI) concentration 200 mg L^{-1} . The removal was rapid in initial stages. Mass transfer studies confirmed that the rate of mass transfer from adsorbate to adsorbent was rapid enough. Thermodynamic studies confirmed that the process was spontaneous and endothermic. Experimental data fitted Langmuir monolayer model and pseudo-first-order kinetic model. Desorption of Cr(VI) took place at pH 9.5.

Removal of Cr(VI) with a lignocellulosic substrate extracted from wheat bran was performed by Dupont and Guillon [31]. The adsorption reaction of Cr(VI) onto the substrate consumed a large

amount of H⁺ along with the reduction of Cr(VI) to Cr(III). IR spectroscopy suggested that Cr(VI) induced oxidation of only lignin components and that the retention of Cr ions occurred through a complexation reaction involving carboxylate moieties (lignin and fatty acids). The bands characteristic of carbohydrate and fatty acids units remained unaltered by the adsorption of Cr(VI). The oxidation of lignin moieties took place concurrently to the chromium reduction and lead to the formation of hydroxyl and carboxyl groups, contributing to an increase of adsorption sites for Cr(III). The results demonstrated that the adsorption reaction of Cr(VI) onto lignocellulosic substrate involved lignin moieties. The maximum adsorption capacity was about 35 mg g⁻¹ at pH 2.1. IR and XPS spectroscopy were used to identify carboxylic and phenolic moieties as the main functional groups in the lignocellulosic substrate, and EXAFS spectroscopy to characterize the structure of the sorption complex formed on the biomaterial. Dupont et al. [100] used transmission electron microscopy (TEM) coupled with energy-dispersive X-ray spectroscopy (EDXS) to determine the speciation of Cr on the lignin entities of the lignocellulosic substrate. The use of a staining agent sensitive to unsaturation (OsO₄) allowed the differentiation between microstructures rich in lignin and rich in cellulose. The EDX analysis showed that Cr was adsorbed in the microstructures rich in lignin moieties. The energy electron loss spectroscopy (EELS) was used to determine the oxidation state of Cr adsorbed in the lignin moieties. The sorption process of Cr(VI) required the reduction of Cr(VI) to Cr(III) and the probably oxidation of lignin moieties.

8.1.5. Cake

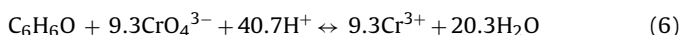
The studies on Cr(VI) removal by *Jatropha* oil cake were mentioned before [43].

The influence of pH, contact time, Cr(VI) concentration, type of adsorbent (olive cake, sawdust, pine needles, almond shells and cactus leaves) and adsorbent dose on the removal process was investigated by Dakiky et al. [58]. The adsorption process followed first-order mechanism and the rate constant was calculated at 30 °C. Each system data fitted Langmuir and Freundlich isotherms. Thermodynamic parameters such as equilibrium constant and Gibbs free energy were also evaluated for each adsorbent.

Reduction of Cr(VI) to Cr(III) using soya cake as reductive agent was performed at pH < 1.0 by Daneshvar et al. [28]. Better yields were obtained increasing temperature. The optimum time and soya cake mass were 5 h and 0.7 g, respectively. Soya cake was also used as an adsorbent for Cr(VI) at pH < 1.0. Adsorption data fitted Langmuir and Freundlich isotherms but the *R_L* value obtained (0.03) indicated that soya cake was not a very strong adsorbent for chromium.

8.1.6. Coir

Coconut coir was used as a biosorbent for Cr(VI) removal from wastewater by Gonzalez et al. [66]. The ideal pH, the sorption kinetics and sorption capacities were studied. After testing five different isotherm models, Redlich–Peterson and Toth models were the best fit for the experimental data. The sorption maximum capacity was 6.3 mg g⁻¹. Acid–base potentiometric titration indicated that around 73% of sorption sites were phenolic and lignin was the main phenolic component present in the coconut coir. FT-IR studies indicated that the sorption mechanism involved organic matter oxidation and chromium uptake. The stoichiometric relationship for complete oxidation of phenol to carbon dioxide coupled to Cr(VI) reduction to Cr(III) was represented by the following equation:



Coir pith, a waste material from padding used in mattress factories was used as an adsorbent for Cr(VI) adsorption from elec-

troplating wastewater [44]. The removal percentage depended on the adsorbent dose, contact time, temperature and pH. Cr(VI) was 99.99% adsorbed at pH 2.0. The adsorption data fitted Langmuir isotherm. The maximum adsorption capacity was 197.23 mg g⁻¹ at 30 °C and 317.65 mg g⁻¹ at 60 °C. Thermodynamic parameters indicated an endothermic process. The adsorption mechanism proposed was electrostatic attraction between negative charged HCrO₄⁻ and positive charged coir pith at low pH and also, the direct reduction of Cr(VI) to Cr(III) in the solution. However, Cr³⁺ in the solution could not be adsorbed at pH 2.0 onto coir pith due to electrostatic repulsion between Cr³⁺ ions and positive charged coir pith. Desorption studies and XANES indicated that most of the Cr bound on the coir pith was as Cr(III). The Cr(VI) adsorption on lignin extracted from coir pith confirmed that lignin was involved in the mechanism of Cr adsorption. FT-IR analysis indicated that carbonyl (C=O) and methoxy (-O-CH₃) groups bonded Cr(III) through a coordinate covalent bond (chemisorption) in which a lone pair of electrons in the oxygen atoms of the methoxy and carbonyl groups could be donated to form a shared bond with Cr(III).

Further studies [45] were performed to determine the oxidation state of chromium in coir pith after Cr(VI) adsorption from aqueous solution by using electron spin resonance (ESR). The principal components of coir pith, lignin, α-cellulose and holocellulose were extracted and Cr(VI) adsorption was conducted on them. ERS spectra of lignin confirmed Cr(III) signal, but ERS spectra of α-cellulose and holocellulose confirmed the presence of Cr(V). So, the researchers concluded than lignin reduced Cr(VI) to Cr(III) and α-cellulose and holocellulose Cr(VI) to Cr(V). The Cr(V) signal might be bound with glucose in cellulose moiety of coir pith, while xylose should be involved in the complex with the pentosan moiety. The percentages of Cr(VI), Cr(V) and Cr(III) in coir pith were 15.63, 12.89 and 71.48%, respectively.

Batch and column experiments were performed by Sumathi et al. [36] to study the Cr(VI) adsorption by sawdust, rice husks and coir pith. Experimental sorption data fitted Freundlich isotherm and sawdust was found to exhibit the higher adsorption capacity. The retention capacity was also calculated on the basis of the distribution coefficient *K_D*. The higher *K_D* was achieved with coir pith (*K_D* = 66.2) followed by sawdust (*K_D* = 32.8) at pH 3.0.

8.1.7. Husk and hull

The husk of Bengal gram (*Cicer arietinum*) was used by Ahalya et al. [34] to perform studies on Cr(VI) biosorption in batch experiments. The experimental data followed Langmuir and Freundlich isotherms; the maximum adsorption capacity was 91.64 mg g⁻¹ at pH 2.0. Results of FT-IR studies suggested that the presence of Cr(VI) in the biomass affected the bands corresponding to hydroxyl and carboxyl groups in the lignocellulosic moieties.

Tan et al. [96] investigated the removal of Cr(VI) from aqueous solutions by coconut husk fibers (CHF) and palm pressed fibers (PPF) using batch and column techniques. Batch tests showed that pH range for effective Cr(VI) removal was between 1.5 and 5 for CHF and between 1.5 and 9 for PPF. The Cr(VI) adsorption capacities of CHF and PPF were 29 and 14 mg g⁻¹ at pH 2.0. In column studies, breakthrough curves of various columns containing PPF were obtained for various flow rates and bed depths and the results were compared with Hutchin's model for adsorption column.

Removal of Cr(VI) from sea water was accomplished by 5 products prepared from coconut husk: raw coconut husk fiber, dried coconut husk fiber, dried coconut husk powder, charred (250 °C) coconut husk powder and coconut husk charred with sulphuric acid [99]. The efficiency of the materials was evaluated on the basis of the percentage of removal, the quantity of material used, the removal time and on the effect on other quality parameters. It was concluded that oven dried coconut husk powder in a concentration

6 g L^{-1} was the most effective. No mechanism was postulated or adsorption isotherm fitting was presented.

Low et al. [57] reported the removal of Cr(VI) from a synthetic solution, electroplating waste and wood preservative by quartered rice hulls using a column technique under various conditions (bed depth, flow rate, presence of SO_4^{2-} ions). Cr(VI) could be quantitatively recovered by eluting with NaOH solution. The column could be used at least 5 cycles.

Park et al. [51] studied the Cr(VI) removal efficiency by different lignocellulosic wastes such as banana skin, oak leaf, walnut shell, peanut shell and rice husk. The removal rate of Cr(VI) was banana skin > oak leaf > walnut shell > peanut shell > rice husk. Removal efficiency of total chromium by each biomaterial was not related to Cr(VI) removal rate. Banana skin completely removed 50 mg L^{-1} of Cr(VI) in 0.5 h. The removal mechanism proposed was mentioned before (Section 7.1.2). The removal rate of Cr(VI) was remarkably pH dependent, decreasing with increasing pH value. XPS analysis was employed to ascertain the oxidation state of the chromium bound on the surface of the banana skin at various pH values. Cr(III) was found bounded to the banana skin surface. Although banana skin could rapidly reduce Cr(VI) to less toxic Cr(III) it could not efficiently remove the reduced Cr(III) and thus showed poor removal efficiency for total Cr. Also, leaching of soluble organic compounds was observed during the adsorption process. These problems were solved by immobilizing the banana skin biomass within Ca-alginate bed. This new biosorbent showed very fast rate and high efficiency of Cr(VI) and total Cr removal. Mechanism of Cr(VI) biosorption was its reduction to Cr(III) through direct and/or indirect reduction reactions under acidic conditions and adsorption of Cr(III) ions at high pH values. A kinetic model was derived that described Cr(VI) and total Cr adsorption by the alginate bead adsorbent.

Krishnani et al. [49] used rice husk, a lignocellulosic waste from agro-industry for the removal of Cr(VI) from aqueous solution. The effect of time on reduction of Cr(VI) in contact with the adsorbent at pH 2.0 was investigated. The Cr(VI) concentration in solution decreased slowly and simultaneously, Cr(III) appeared in the acidic solution and also bound to the adsorbent surface. Carboxylic and hydroxyl groups present in the biomaterial might act as electron-donors. It was concluded that Cr(VI) induced oxidation of only the lignin components of the biomaterial and that the retention of Cr ions occurred through a complexation reaction involving the carboxylate moieties of lignin. Speciation of Cr loaded in the biomatrix was determined by XPS.

Cr(VI) adsorption studies by rice husk were previously mentioned [36].

Removal of Cr(VI) from aqueous solution by walnut hull was performed under different experimental conditions (pH, contact time, adsorbent dose, Cr(VI) initial concentration, temperature, and ionic strength) [56]. Adsorption data followed Langmuir and Freundlich isotherms; the maximum adsorption capacity was 98.13 mg g^{-1} at pH 1.0. The kinetic data were fitted to the first-order model, to intraparticle diffusion and Elovich models. The estimated Arrhenius activation energy indicated that the rate limiting step might be a chemically controlled process.

8.1.8. Leaves

The studies on Cr(VI) removal by cactus leaves were mentioned before [58].

Ficus religiosa leaves were reported to be a good adsorbent for Cr(VI) [64]. The sorption maximum capacity was 26.25 mg g^{-1} at pH 1.0. The sorption process followed Langmuir model. Main removal mechanism was ion exchange between metal anions and hydroxyl groups. The kinetics of the process was represented by pseudo-second-order kinetics model.

Aoyama [30] studied the removal of Cr(VI) by London plane leaves under different experimental conditions. Adsorption data fitted Langmuir isotherm. Evaluation of thermodynamic parameters confirmed the endothermic and spontaneous nature of adsorption process. Adsorption data were fitted to Lagergren equation. The adsorption mechanism postulated was chemisorption.

The studies on Cr(VI) removal by oak leaves were mentioned before [51].

The equilibrium removal of Cr(VI) by use of lignocellulosic solid wastes such as sawdust and pine leaves under different experimental conditions (pH, temperature, contact time, initial Cr(VI) concentration and particle size) was investigated [38]. The adsorption mechanism proposed was electrostatic attraction between Cr(VI) negative charged species and positively charged surface sites.

8.1.9. Sawdust

The removal of Cr(VI) by treated sawdust (*Acacia arabica*) under different experimental conditions was analyzed by Meena et al. [67]. The sawdust was treated with NaOH and H_2SO_4 to remove lignin; although other authors have shown that lignin was the main component in the adsorption process. Treated sawdust showed 100% removal capacity for solutions up to Cr(VI) initial concentration 3 mg L^{-1} in 48 h period. Adsorption data fitted Langmuir and Freundlich isotherms. The adsorption process followed first-order kinetics. It is interesting to note that the Cr(VI) removal capacity was higher at pH 6.0 although almost all other authors found that sorption capacity was higher at pH 1.0–3.0 and that above pH 3.0, the removal of Cr(VI) decreased. Ionic exchange was the mechanism proposed.

The adsorption of Cr(VI) from aqueous solutions on formaldehyde treated sawdust of Indian Rosewood, a timber industrial waste, was studied at different experimental conditions (adsorbent dose, pH, agitation time, initial Cr(VI) concentration) by Garg et al. [33]. The experimental data followed first-order kinetics Lagergren model.

Other studies on Cr(VI) removal by sawdust were mentioned before [24,38,58].

Utilization of waste material such as sawdust for the removal of Cr(VI) from industrial wastewater streams was investigated by Gupta and Babu [55]. It was reported that sawdust was better adsorbent than other low cost and commercially available adsorbents with the exception of activated carbon and bentonite clay. The maximum adsorption capacity was 41.52 mg g^{-1} at pH 1.0. The applicability of Langmuir, Freundlich, Tempki, Redlich–Peterson, Dubinin–Radushkevich and other isotherms was tested. Adsorption data fitted better Langmuir isotherm, confirming the monolayer adsorption. The adsorption process followed second-order kinetics and the corresponding rate constants were calculated. The adsorption mechanism proposed was electrostatic attraction between positively charged groups at the adsorbent surface and HCrO_4^- , the principal species at low pH value. At low pH, the reduction of Cr(VI) to Cr(III) was also possible. As the size of Cr(III) ions is small, they could easily replace positively charged ions on the sawdust surface, confirmed by the fact that the presence of Cr(III) ions in the final solution was insignificant.

Continuous adsorption experiments in a fixed-bed column for removal of Cr(VI) by sawdust were performed by Gupta and Babu [107]. The effect of flow rate, mass of adsorbent, initial Cr(VI) concentration was investigated through the breakthrough curves. The fixed bed process parameters, breakthrough time, total percentage removal of Cr(VI), adsorption exhaustion rate and fraction of unused bed were obtained. A mathematical model for fixed bed adsorption was proposed by incorporating the effect of velocity variation along the bed length in the Bautista et al. [108] model.

The proposed model was successfully validated with the literature data and the experimental data obtained. The pore diffusion and solid diffusion models were found to be suitable for explaining the breakthrough behavior of Cr(VI) removal by sawdust.

Maple sawdust was used as Cr(VI) adsorbent from aqueous solutions [59]. Effect of experimental conditions (adsorbent dose, initial metal concentration, contact time, pH) was studied. Adsorption data best fitted Freundlich isotherm. The pH dependence of adsorption suggested that Cr(VI) ions were adsorbed according to the ion-exchange mechanism and the dependence of adsorption on sorbent deacetylation indicated the chelation mechanism.

The adsorption of Cr(VI) from aqueous solution by oak (*Quercus coccifera*) sawdust modified by HCl treatment was studied by Argun et al. [63]. The optimal experimental conditions were determined (shaking speed, adsorbent mass, contact time and pH). Experimental data fitted Langmuir and Dubinin–Radushkevich isotherms. The mean adsorption energy calculated from the latter (4.26 kJ mol^{-1} , $T 293 \text{ K}$) suggested that the adsorption process was physical. Thermodynamic parameters suggested that the adsorption process was spontaneous and endothermic. Kinetic data were best modeled by a pseudo-second-order kinetics equation, and external mass transfer appeared to control the rate of adsorption. The maximum removal capacity for Cr(VI) was 84% (pH 3.0).

Thermodynamic and kinetic parameters of the Cr(VI) removal from aqueous solution by treated pine sawdust were determined by Uysal and Ar [46]. Sawdust was treated with 1,5-disodium hydrogen phosphate before adsorption experiments. The effect of different experimental conditions (pH, temperature, adsorbent dose, initial metal concentration) was investigated. Adsorption data fitted Langmuir and Freundlich isotherms and Lagergren kinetic model. The adsorption of Cr(VI) on pine sawdust was spontaneous and endothermic. The adsorption mechanism postulated was electronic attraction between positive charged sites on the adsorbent surface and Cr(VI) anionic species.

The adsorption of Cr(VI) from aqueous solution by sawdust (SD), base extracted sawdust (BESD) and tartaric acid modified sawdust (TASD) of red pine tree (*Pinus nigra*) was studied by Gode et al. [79]. Batch studies were performed at different Cr(VI) initial concentrations, adsorbent dose, modifier concentration and pH. Adsorption data fitted better Freundlich isotherm. The adsorption mechanism proposed was chelation and ion exchange. Percentage removal of Cr(VI) was higher at pH 3.0: 87.7, 70.6, and 55.2% by TASD, BESD and SD, respectively.

Polyacrylamide-grafted sawdust from rubber wood (*Hevea brasiliensis*) was effectively used for the removal of Cr(VI) from aqueous solution [25]. Experimental data fitted Freundlich isotherm and followed first-order kinetics. The percentage removal depended on experimental conditions. An empirical relationship was obtained that predicted the removal percentage with sorbent dose and initial metal concentration. The presence of diverse ions did not affect the adsorption of Cr(VI). The thermodynamic parameters showed the spontaneous and exothermic nature of the adsorption process.

Also Baral et al. [39] used sawdust as Cr(VI) biosorbent after chemical treatment with formaldehyde. Adsorption experiments were conducted by varying contact time, adsorbent dose and adsorbate concentration.

The removal of Cr(VI) by Beech (*Fagus orientalis*) sawdust was investigated by Acar and Malkoc [32]. Maximum removal (100%) was observed near pH 1.0. Removal of Cr(VI) increased with adsorbent dose. Adsorption data fitted Freundlich and Langmuir isotherm. No Cr(VI) adsorption mechanism was proposed by the authors.

The studies on Cr(VI) removal by teak sawdust were mentioned before [36].

8.1.10. Shell

Agarwal et al. [37] reported the effectiveness of low cost agro-based materials such as *Tamarindus indica* seed, coconut shell, almond shell, ground nut shell and walnut shell for Cr(VI) removal from aqueous solution. Tamarind seed showed the better Cr(VI) removal capacity. The removal capacity decreased with an increase of pH and ionic strength and increased with temperature. The authors stated that the removal mechanism was chemisorption. Sorption equilibrium fitted better Freundlich than Langmuir isotherms. Sorption kinetic data followed first-order reversible kinetic model for all tested materials.

Studies on Cr(VI) removal by almond shell were mentioned before [58].

The potential to remove Cr(VI) from aqueous solution using walnut, hazelnut and almond shells was investigated by Pehlivan and Altun [53]. Adsorption data fitted Langmuir isotherm, being the sorption maximum capacities 8.01, 8.28 and 2.40 mg g^{-1} , and the removal percentage 85.32, 88.46 and 55.0% for walnut, hazelnut and almond shells, respectively. The proposed mechanism for Cr(VI) adsorption was physical adsorption by electrostatic attraction between positively charged groups of biomaterial surface and the HCrO_4^- ion, which is the predominant species at low pH value.

Other studies on coconut, ground nut and walnut shells [37] and on walnut and peanut shells [51] were mentioned before.

8.1.11. Various

Studies on Cr(VI) removal by banana skin [51], maize cob [24], maize corn cob [43], needle pines [58] and indica seeds [37] were mentioned before.

Residual lignin from paper industry was used as a low cost material to remove Cr(VI) ions from wastewaters [17]. The optimum pH was 3.0 because at this pH, the Cr(VI) principal species was negatively charged (HCr_2O_7^-) and was able to be adsorbed to positively charged lignin surface by electrostatic attraction. Efficiency was about 90% at optimum conditions (contact time 7 h, 0.5 g adsorbent and Cr(VI) initial concentration 25 mg L^{-1}).

Pine needles, capable of removing Cr(VI) from aqueous solution were used as a new kinetic model to study the Cr(VI) removal by biomaterials [50]. Analysis of chromium species in aqueous and solid phases revealed that the removal mechanism was reduction of Cr(VI) to Cr(III). The kinetic model successfully predicted that the rate of Cr(VI) removal increased with a decrease in pH or with an increase in the temperature. A kinetic equation in the form: $-d[\text{Cr(VI)}]/dt = Ae^{E_a/RT}[\text{H}^+]^n[\text{Cr(VI)}][\text{OC}]$ was derived and successfully predicted the time-dependence of Cr(VI) concentration at various pHs and temperatures.

Malkoc et al. [40] studied the Cr(VI) removal from solution by pomace using batch and column experiments. The effect of different experimental conditions (pH, adsorbent mass, initial Cr(VI) concentration and temperature) was investigated in batch experiments. The Cr(VI) adsorption increased with temperature, with adsorbent mass and decreased with pH. Adsorption data fitted both Langmuir and Freundlich isotherms. Thermodynamic calculations showed that Cr(VI) adsorption process was endothermic and spontaneous. Column experiments showed that Cr(VI) adsorption decreased with increasing flow rate and increased with increasing inlet feed Cr(VI) concentration. Batch experiments resulted more effective.

The removal of Cr(VI) by rice straw was investigated by Gao et al. [10]. The effect of pH, initial Cr(VI) concentration, temperature, straw particle size and ionic strength was studied. The optimal initial pH was 2.0 and the Cr(VI) removal increased when Cr(VI) initial concentration and straw particle size decreased and increased when temperature increased. The studies on the effect of chemical pretreatments indicated that carboxyl groups present on the biomass took part in the Cr(VI) removal, but no mechanism was proposed. The maximum adsorption capacity was 3.15 mg g^{-1} .

Table 3
Cr(III) adsorption by lignocellulosic wastes.

Adsorbent material	Q_{\max} (mg g ⁻¹)	pH optimal	Type of study	Isotherm	Kinetic model	Mechanism proposed	Adsorbent characterization, metal speciation, functional groups	Reference
<i>Biomass</i> Alfalfa						Binding through carboxyl groups Ion exchange	FT-IR, EXAFS, XANES	Gardea-Torresdey et al. [86] Romero-Gonzalez et al. [88]
<i>Agave lechuguilla</i>	11.31	4.0	E, T	L, F				Bernardo et al. [101]
<i>Agave bagasse</i>	11.44	4.0	E, T	L, F		Ion exchange and complexation	ATR-FT-IR	Bernardo et al. [101]
<i>Husk</i> Peanut husk modified <i>Sawdust</i> Meranti	7.67	4.0	E, K	L, F	Pseudo-second order		FT-IR	Li et al. [78]
Poplar tree	37.88	6.0	E, K	L, F, D–R	Pseudo-second order	Ion exchange	FT-IR, SEM	Rafatullaha et al. [90]
Sawdust grafted poly(methacrylic acid)	5.52	4.0	E, K	L, F	Pseudo-second order		FT-IR	Li et al. [78]
Spruce	36.63	7.0	E, K	L, F, T	Pseudo-second order	Electrostatic attraction	FT-IR	Anirudhan and Radhakrishnan [77]
	0.30	7.0	E, K, T	L, F, D–R	Lagergren first-order model, intraparticle diffusion			Ahmad [71]
<i>Straw</i> Sorghum	6.96	4.0	E, T	L, F		Ion exchange and complexation	ATR-FT-IR	Bernardo et al. [101]
Oats	12.97	4.0	E, T	L, F		Ion exchange and complexation	ATR-FT-IR	Bernardo et al. [101]
<i>Various</i> Lignin from black liquor	17.97	5.0	E, K	L	Pseudo-second order, mass transfer, intraparticle diffusion	Ion exchange		Wu et al. [89]
Lignin from wheat straw			E			Inner-sphere surface complexes	XRD, TEM-EDX, EPR, XANES, EXAFS	Flogeac et al. [75]
Sunflower stem	6.24	3.0	E, K, T	L, F, D–R	Lagergren first-order model, intraparticle diffusion	Ion exchange		Malik et al. [72]

E: equilibrium; K: kinetic; D: dynamic; T: thermodynamic.

L: Langmuir; F: Freundlich; T: Tempkin; D–R: Dubinin–Radushkevich isotherms.

X-ray diffraction (XRD); scanning electron microscopy (SEM); X-ray absorption near-edge structure (XANES); extended X-ray absorption fine structure spectroscopy (EXAFS); transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (TEM-EDX); infrared spectroscopy (IR); Fourier transform infrared spectroscopy (FT-IR); attenuated total reflection Fourier transform infrared (ATR-FT-IR).

Cr adsorption onto a lignocellulosic sorbent prepared from paddy straw was carried out by Krishnani et al. [103]. The biosorbent was characterized by SEM technique. XPS analysis was used to determine the presence of exchangeable cations in the sorbent and to determine the Cr speciation in the agrowaste. Interpretation of Dahlquist [104] and Scatchard [105] models confirmed binding site heterogeneity, due to the fact that the plot Q_e/C_e vs Q_e was a concave curve instead of a straight one. A concave curve indicated the presence of two different types of binding sites and also indicated negative cooperativity between strong and weak binding sites. It was found that reduction of Cr(VI) to Cr(III) was higher at pH 2 and involved the lignin moieties as electron-donors. Previous studies [106] had showed that Cr(III) ions were adsorbed onto the biosorbent via an ion-exchange mechanism with Ca^{2+} , but Krishnani et al. [103] found that Ca^{2+} was only partly involved in the ion-exchange mechanism with Cr(III) ions as the concentration of Ca^{2+} ions released ($0.484 \text{ mmol g}^{-1}$) was lower than the concentration of Cr(III) ions adsorbed ($0.112 \text{ mmol g}^{-1}$) after 2 h.

The studies on Cr(VI) adsorption by different lignocellulosic materials reported before showed that the adsorption data followed the usual isotherms and mainly first-order kinetics. The optimal adsorption pH was in the acidic range. The adsorption process was spontaneous and endothermic and the adsorption mechanism reported was electrostatic attraction (51% of the studies) and/or Cr(VI) reduction to Cr(III) (40% of the studies). Lignin was the main component involved in the adsorption process, mainly through carboxyl groups, methoxy and/or carbonyl groups acting as electron-donors.

8.2. Cr(III)

Reported results on Cr(III) adsorption onto lignocellulosic wastes are shown in Table 3.

8.2.1. Biomass

Alfalfa biomass was used as a biosorbent for Cr(III) removal from contaminated waters [86]. The aim of the researchers was to determine the mechanism through which Cr(III) binds to alfalfa biomass. Studies were conducted to determine how modification (esterification, hydrolysis) of chemical groups present on the alfalfa biomass affected the Cr(III) binding. A comparison with ion exchange resins containing different functional groups was also performed. Results confirmed that Cr(III) was bound through carboxyl ligands similar to a carboxyl resin. FT-IR analysis showed that Cr(III) coordination with carboxyl ligands was through a bridging bidentate complex. XAS studies confirmed the previous results.

Romero-Gonzalez et al. [88] performed thermodynamic studies on the Cr(III) removal by *Agave lechuguilla* biomass from aqueous solution. Experimental adsorption data fitted both Langmuir and Freundlich isotherms. Thermodynamic parameters suggested the spontaneous and endothermic nature of adsorption process. The E_a value ($10.20\text{--}14.74 \text{ kJ mol}^{-1}$) supported the idea that the sorption of Cr(III) into *lechuguilla* biomass might proceed through and ion exchange reaction via carboxyl groups located on the surface of the bioadsorbent.

The use of sorghum straw (*S. bicolor*), oats straw (*A. sativa*) and agave bagasse for Cr(III) removal from aqueous solution was reported by Bernardo et al. [101]. Attenuated total reflection Fourier transform infrared analysis (ATR-FT-IR) was used to identify the surface groups in the agrowastes materials. Carboxyl and hydroxyl groups were capable of binding Cr(III) from aqueous solution. Agave bagasse presented higher sorption capacity at pH 4. At pH 3, the adsorption capacity diminished due to H^+ competition with Cr(III) ions. The adsorption process was probably endothermic, although ΔH° was not calculated. The partially saturated agrowastes materials could be efficiently regenerated by an EDTA solution at 55°C .

The adsorption/desorption experiments allowed to infer that the possible Cr(III) sorption mechanism onto agrowastes materials was ion exchange and complexation.

8.2.2. Husk

Sawdust from poplar tree and modified peanut husk were used as Cr(III) adsorbents [78]. Three kinetic models were tested, intraparticle diffusion, Lagergren first-order and second-order models. The experimental data best fitted second-order model, being adsorption the rate limiting step. Also, experimental data fitted Langmuir and Freundlich isotherm. No adsorption mechanism was proposed.

8.2.3. Sawdust

Sawdust from meranti was used as adsorbent for Cr(III) removal from aqueous solution [90]. The effect of contact time, initial metal concentration, pH, temperature and adsorbent dose was studied. The adsorption kinetics followed pseudo-second-order kinetic model and the rate controlling step was mainly intraparticle diffusion. Adsorption data fitted Langmuir and Dubinin–Radushkevich isotherms.

The adsorption of Cr(III) by poplar tree husk was mentioned already [78].

Cr(III) was removed from wastewater using a cation exchanger prepared through graft copolymerization of methacrylic acid on sawdust [77]. The effect of experimental conditions (pH, contact time, adsorbent dose, metal initial concentration and temperature) on the adsorption process was studied. The maximum Cr(III) removal was observed at initial pH 7.0. Kinetic data fitted the pseudo-second-order rate expression. The experimental adsorption data fitted Langmuir isotherm. The maximum adsorption capacity was 36.63 mg g^{-1} . The adsorption mechanism proposed was electrostatic attraction of chromium main species $\text{Cr}(\text{OH})_2^+$ and the negatively charged adsorbent surface at $\text{pH} > 5.2$.

Cr(III) ions sorption onto sawdust of spruce (*Picea smithiana*) was studied using radiotracer technique by Ahmad [71]. The results showed that the sorption of Cr(III) ions followed Reichenberg, Morris–Webber and Lagergren kinetic models. Data fitted Freundlich and Dubinin–Radushkevich isotherms over entire range of concentration and Langmuir isotherm at lower concentrations. The thermodynamic parameters calculated showed the spontaneous and exothermic nature of the adsorption process. The sawdust column could be used to separate Cr(III) ion from Cs(I), I(I), Tc(VII) and Se(IV). The presence of Y(III), Ce(II) and Ca(II) reduced the Cr(III) sorption capacity, and also the sorption capacity was decreased by the presence of anions such as oxalate, citrate, carbonate and borate.

8.2.4. Straw

The studies on removal of Cr(III) by sorghum straw (*S. bicolor*), oats straw (*A. sativa*) performed by Bernardo et al. [101] were mentioned before.

8.2.5. Various

The adsorption of Cr(III) on lignin isolated from black liquor, a waste product of paper industry, was studied by Wu et al. [89] under different experimental conditions. The pH dependence of adsorption indicated that the adsorption mechanism was ionic exchange, and the independence of adsorption on ionic strength suggested that Cr(III) formed inner-sphere complexes with lignin. Equilibrium data fitted Langmuir two-surface isotherm. The adsorption process followed pseudo-second-order kinetics.

Flogeac et al. [75] studied the binding ability of Cr(III) into a lignocellulosic substrate extracted from wheat straw. The adsorbent was characterized using XRD and TEM-EDX. The effect of

Table 4
Cr(VI) and Cr(III) adsorption by lignocellulosic wastes.

Adsorbent material	Q_{\max} (mg g ⁻¹)		pH optimal		Type of study	Isotherm	Kinetic model	Mechanism proposed	Adsorbent characterization, metal speciation, functional groups	Reference
	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)						
<i>Biomass</i>										
<i>Agave lechuguilla</i>	33.55	63.69	2.0	4.0	E, K	L, F	Pseudo-second order	Cr(VI) reduction to Cr(III) Electrostatic attraction	IR	Romero-Gonzalez et al. [61] Li et al. [70]
Herb (<i>Leersia hexandra</i>)	2.51	28.64	2.0	5.0	E, K	L	Pseudo-second order			
<i>Cassia fistula</i>	121.95	107.50	2.0	5.0	E, K	L, F	Pseudo-second order	Electrostatic attraction		Abbas et al. [65]
<i>Cassia fistula</i> (pretreated)	131.50	114.90	2.0	5.0	E, K	L, F	Pseudo-second order	Electrostatic attraction		Abbas et al. [65]
<i>Citrus reticulata</i>	263.15	232.50	2.0	5.0	E, K	L, F	Pseudo-second order	Electrostatic attraction	EXAFS, XANES SEM, EDX, IR, TGA	Zubair et al. [68] Parsons et al. [84] Barrera et al. [73]
Hops								Cr(VI) reduction to Cr(III)		
<i>Opuntia ectodermis</i>	6.22	11.72	4.0	4.0	E	L, F		Electrostatic attraction and/or reduction Cr(VI) to Cr(III)		
<i>Various</i>										
Aquatic weeds	8.87	6.07–7.19	4.5–5.5	4.5–5.5	E, K	L, F	Pseudo-second order	Cr(VI) reduction to Cr(III)	FT-IR	Elangovan et al. [48] Cimino et al. [26]
Hazelnut shell	17.70	3.08	<3.0	4.0	E	L, F		Electrostatic attraction and/or reduction Cr(VI) to Cr(III)		
Lignin	5.64	6.59	<2.0	>3.0	E, K	L	Second order	Electrostatic attraction		Lalvani et al. [21]
Modified lignin from wood sawdust	7.60	23.60	2.0	4.5–5.5	E	L		electrostatic attraction		Demirbas [82]
Palm flower	4.90	5.99	4.5	4.5	E, D, K	L, F, R–P, T, etc.	Pseudo-second order; intraparticle diffusion	Cr(V) reduction to Cr(III)	FT-IR	Elangovan et al. [47]
Palm flower pretreated	7.13	1.41	4.5	4.5	E, D, K	L, F, R–P, T, etc.	Pseudo-second-order; intraparticle diffusion	Cr(V) reduction to Cr(III)	FT-IR	Elangovan et al. [47]
Rice bran			2.0	5.0	E, K, T	F	Pseudo-second-order; intraparticle diffusion			Oliveira et al. [60]
Saltbush leaves	10.92	99.84	2.0	5.0	E, T	L, F		Ionic exchange		Sawalha et al. [62]

E: equilibrium; K: kinetic; D: dynamic; T: thermodynamic.

L: Langmuir; F: Freundlich; T: Tempkin; R–P: Redlich–Peterson isotherms.

X-ray diffraction (XRD); scanning electron microscopy (SEM); X-ray absorption near-edge structure (XANES); extended X-ray absorption fine structure spectroscopy (EXAFS); infrared spectroscopy (IR); Fourier transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA).

experimental conditions (pH, contact time, metal initial concentration) was analyzed. Depending on experimental conditions, adsorption, co-precipitation and precipitation were able to occur. The speciation of Cr was also investigated by EPR, EXAFS, and XANES, revealing that Cr(III) surface complexes had an octahedral geometry. Chromium ions were held in inner-sphere complexes, coordinated to six oxygen atoms.

Malik et al. [72] used Cr radiotracer technique to study the adsorption potential of sunflower stem for Cr(III) ions. The maximum adsorption capacity (85%) was achieved from 0.001 M HNO₃ solution; the dominant species of Cr(III) present in this acidic solution (pH 3) were Cr³⁺ (95%) and Cr(OH)²⁺ (5%). The adsorption process followed Reichenberg and Lagergren kinetic model over the entire contact time studied. Sorption data fitted Dubinin–Radushkevich, Freundlich and Langmuir isotherms. Bisulphate, citrate, molybdate, Fe(II), Fe(III) and Y(III) decreased the sorption capacity. The thermodynamic parameters showed that the process was spontaneous and exothermic.

The studies on Cr(III) adsorption by different lignocellulosic materials reported before showed that the adsorption data followed the usual isotherms and mainly pseudo-second-order kinetics. The adsorption mechanism was electrostatic attraction and the optimal adsorption pH was >4.0.

8.3. Cr(VI) and Cr(III)

Reported results on Cr(VI) and Cr(III) adsorption onto lignocellulosic wastes are shown in Table 4. It is important to note that Cr(VI) and Cr(III) adsorption by different adsorbent materials were performed in different set of experiments.

8.3.1. Biomass

Romero-Gonzalez et al. [61] investigated the adsorption of Cr(VI) and Cr(III) onto *A. lechuguilla* biomass. Batch experiments determined that pH 4.0 and 2.0 were optimum for Cr(III) and Cr(VI) adsorption, respectively. The adsorption of Cr(VI) was time dependent and followed pseudo-second-order kinetic model but adsorption of Cr(III) was not time dependent. Cr(VI) adsorption followed Freundlich isotherm and Cr(III) Langmuir one. The authors proposed an electrostatic surface binding model.

The biosorption properties of the plant *Leersia hexandra* biomass was analyzed for Cr(VI) and Cr(III) ions by Li et al. [70]. The IR results indicated that the binding process of the chromium ions involved the active participation of functional groups present in the biomass surface, Cr(VI) was mainly complexed with amino groups and Cr(III) with carboxyl and amide functional groups. Adsorption data fitted Langmuir and Freundlich equations. The adsorption process was rapid and followed the pseudo-second-order kinetic model.

Cassia fistula (an ornamental tree) biomass untreated and pretreated was used for the sorption of Cr(VI) and Cr(III) [65]. *C. fistula* biomass was pretreated physically by heating, autoclaving, boiling and chemically with sodium hydroxide, formaldehyde, gluteraldehyde, benzene, acetic acid, hydrogen peroxide, commercial detergent, orthophosphoric, sulphuric, nitric and hydrochloric acids. Gluteraldehyde and benzene improved significantly the adsorption capacity, which depended on pH, initial metal concentration, sorbent dose, and temperature. The adsorption mechanism proposed was electrostatic attraction as previously reported by other authors. Experimental data fitted better Langmuir isotherm. The kinetic studies showed that sorption rates were better described by a second-order model.

In a similar way, *Citrus reticulata* waste biomass was used for Cr(VI) and Cr(III) removal from aqueous solutions as a raw material and after physical and chemical (acid and base) treatment [68]. The effect of pH, biosorbent dosage, particle size, initial metal concentration, temperature, shaking speed and sorption time was

determined. Adsorption data fitted Freundlich isotherm and the pseudo-second-order kinetic model for Cr(III) and Cr(VI).

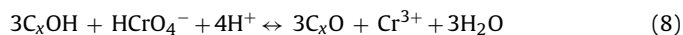
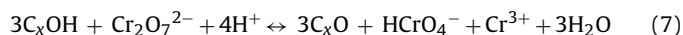
The binding mechanism of Cr(VI) and Cr(III) to hops biomass was investigated by XAS spectroscopy [84]. Results showed that Cr(III) remained in the same oxidation state when it reacted to hops biomass. However the reaction of Cr(VI) with hops biomass resulted in the reduction of Cr(VI) to Cr(III). Analysis of the XAS spectra (XANES and EXAFS) showed that Cr(III) and Cr(VI) were bound to the biomass through oxygen atoms. The Cr(III) was bound to the biomass with a molecular geometry that matched that of Cr(III) acetate.

Barrera et al. [73] used *Opuntia* ectodermis for Cr(III) and Cr(VI) removal from aqueous solution. The authors reported that at pH 4.0, the principal Cr(VI) anionic species were HCrO₄⁻ (80%) and Cr₂O₇²⁻ (20%). They were adsorbed by electrostatic attraction to the sorbent surface which was positively charged due to protonation. They also proposed the reduction of Cr(VI) to Cr(III) under acidic conditions, as above described. In the case of Cr(III), at pH values below 4.0, the main species was Cr³⁺. The hydroxyl groups of cellulose were responsible of metal binding between Cr³⁺ and 3 vicinal cellulosic OH groups. Experimental sorption data correlated with Langmuir model. SEM analysis indicated that the Cr sorption took place on the surface of the biomass. EDX analysis confirmed the Cr presence after biomass contact with Cr solutions.

8.3.2. Various

Elangovan et al. [48] studied the Cr(VI) and Cr(III) removal from aqueous solutions by different aquatic weeds as biosorbents (reed mat (*Cannomois Vvirgata*), water lettuce (*Pistia stratiotes*), arrow-leaved tear thumb (*Polygonum sagittatum*), lotus flower (*Nelumbo nucifera*), green taro (*Colocasia esculenta*), water lilyflower (*Nymphaea* sp.), water hyacinth (*E. crassipes*), and mangrove leaves (*Rhizophora mangle* L.)). Batch kinetic and equilibrium experiments were performed to determine the adsorption rate and adsorption capacities of the biosorbents. Reed mat showed maximum Cr(III) adsorption capacity and mangrove leaves maximum Cr(VI) adsorption capacity. Adsorption followed second-order kinetics. The adsorption mechanism proposed after the FT-IR studies was reduction of Cr(VI) to Cr(III) by tannin, phenolic compounds and other functional groups on the sorbent surfaces and subsequently adsorption.

Removal of Cr(III) and Cr(VI) from aqueous solutions using hazelnut shell as biosorbent substrate was performed by Cimino et al. [26]. The authors reported good fit of adsorption data to Langmuir and Freundlich isotherms, being the maximum sorption capacity 3.08 mg g⁻¹ for Cr(III) at pH 4.0. Hazelnut shell also showed effective capacity for Cr(VI) removal within the limits of a short acid pH interval: 2.5–3.5 where the reduction reactions of Cr(VI) and the sorption process of Cr³⁺, HCrO₄⁻ and CrO₄²⁻ ion species were maximized. In the presence of a reducing substrate (C_xOH), the following reactions took place:



According to the above equations only the acid chromate ion species could be sorbed on the protonated active sites of the biosorbent surface following Eq. (7) and Cr³⁺ ions remained not sorbed at these low pH values:



On the whole, the results were a low removal of total chromium but an almost total reductive removal of Cr(VI). The maximum Cr(VI) sorption capacity was 17.7 mg g⁻¹ at pH 2.0.

A commercially available lignin was used for the removal of Cr(VI) and Cr(III) from aqueous solution by Lalvani et al. [21]. It

was found that lignin could remove up to 63% of Cr(VI) present as anionic species in the solution at pH 2.0. The mechanism proposed was adsorption due to electrostatic attraction between anionic Cr(VI) species and positively charged sites in lignin surface. Lignin removed 100% of Cr(III) at pH > 4.0 due to electrostatic attraction between Cr³⁺ species and negatively charged sites on lignin surface.

The Cr(VI) and Cr(III) removal from aqueous solutions by modified lignin from wood sawdust was studied by Demirbas [82]. Modified lignin was obtained by HCl precipitation of the sulphate pulping waste material (black liquor). The Cr(III) adsorption increased as pH increased from 2.0 to 6.0, with optimum adsorption between pH 4.5 and 5.5. Above pH 4.0, the carboxyl groups were deprotonated and able to adsorb Cr³⁺ species. CrO₄²⁻, HCrO₄⁻ and Cr₂O₇²⁻ species adsorption was unlikely at these pH values. The maximum adsorption capacities were 7.6 and 23.6 mg g⁻¹ for Cr(VI) and Cr(III), respectively at 330 K, and increased to 9.3 and 15 mg g⁻¹ when temperature decreased to 290 K.

Elangovan et al. [47] studied the Cr(VI) and Cr(III) sorption from aqueous phase by palm flower (*Borassus aethiopicum*). Both, Cr(VI) and Cr(III) followed second-order kinetics. The maximum Cr(III) adsorption capacity was 6.24 mg g⁻¹, but acid treatment of the adsorbent lowered it to 1.41 mg g⁻¹. In the case of Cr(VI), the adsorption capacities were 4.9 and 7.13 mg g⁻¹ for raw and acid treated biomass, respectively. The Cr(VI) adsorption mechanism proposed was reduction of Cr(VI) to Cr(III) by tannin and phenolic compounds and subsequent adsorption on the biomass. Alkali pretreatment of the biomass reduced the adsorption capacities for both Cr(VI) and Cr(III). Adsorption equilibrium data fitted well with most of the well-known models.

The capacity of raw rice bran for Cr(VI) and Cr(III) removal from aqueous solution was investigated [60]. Sorption experimental data fitted Freundlich isotherm model. The kinetics data followed pseudo-second-order model. ΔG° values were calculated and it was found that Cr(III) adsorption was spontaneous but Cr(VI) adsorption was not favorable. However, the authors postulated that Cr(VI) species were adsorbed due to the strong interactions with the active sites of the sorbent.

The results of the study by Sawalha et al. [62] on biosorption of Cr(VI) and Cr(III) onto saltbush leaves biomass (*Atriplex canescens*) showed that adsorption data fitted both Freundlich and Langmuir isotherms and the maximum adsorption capacity was higher for Cr(III) (1.06 mmol g⁻¹) than for Cr(VI) (0.21 mmol g⁻¹). Thermodynamic parameters showed that adsorption process was spontaneous for Cr(III) but non-spontaneous for Cr(VI). The mean free energy calculated suggested that the adsorption mechanism was ionic exchange.

9. Conclusions

In recent years, increasing costs and environmental considerations have led to the use of new low cost adsorbents derived from renewable resources. More than 100 papers on Cr removal from aqueous solution by adsorption onto lignocellulosic wastes were discussed in this review in order to provide recent information on the remediation process. Previous studies have shown that lignocellulosic wastes are comparable to sorbents from other natural sources, but have advantages derived from their great availability, very low cost and simple operational process [4,7]. Performance comparison of different low cost adsorbents is difficult because of inconsistencies in data, principally due to different experimental conditions (pH, temperature, ionic strength, particle size, presence of competing ions, etc.). Cost information of low cost adsorbents is seldom reported in the publications

because it depends on local availability and on the technology applied.

As shown in Tables 2–4, Cr(VI) maximum adsorption capacity ranged from 0.20 mg g⁻¹ by sawdust [38] to 285.71 mg g⁻¹ by rice bran [83] and Cr(III) maximum adsorption capacity ranged from 0.30 mg g⁻¹ by spruce sawdust [71] to 232.50 mg g⁻¹ by *C. reticulata* biomass [68]. It is important to note that some of the results shown in Tables 2–4 may be incorrect, as some researchers determined total Cr in aqueous solution by AAS or ICP and reported it as Cr(VI) not considering the Cr(VI) reduction to Cr(III) at low pH values.

Experimental data were fitted to several isotherms, Langmuir and Freundlich models were the most used in the studies reported here. Experimental data followed pseudo-first-order and pseudo-second-order kinetic models in most of the reported studies.

The adsorption mechanism of Cr(VI) and Cr(III) on lignocellulosic wastes was discussed in most of the papers. Nowadays the “adsorption-coupled reduction” mechanism is truly accepted as the true mechanism of Cr(VI) biosorption by natural lignocellulosic and other biomaterials under acidic conditions [50–52]. The reduction of Cr(VI) into lignocellulosic substrate clearly involves lignin moieties, mainly through carboxyl groups or methoxy and carbonyl groups as electron-donors [31,44,45,49,103]. Spectroscopic analyses were carried on in a great number of studies in order to have a better understanding of the mechanism of Cr adsorption onto the lignocellulosic materials. IR, FT-IR techniques were used for the determination of the functional groups in the lignocellulosic materials and XPS, XANES, EXAFS, ESR and EELS to determinate the oxidation state of chromium bound on the biomaterial.

The studies on Cr(III) adsorption by different lignocellulosic materials reported before showed that the adsorption mechanism was electrostatic attraction and the optimal adsorption pH was >4.0. Cr(III) adsorption was almost negligible at pH < 2.0. At a pH higher than the pK_a (~3.5), carboxylic groups were negatively charged and Cr³⁺ ion was bound to negative charged groups by electrostatic attraction. At pH lower than pK_a, functional groups were protonated, and metal uptake decreased.

In general, raw lignocellulosic biosorbents can be modified by various methods to increase their sorption capacities because the Cr binding to the surface of these materials takes place through chemical groups such as hydroxyl, carboxyl, amino or phenol by electronic attraction or as it is nowadays believed, through the presence of electron-donor functional groups that take part in the reduction of Cr(VI) to Cr(III). Although chemically modified plant wastes may enhance Cr adsorption, the cost of chemicals and technologies used have to be taken into consideration in order to produce ‘low-cost’ adsorbents.

The biomaterials reported in this review were able to completely remove toxic Cr(VI) under low pH conditions but most of the studies were limited to an initial evaluation of the adsorption capacity. More studies are needed to transfer the process to pilot-plant scale and industrial scale.

As mentioned by Park et al. [51] some problems that need to be resolved are: the slow rate of Cr(VI) reduction by biomaterials compared with chemical reductants; the soluble organic products that are released during biosorption and must be eliminated (this can be accomplished by immobilizing the biomass within Ca-alginate bed [51]); and the fact that not only Cr(VI) but Cr(III) must be removed being the best removal conditions for each other different (the removal efficiency for Cr(VI) increases with the decrease of pH, and the removal efficiency for Cr(III) increases with the increase of pH).

This review of recent literature shows that lignocellulosic wastes can offer an effective and economic alternative to more expensive treatments for the removal of Cr(VI) from wastewaters, due to their high adsorption capacity, abundance and low cost.

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