Removal of Toxicant Chromium (VI) from Aqueous Solution Using Different Adsorbents

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Summary: The presence of Cr (VI) in aqueous solution, particularly waste water and its detrimental effect to human and aquatic organisms has led to the search for more readily available low cost adsorbents. Chromium is one of the main contaminants in the environment which originates from industries and it is known to be carcinogenic or mutagenic to man and aquatic organism, hence its removal becomes inevitable. This review paper discusses the use of agricultural wastes, synthetic materials and aquatic organisms as adsorbents for the removal of Cr (VI) from aqueous solution. Among other factors, it was noted that the adsorption of the Cr (VI) onto these adsorbents is largely influenced by the pore size of the adsorbent and the pH of the solution. Conclusively, there is need for more research on other inexpensive and readily available adsorbents for the removal of Cr (VI) from the environment.

Keywords: Adsorbent, Waste water, Agricultural waste, Heavy metals, Synthetic materials.

Introduction

Chromium is a redox-active element with oxidation states from −2 to +6, but only the +3 and +6 states are prevalent in the aqueous phase. The two environmentally stable oxidation states, Cr (III) and Cr (VI), exhibits great difference in toxicities and mobilities. Cr (III) is relatively insoluble in aqueous systems (above pH 5) and exhibits little or no toxicity. In contrast, Cr (VI) usually occurs as highly soluble and highly toxic chromate anions ($HCrO^{4-}$ or $Cr2O_7^{2-}$) [1]. The tanning process is one of the major sources of chromium pollution at global scale. In the chromium tanning process, the leather takes up only 60–80 % of applied chromium, and the rest is usually discharged into the wastewaters causing serious environmental impact. Chromium ion in liquid tanning wastes occurs mainly in trivalent form, which gets further oxidized to hexavalent form [2, 3]. The maximum levels permitted for trivalent and hexavalent chromium in wastewater is 5 mg/l and 0.05 mg/l respectively [4].

The removal of toxic heavy metals from industrial wastewaters using conventional chemical approaches such as oxidation, reduction and chemical precipitation, among others, proves to be costly. These processes require large quantities of reagents and result in the production of considerable amounts of toxic sludge and secondary pollutants, thereby affecting the sustainability of these technologies. Operational costs for the treatment of wastewater treatment processes increase for waste streams with complex characteristics like complex organic matters and relatively low metal concentrations [5]. Adsorption has evolved as the front line of defense for chromium removal. Selective adsorption by biological materials, mineral oxides, activated carbons, or polymer resins has generated increasing excitement [6-15]. Among these heavy metals, chromium is one of the priority contaminants in the environment, which originates from the emissions from industrial process including electroplating, pigment, metal cleaning, leather processing and mining [16]. There are various methods for removing heavy metals, these includes chemical precipitation, membrane filtration, ion exchange, liquid extraction or electro dialysis, reverse osmosis [17, 18]. Production of commercial activated carbon is still an expensive process. Therefore a search for a more cost effective adsorbent material is of immense interest in waste water treatment. Recently, utilizing agricultural by-product, synthetic material and aquatic organism for fabrication of adsorbent for the removal of heavy metal has been reported [19-30].

The conventional chromium treatment method consists of four steps: reduction of Cr (VI) – Cr (III), precipitation of Cr (III) as $Cr(OH)_3$ at high pH, settling of the insoluble metal hydroxide, disposal of the dewatered sludge. As a result of the shortcomings of conventional treatment methods such as the high cost of sludge disposal, expensive chemicals necessary for Cr (VI) reduction and incomplete reduction of Cr (VI), adsorption processes are considered to be the most appropriate method [31]. A number of low cost adsorbents have been

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used earlier for the removal of toxic pollutants from waste waters [32-37]. Using different low cost and readily available absorbent in substitute for the expensive commercially activated carbon for the removal of Cr (VI) in the environment is the main priority in this review paper.

Effect of Chromium to Man and Aquatic Organisms

Chromium was discovered in 1797 by the French chemist Louis Vauquelin. It was named chromium (Greek chroma, "color") because of the many different colors found in its compounds [38]. Cr (III) is the most thermodynamically stable oxidation state; under reducing conditions Cr (VI) can remain stable for significant periods of time [39]. Chromium has both beneficial and detrimental properties. Cr (VI) occurs as highly soluble and toxic chromate anions ($HCrO^{4-}$ or $Cr_2O_7^{2-}$), which causes epigastric pain, nausea, vomiting, severe diarrhea, hemorrhaging and is suspected to be carcinogens and mutagens [40-42]. It is also considered powerful agent that modifies DNA transcription process causing important chromosomic aberration [43, 44]. Chromium has adverse effects on aquatic species as it accumulates in fish tissues and causes reduction in fish production at higher concentration [45, 46]. Trivalent chromium is an essential element in humans and is much less toxic than the hexavalent one, but due to its possible oxidation to the harmful Cr (VI), environmental regulations usually define limiting values for both [47], the hexavalent form is 500 times more toxic than the trivalent form [48]. It is highly mobile in soil and aquatic system and also a strong oxidant capable of being absorbed by the skin [49]. Human toxicity includes lung cancer, as well as kidney, liver, and gastric damage [50].

Industrial processes that produce aqueous effluents rich in chromium and other heavy metals are given in Table-1 [51]. Chromium compounds are widely used in electroplating, metal finishing, magnetic tapes, pigments, leather tanning, wood protection, chemical manufacturing, brass, electrical and electronic equipment. Table-2 [52], gives the summary of the total quantity of contaminant released to the environment (air, soil and water).

Agricultural Waste used as Adsorbent for Cr (VI) Removal from Aqueous Solution

Helianthus annuus

The efficiency of Cr (VI) removal using sunflower waste from aqueous system under different process conditions was investigated by Jain and co-worker [53].Two adsorbents were prepared by pre-treating the sunflower stem waste. The first adsorbent was prepared by boiling it while the second was prepared by treating it with formaldehyde. Batch mode experiments were carried out as a function of solution pH, adsorbent dosage, Cr (VI) concentration and contact time. FT-IR spectra and SEMs of the adsorbents were recorded to explore the number and position of functional groups available for the binding of Cr (VI) ions and morphology of the adsorbents studied. The removal of chromium was dependent on the physicochemical characteristics of the adsorbent, adsorbate concentration and other process parameters. Maximum metal removal was observed at pH 2.0. The results obtained in this study fitted the Langmuir isotherm than Freundlich (Table-3) and D–R adsorption isotherms. Their result shows that there is a little difference in the adsorption capacity of BSS (pre-boiled sunflower stem) and FSS (formaldehyde treated sun flower stem) at equilibrium time. A list showing the adsorption capacity of different adsorbents for the adsorption of hexavalent chromium from aqueous solutions is given in Table-4, where it is observed that the adsorption capacity of sunflower stem waste for hexavalent chromium is comparable with other low-cost adsorbents [53].

Table-1: Industrial processes that produce aqueous effluents rich in chromium and other heavy metals [51].

Industry Source	Al	Zn	As	Sn	Ag	Sb	Cd	Cr	Cu	Fe	Hg	Mn	Pb	Ni	Bi
Automobile		X		X			X	X		X			X	X	
Petroleum Refining		X	X					X	X	X			X	X	
Pulp and Paper		X						X	X		X		X	X	
Textile								X							
Steel		X	X			X	X	X		X			X	X	
Organic Chemicals	X	X	X	X			X	X		X	X		X		
Inorganic Chemicals	X	X	X				X	X		X	X		X		
Fertilizers	X	X	X				X	X	X	X	X	X	X	X	
Plastic and Synthetics										X					
Leather tanning and Finishing								X							
Steel Power Plants		X						X							
Mining			X				X		X		X	X	X		
Acid mine drainage	X	X							X	X		X			
Metal Plating		X					X	X	X						
Glass			X												
Nuclear Power															X
Coal and gasoline											X		X		X

X- Present; Blank: Absent

Table-2: Global discharge of trace metals (1000 metric tonnes/year) [52].

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

Table-3: Langmuir, Freundlich and D–R parameters for BSS and FSS for Cr (VI) removal [53].

Adsorbent	Langmuir parameters			Freundlich parameters			D–R parameters			
	Q_0 (mg/g)	b (l/mg)	R^2	K_f (mg/g)	n	R^2	q_D (mg/g)	B_D (mol^2/kJ^2)	E_D (kJ/mol)	R^2
BSS	5.37	0.109	0.934	0.86	1.78	0.617	5.8	0.27	1.37	0.9779
FSS	4.81	0.071	0.808	0.562	2.0	1.0	3.9	0.17	1.70	0.8308

Table-4: Adsorption capacity of different adsorbents for Cr (VI).

Adsorbent	Optimum dose (g/L)	Initial concentration (mg/L)	Optimum pH	q_e (mg/g)	Ref.
Hazelnut shell	2.5	1000	1.0	170	[54]
Almond shell	2.4	100	2.0	10.62	[55]
Saw dust	2.4	100	2.0	15.82	[55]
Wool	2.4	100	2.0	41.15	[55]
Maple waste	50	10	5.0	5.1	[56]
Bagasse	4.0	100	6.0	0.03	[27]
Flyash	4.0	90	6.0	0.01	[27]
Wallastonite	20	10.4	2.5	0.52	[57]
Waste tea	–	–	–	1.55	[58]
BSS	4.0	50	2.0	4.9	[53]
FSS	4.0	50	2.0	3.6	[53]

Rice Husk

Rice husk is an agricultural waste material generated in rice producing countries, especially in Asia. The annual world rice production is approximately 500 million metric tons, of which 10 – 20% is rice husk. Dry rice husk contains 70 – 85% of organic matter (lignin, cellulose, sugars, etc) and the remainder consists of silica, which is present in the cellular membrane [59]. In recent years, attention has been focused on the utilization of unmodified or modified rice husk as an adsorbent for the removal of pollutants. Srinivasan *et al.*, [60] studied on chromium removal by rice husk carbon. The activated carbon prepared by carbonization of rice husk with sulphuric acid followed by CO_2 activation showed 88% removal of total chromium and greater than 99% removal of hexavalent chromium. Column studies showed capacity of 8.9 mg/g and 6.3 mg/g for rice husk and commercial carbons respectively, for Cr (VI) removal.

Munaf and Zein, [61] studied the use of rice husk for removal of toxic metals from wastewater. They have reported, at optimal conditions, the chromium, zinc, copper and cadmium ion removals from aqueous solution and stated as 79%, 85%, 80% and 85% respectively. Guo *et al.*, [62] studied on adsorption of Cr (VI) on micro- and mesoporous rice husk-based activated carbon. They have concluded that the rice husk carbon is a good sorbent for the removal of Cr (VI) from aqueous solution range from 5 to 60 mg/l with adsorbent dose of 0.8 g/l at pH < 5 under the minimum equilibration time of 2 hours. There is a sharp decrease in adsorption above pH 5.0 and the adsorption in the higher pH range would be negligible. Maximum reported adsorption is > 95% removal of Cr (VI). A study on utilization of agro-residues (rice husk) in small waste water treatment plans was done by Daifullah *et al.*, [63].

Subramaniam *et al.*, [64] studied on raw rice for the removal of Cr (VI). The overall result indicated that the maximum removal (66%) of Cr (VI) for raw rice husk was obtained at pH 2, when it is given adsorbent dose of 70 g/l for 2 hours. Ahmed *et al.*, [65] studied the adsorption of hexavalent chromium from aqueous medium by rice husk activated carbon prepared by physical method as a function of pH , contact time , adsorbent dose , and initial adsorbed concentration. Where the optimum results were found to be 150 minutes, 20 mg/l, 2, and 5g/l for time contact .initial concentration ,pH, and adsorbent dose respectively at optimal conditions, the adsorption of hexavalent chromium was found to be 95.2%

Tea Leaf

Hossain and Kumita, [66] studied the dynamic characteristics of Cr (IV) sorption using black tea leaves as adsorbent. Batch experiments were conducted to evaluate the effects of Cr (VI). Experimental and calculated kinetics data for

equilibrium were expressed by Langmuir effect on the adsorption rate. The potential to remove Cr (VI) from aqueous solutions through biosorption using the nusk of Bengal gram (Cicer arientinum) was investigated in batch experiments by Ahalya *et al.*,[67]. The results showed 99.9% removal of Cr from 10mg/L Cr solution; the biomass required at saturation was 1g/mg. The adsorption data fitted well with the Langmuir and Freundlich isotherm models. Yohimbe bark and grape stalks waste were used as ligands in composite and PVC- based membranes for the development of Cr (VI) and Hg (II) selective electrodes by Fiol *et al.*,[68]

Nutshell

The carbon derived from the nutshell can be used as an adsorbent for the removal of toxic Cr (VI) from aqueous solution. Conformation of data to the equation indicates first order kinetics for Cr (VI) removal by adsorption [69]. The activated carbon prepared from the nutshell is inexpensive and use of the same provides an effective solution for treatment of effluents containing hexavalent chromium. Hence, the use of low cost carbon prepared and used as an adsorbent for Cr (VI) removal in this study is of practical importance and is expected to be economical. The carbon derived from the nutshell can be used as an efficient sorbent for the removal of toxic Cr (VI) from aqueous solution [69]. Percentage removal of Cr (VI) increased with decrease in pH and it was found to increase from 65% to 80% for the variation of pH from 7.4 to 1.2 (Fig. 1). The maximum removal of Cr (VI) was observed at pH 1.2. Some literatures are available on the use of nutshell for the removal of Chromium [69-78].

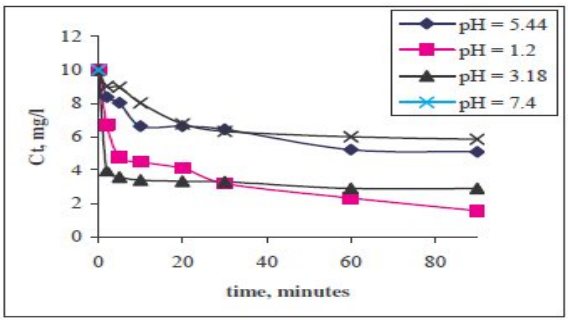

Fig. 1: The pH value influence on Cr (VI) adsorption efficiency on active carbon (nutshells) [69].

Activated Terminalia Arjuna nut

Terminalia arjuna nuts used for different structured activated carbons for the removal of Cr (VI) was investigated by Mohanty *et al* [79], Several activated carbons were prepared from *Terminalia arjuna* nuts, an agricultural waste, by chemical activation with zinc chloride and then tested for aqueous Cr (VI) remediation. The most important parameter in chemical activation was found to be the chemical ratio (activating agent/precursor, g/g). Carbonization temperature and time are the other two important variables, which had significant effect on the pore structure of carbon. The activated carbon developed shows substantial capability to adsorb Cr (VI) from dilute aqueous solutions. The parameters studied include pH, adsorbent dosage, contact time, and initial concentrations. The kinetic data were best fitted to the Lagergren pseudo-first-order model. The isotherm equilibrium data were well fitted by the Langmuir and Freundlich models. The maximum removal of chromium was obtained at pH 1.0. For the carbonization of the $ZnCl_2$ treated sample, $ZnCl_2$ plays an important role in retarding tar escape during carbonization. It was found that acid washing is a necessary step for the preparation of high-porosity carbons. The uptake of the Cr (VI) was greatly affected by the solution pH. The data obtained could be used for designing and establishing a continuous treatment plant for water and wastewaters contaminated with Cr (VI).

Jungias regta (walnut) Hull

In this study, removal of chromium (VI) from aqueous solution by walnut hull (a local low-cost adsorbent) was studied and investigated by Wang and co workers, as a function of solution pH, contact time, adsorbent and adsorbate concentration, reaction temperature and supporting electrolyte (sodium chloride) [80]. The Cr (VI) removal was pH-dependent, reaching a maximum adsorption of 97.3% at pH 1.0. The kinetic experimental data were fitted to the pseudo first-order, modified Freundlich, intraparticle diffusion and Elovich models and the corresponding parameters were obtained. Both the Langmuir and Freundlich isotherms were suitable for describing the biosorption of chromium (VI) onto walnut hull. The uptake of chromium (VI) per weight of adsorbent increased with increasing initial chromium (VI) concentration and decreased sharply with increasing adsorbent concentration. An increase in sodium chloride (as supporting electrolyte) concentration was found to induce a negative effect while an increase in temperature was found to give rise to a positive effect on the Cr (VI) adsorption process. The increased equilibrium adsorption capacity with rise in temperature indicated that the nature of adsorption process is endothermic, which is further supported by the thermodynamic parameters calculated from the Langmuir isotherm at various temperatures.

Rubber Wood Sawdust

The ability of untreated local rubber wood sawdust (RWS) to remove Cr (VI) was carried out by Zakaria and co-worker, under a bench-scale shaking condition by varying parameters such as initial Cr (VI) concentrations, adsorbent dosage, pH, temperature and eluting agent. Complete Cr (VI) removal was achieved at pH less than 2 [81]. The point of zero charge (pH_{PZC}) of 4.90 explained the decrease in Cr (VI) removal capacity by RWS, When pH (3–9) and initial Cr (VI) concentrations (200–500 mg/L) were increased (Fig. 2). Shorter time was needed when 1 M HCl was used to recover Cr (VI) from RWS. FTIR analysis suggests the importance of functional groups such as amino, hydroxyl and carboxyl during Cr (VI) removal. Results suggest that the Cr (VI) removal by RWS is an endothermic process with positive entropy and occurs non-spontaneously (Table-5). The utilization of sawdust for the treatment of Cr (VI) from aqueous solution is gaining importance as a useful, simple yet effective alternative method for commercial activated carbon. Various sources of sawdust have been used with varying Cr (VI) removal capacity (Table-6). Together with its high surface areas and high concentration of active functional groups, the abundance and availability of rubber wood sawdust makes it economically feasible [82]. Sawdust is a waste by-product of the timber industry that is either used as cooking fuel or a packing material. Wood sawdust, a solid waste product obtained from mechanical wood processing, can be used as a low-cost adsorbent of heavy metals, largely due to its lignocellulosic composition. It is mainly composed of cellulose (45–50%) and lignin (23– 30%), both with a capacity for binding metal cations due to hydroxyl, carboxylic and phenolic groups present in their structure [83]. A number of publications have reported on the use of wood sawdust to remove Cr (VI) from solution [82-85].

Ocimum americanum

Boiled mucilaginous seeds of *O. americanum* have shown a reasonable chromium adsorption capacity which was comparable with adsorption capacity of various agricultural by-products that have been reported. Investigations were carried out to study the chromium removal efficiency [90]. Batch experiments were conducted to study the biosorption kinetics of chromium removal for various concentrations of Cr (VI) solutions. The biosorbent dosage was 8 g dry seeds/L. The toxic hexavalent chromium was reduced to less toxic Cr (III) in the presence of seeds and the reduced chromium was adsorbed on the mucilage of seeds. The optimum chromium reduction and adsorption was observed at the pH value of 1.5. The biosorption data fitted well with Langmuir isotherm. Thus, the naturally immobilized polysaccharides on the seeds mimic the microbial polysaccharides in terms of their ability to absorb heavy metals with an added advantage of making the immobilization step unnecessary. Compared to the other biosorbents, *O. americanum* seeds have uniform size and spherical in shape and are amenable to use in packed bed reactors.

Table-5: Thermodynamic parameters of RWS at initial Cr (VI) 50 mg/L [81].

T (K)	ΔG^0 (kJ / mol)	ΔH^0 (kJ / mol)	ΔS^0 (J/mol K)
298.15	- 8.414		
303.15	- 8.774	4.534	43.39
310.15	-10.522		
318.15	-11.225		

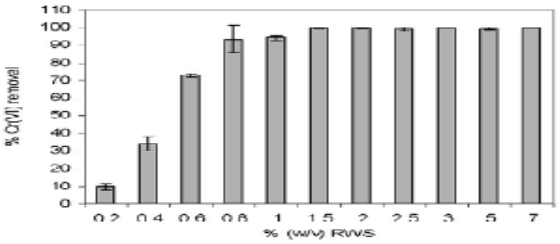

Fig. 2: Removal of Cr (VI) by different concentration of RWS (initial Cr (VI) concentration 150 mg/L) [81].

Fagus orientalis L

The removal of Cr (VI) from aqueous solution under different conditions using Beech sawdust *(Fagus orientalis L.)* as an adsorbent was investigated and studied by Acar *et al* using batch techniques [91]. Batch studies indicated that the percent adsorption decreased with increasing initial concentration of Cr (VI). A contact time of 80 min was found to be optimum. Maximum Cr (VI) removal was observed near a pH of 1.0. Adsorption data was tested using Freundlich and Langmuir isotherms. Maximum adsorption efficiency of 100% was obtained at pH=1. Removal of Cr (VI) increased with increasing adsorbent dose.

Table-6: Capacities of different sources of sawdust in the removal of Cr (VI).

Source of sawdust	Treatment	pH	Initial Cr (VI), g/L	Cr removed mg/g	References
Teak (*Teclona grandis Linn. F*)	None	5.72	184.90	0.89	[86]
Sal tree (*S.robusta)*	Physicochemical	3.5	40	9.55	[87]
Rubber wood	Chemical	3.0	40	158.7	[88]
Maple	None	6.0	10	5.1	[56]
Rubber wood(*Hevea brasiliensis*)	None	2.0	150	4.87	[81]

Agricultural and Timber Waste Carbons

This paper reports the feasibility of using agricultural waste and timber industry waste carbons to remove Cr (VI) from synthetic wastewater under different experimental conditions. Rice husk and saw dust have been used as adsorbent after sulphuric acid treatment [92]. Effect of various process parameters, namely, pH, adsorbent dose, initial chromium concentration and contact time were studied in batch systems (Fig. 3, 4). Maximum metal removal was observed at pH 2.0. The efficiencies of rice husk carbon (RHC) and sawdust carbon (SDC) for Cr (VI) removal were 91.75 % and 94.33 %, respectively. Adsorption capacities of RHC and SDC at different adsorbent doses are reported in Table 7, while the adsorption capacities of RHC and SDC at different initial concentrations of Cr (VI) are presented in Table 8. The experimental data was analyzed using Freundlich, Langmuir, Dubinin–Redushkevich (D–R) and Temkin isotherm models. It was found that Langmuir, D–R and Tempkin models fitted well. The results revealed that the hexavalent chromium is considerably adsorbed on RHC and SDC and it could be an economical method for the removal of hexavalent chromium from aqueous systems. FTIR and SEM characterization of the adsorbents has shown a clear difference in the native and Cr (VI)-loaded adsorbents. The results obtained can be used by small scale industries having low concentrations of Cr (VI) in wastewater using batch or stirred-tank flow reactors where standard material, such as activated carbon, is not available [92].

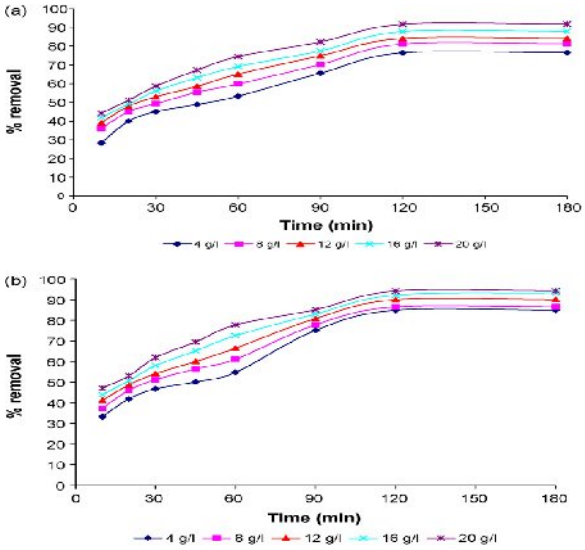

Fig. 3: (a) Effect of adsorbent dose with contact time on Cr (VI) removal by RHC and (b) effect of adsorbent dose with contact time on Cr (VI) removal by SDC [92].

Table-7: Adsorption capacities of RHC and SDC at different adsorbent doses. [92].

Adsorbent dose (gL^{-1})	RHC (q_e,mgg^{-1})	SDC (q_e, mgg^{-1})
4	47.89	53.09
8	25.43	27.07
112	17.54	18.76
16	13.74	14.42
20	11.47	11.79

Table-8: Adsorption capacities of RHC and SDC at different initial concentrations of Cr (VI) [92].

Initial Cr (VI) conc. (mgL^{-1})	RHC (q_e,mgg^{-1})	SDC (q_e mgg^{-1})
100	24.4	24.96
150	35.18	36.22
200	39.95	44.6
250	47.89	53.09

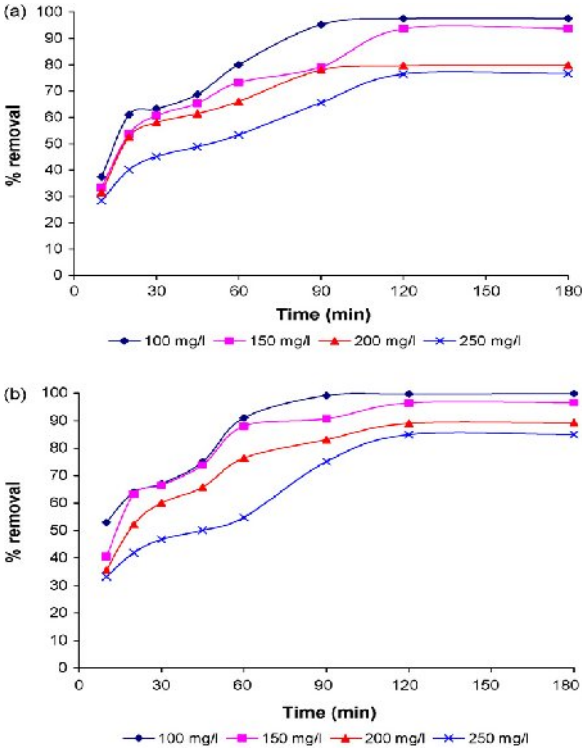

Fig. 4: (a) Effect of initial metal concentration and contact time on Cr (VI) removal by RHC and (b) effect of initial metal concentration and contact time on Cr (VI) removal by SDC [92].

Synthetic materials as adsorbent for the removal of Cr (VI)

Clay Mineral

Finely divided clay minerals and oxides exhibit large surface area. Clay minerals and oxides adsorb cationic, anionic, and neutral metal species. Many studies of Cr (III) and Cr (VI) removal from water by oxides and clay minerals were reported [93-100]. The removal of Cr (VI) from aqueous solutions

by *Fagus orientalis L. Vermiculite*, a 2:1 clay mineral, was applied as adsorbent for removal of chromium and some selected element from aqueous solutions. Parameters such as time of reaction, effect of pH and cation concentration were investigated [101]. The adsorbent showed good sorption potential for these cations. The experimental data was analyzed by Langmuir isotherm model showing reasonable adjustment. This study revealed that vermiculite could be used as an effective adsorbent for the sequestration of Cr (VI) in aqueous solution.

Alginate–goethite beads

In this study, the removal of hexavalent and trivalent chromium ions from binary aqueous solutions by composite alginate–goethite beads was investigated in a batch mode by Lazaridis *et al* [102]. Equilibrium sorption experiments were carried out at different temperatures and pH values. The data were correlated with Langmuir and Freundlich equations. The thermodynamic parameters calculated were: ΔG^o, ΔH^o, ΔS^o and the heat of adsorption. The influence of mixing rate, sorbent concentration and sorbent particle size was studied at different kinetic runs. Equilibrium uptakes, time courses of both metal ions as well as desorption of the loaded material were tested. The thermodynamic parameters revealed that the process was endothermic and spontaneous at room temperature. An increase of Cr (VI) and Cr (III) uptake by alginate–goethite beads was observed with (i) higher mixing rate (ii) smaller bead size and (iii) higher sorbent concentration. These properties showed the potential applicability of composite sorbent in large-scale operations as well as in effluents bearing various anions and cations.

Tea Factory Waste (TWF)

Emine Malkoc and co-worker investigation was aimed at heavy metal adsorption from synthetic wastewaters with another pollutant matter (tea factory waste) [103]. The study investigates the effects of process parameters such as pH, initial concentration of Cr (VI) ion, temperature, agitating rate and adsorbent mass. The nature of the possible adsorbent and metal ion interactions was examined by the FTIR technique. Zeta potential values of the TFW were defined at different values of pH according to deionized water. Maximum adsorption was noted at pH 2.0. The adsorption data follow the Langmuir model better than the Freundlich model and the adsorption equilibrium was well described by the Langmuir isotherm model with maximum adsorption capacity of 54.65 mg g^{-1} of Cr (VI) ions on TFW at 60^0C. The adsorption of Cr (VI) ions increased with increasing temperature indicating endothermic nature of the adsorption process. This study indicated that the TFW can be used as an effective, environmentally friendly and inexpensive biosorbent for the treatment of Cr (VI) containing aqueous solutions. As the pH in the solution decreases, the percentage of Cr (VI) removed increases considerably, the pseudo first order kinetic model was successfully applied to the experimental data, confirming that adsorption was controlled by intra-particle diffusion.

Cellulose acetate and sulfonated poly (ether ether ketone) blend

In this work, it has been demonstrated that ultra filtration assisted by complexation is a promising separation technique applied to purification of effluents containing heavy metals such as chromium [104]. Chromium salts are largely used in various industries including leather-manufacturing industry. Ultrafiltration membranes were prepared by precipitation phase inversion technique in 100/0, 90/10, 80/20 and 70/30 % polymer blend compositions and subjected to the rejection of chromium at different concentrations with a water-soluble macroligand (polyvinylalcohol). Factors affecting the percentage rejection and permeate flux such as pH, concentration of solute, concentration of poly vinyl alcohol, transmembrane pressure and composition of blend membranes were investigated. It was found that percentage rejection improved at pH 6 and a macro ligand concentration of 2 wt % using a membrane of 100 % CA at 345 kPa. In principle, it would be possible to decomplex the chromium–PVA by acidifying the solution to a pH below 1. The study allows separating the chromium from macroligand for its possible reuse [104].

Micellar Compounds

The experimental result of the metal ion which is bound on micellar compounds and then retained by ultrafiltration membrane has been reported [105]. A well known surfactant cetyltrimethylammonium bromide (CTABr) was used as an adsorbent to remove hexavalent chromium from wastewaters. The effect of various experimental parameters on equilibrium adsorption of Cr (VI) on the surfactant was investigated using batch adsorption experiments. It was found that the capacity of chromium adsorption on CTABr increases with initial metal concentration and to a lesser extent with pH solution [105]. Total chromium adsorption decreased slightly with a rise in temperature suggesting an exothermic adsorption of

chromium, thermodynamic parameters were calculated. It was also observed that the capacity of chromium adsorption decreases with the mass of adsorbent and concentration of other ions present in the solution. The metal ion adsorption on surfactant is well represented by the Freundlich isotherm. Thermodynamic parameters evaluated gave; the enthalpy change, ΔH° and the entropy change ΔS° for the sorption processes to be −33.119 $kJmol^{-1}$ and −92, 59 $Jmol^{-1}K^{-1}$, respectively. The maximum capacities of chromium metal adsorption were calculated using Langmuir adsorption isotherm were 17.89 mgg^{-1} and 13.85 mgg^{-1}obtained at 30 and 45 °C respectively. In addition, kinetic experiments performed pointed out the specific role of the cationic surfactant to the removal of hexavalent chromium from wastewater [105].

Amine-Crosslinked Wheat straw

A new adsorbent was prepared from wheat straw (WS) after the cross linking of amine groups. Its adsorption characteristics and operating parameters for chromium (VI) removal was investigated [106]. BET surface area, elemental, zeta potential and Raman spectrum techniques were measured to elucidate the physicochemical change between AC-WS and WS. Significant variation in Raman shift and its results suggested the differential adsorption mechanisms for chromate (VI) removal by AC-WS. The adverse effect of ionic strength on chromate (VI) uptake suggests the possibility of ion exchange mechanisms being active in the adsorption process. The regeneration capacity for Cr (VI)-loaded AC-WS was 74.8%. In addition, the adsorption capacity of AC-WS for chromate (VI) was 5.68 mol/g, the high adsorption capacity data provided a potential application of AC-WS for toxic heavy metals removal from aqueous solutions [106].

Removal of Cr (VI) using Aquatic Organisms as Adsorbents

Two Marine isolates of Yarrowia lipolytica

The removal of Cr (VI) ions from aqueous solutions by the biomass of two marine strains of *Yarrowia lipolytica* (NCIM 3589 and 3590) was also investigated [107] with respect to pH, temperature, biomass, sea salt concentration, agitation speed, contact time and initial concentration of chromium (VI) ions. Maximum biosorption was observed at pH of 1.0 and at a temperature of 35^0C. Increase in biomass and sea salts resulted in a decreased metal uptake. With an agitation speed of 130 rpm, equilibrium was attained within 2 h. Under optimum conditions, biosorption was enhanced with increasing concentrations of Cr (VI) ions. NCIM 3589 and 3590 gave a specific uptake of Cr (VI) ions of 63.73±1.3mgg^{-1} at a concentration of 950 ppm and 46.09±0.23mgg^{-1} at 955 ppm, respectively. Scatchard plot analysis revealed a straight line allowing the data to be fitted in the Langmuir model. The adsorption data obtained also fitted well to the Freundlich isotherm. The surface sequestration of Cr (VI) by *Y. lipolytica* was investigated with a scanning electron microscope equipped with an energy dispersive spectrometer (SEM-EDS) as well as with ED-Xray fluorescence (ED-XRF). Fourier transform infrared (FTIR) spectroscopy revealed the involvement of carboxyl, hydroxyl and amide groups on the cell surfaces in chromium binding [107]

Algae Boom

A novel approach for the preparation of activated carbon from blue-green algal bloom residue has been reported for its capability to remove Cr (VI) from aqueous solution has been examined by Hong Zhang *et al*. For this algal bloom residue derived activated carbon, the physical characters regarding adsorption capability were analyzed by SEM, EDS, FTIR [108]. Batch studies showed that initial pH of 1.0 (most favorable), adsorbent dosage, and initial concentration of Cr (VI) were important parameters for Cr (VI) adsorption. The higher the proton concentration, the higher the efficiency of the Cr (VI) removal. The adsorption process followed the pseudo-second-order equation and Freundlich isotherm. The evidences from SEM, EDS and FTIR characterization also indicates that the adsorption of Cr (VI) on the ARAC leads to the formation of carboxylic and hydroxyl moieties, which can be attributed to the oxidation of the ARAC when Cr (VI) is reduced to Cr (III). It is in return advantageous to environment protection [108].

Many microorganisms of several genera can biosorb while utilizing a wide range of substrates at near neutral pH [109]. Hence, biological processes may provide an alternative to the conventional technique for Cr (VI) removal. Jean-Francios *et al*. [110] indicate that senescent algae could photoproduce some reductive radicals that induce photodegradation of organic pollutants. It is possible that some oxidative radicals photoproduced from senescent algae can induce metal photoreduction. Algae cellwalls, mainly containing polysaccharides, proteins and lipids, offer many functional groups, which have been shown to sequester metal ions [111-112]. In addition, the cell wall structures of algae contain a large quantity of hydroxyproline and rich

glycoprotein, with arabinose, mannose, galactose, and glucose being the predominant sugars [113]. The functional groups and surface properties of algae that were illuminated with metal halide lamp have a higher level of performance for reduction.

Moreover, *Chlorella vulgaris* existed in the natural water can be used for effective photoreduction of chromium (VI) [114]. It was reported that *Chlorella vulgaris* were able to reduce chromium (VI) under UV/visible light illumination. A greater photoreduction was observed under purging N_2 compared to that under purging air. The rate of Cr (VI) photochemical reduction increased with algae concentration increasing, initial Cr (VI) concentration decreasing and the decrease of pH, and the velocity of the photochemical reduction also increased with alga concentration increasing, the increase of initial Cr (VI) concentration and the decrease of pH [114]. When pH increased to 6, the process nearly vanished. When initial Cr (VI) concentration ranged from 0.4 to 1.0 mg L^{-1} and initial algae concentrations ranged from ABS_{algae} = 0.025 to ABSalgae = 0.180, According to the results of kinetic analyses, the kinetic equation of Cr (VI) photochemical reduction in aqueous solution with alga under 250W MHL was $V_o = kC_0^{0.1718} A_{Algae}^{0.5235}$ (Fig. 5) under the condition of pH 4 [114].

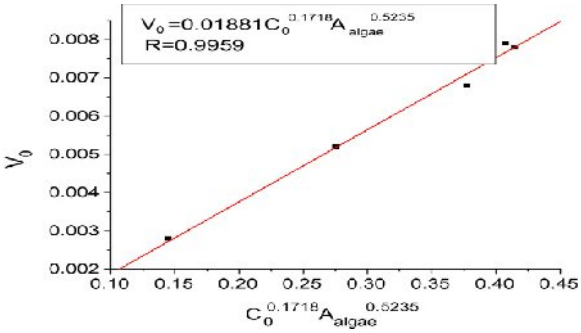

Fig. 5: Effects of initial concentrations of Cr (VI) and algae on the photoreduction of Cr (VI) (pH 4, *R*c = 0.9912, *n*=5, α = 0.001) [114].

Fungi

Fungi and yeast accumulate the non-nutrient metals like chromium, in substantial amounts. Both living and dead fungal cells possess a remarkable ability for toxic and precious metals uptake from wastewater. Fungal biosorbent use in heavy metals removal has been reviewed [115-116]. Fungi are used in a variety of industrial fermentation processes. These processes could serve as economical biomass supply sources for the removal of metal ions. Various types of fungal biomass have been used for the removal and recovery of Cr (III) and Cr (VI) from wastewater. These include unmethylated and methylated yeast [117], *R. arrhizus* [118-119], *Penicillium chrysogenum* [120], dead fungal biomass [121], *Lentinus sajorcaju* mycelia [122-123], *R. nigricans* [124-126], *Neurospora crassa* [127]. The chromium present on the biomass surface was verified by FT-IR and X-ray photoelectron spectroscopy (XPS) analyses. The maximum uptake was dependent on solution pH and increased with biomass. The presence of co-ions in binary, ternary and quarternary combinations decreased the metal uptake.

Bacteria

The use of bacteria for bio adsorption is a fast growing field in metal remediation because of their ubiquity, ability to grow under controlled conditions and smaller size which leads to high surface area and fast rates. Investigations were carried out on the following bacteria: *Zoogloea ramigera* [128], *Bacillus* sp. [129], *Aeromonas caviae* [130, 131], *thuringiensis* [132], *Pantoea* sp. [133], Batch studies were conducted as a function of pH, initial metal ion concentration and temperature, The sorption data fitted to both Langmuir and Freundlich isotherms. In the *Aeromonas caviae* studies on chromium removal, Protonation of functional groups (e.g. carboxyl and amino groups) gives an overall biomass positive charge at 2.5 which enabled adsorption.

The adsorption capacities of Cr (VI) onto different adsorbents are compared in Table 9. The adsorption capacities of Chromium (VI) at different concentrations by SBC – Sugar cane Bagasse, MCC – Maize corn cob, JOC – Jatropha oil cake are reported in Table 10. The effects of both initial concentrations and pH on the adsorption of Chromium (VI) using different adsorbents studied by various researchers are collated in Table 11. Different physical characteristics of some natural adsorbents (Table 12) and the wave number (cm^{-1}) of dominant peaks from FT-IR spectra for Cr (VI) adsorption onto different adsorbents are also reported (Table 13a and b).

Table-9: Comparison of the Adsorption capacity of various adsorbent of Cr (VI)

Adsorbent	$Q_{o\,(mgg^{-1})}$	pH	References
CKW (KOH)	180.3	3	[134]
Acticarbone (H_3PO_4)	124.6	3	[134]
Wood activated carbon	29.9–26.6	2-5	[135]
F400 CAC	26.2–19.1	2-5	[136]
Hazelnut shell activated carbon (H_2SO_4)	52.2	3	[137]
Coconut tree sawdust activated carbon (H_2SO_4)	3.5	3	[137]

CKW – activated carbon treated with KOH and then washed with distilled water.

Table-10: Adsorption of Chromium (VI) by different adsorbents at different initial concentrations [138].

Cr (VI) concentration (mgl^{-1})	SCB (q_e) (mgg^{-1})	MCC(q_e) (mgg^{-1})	JOC(q_e) (mgg^{-1})
5	0.25	0.23	0.25
10	0.50	0.42	0.50
25	1.25	0.95	1.175
50	2.13	1.61	2.30
75	3.15	2.16	3.08
100	3.90	2.56	4.05
250	5.75	3.13	7.75
500	5.75	3.0	11.75

SCB – sugarcane bagasse, MCC – maize corn cob, JOC – jatropha oil cake

Table-11: Adsorption of Chromium (VI) by different adsorbents at different initial concentrations and pH.

Adsorbent	Adsorption capacity mgg^{-1}	Initial Cr (VI) concentration (mgL^{-1})	pH	References
Rubber wood sawdust activated carbon	44.05	200	2	[139]
Tamarind hull activated carbon	85.91	25-75	2	[140]
Terminalia arjuna nuts activated carbon	28.4	10–30	1	[79]
Bael fruit shell	17.27	50–125	2	[141]
Activated carbon	473.91	10	2	[142]
BFS AC				
Green alga Ulva lactuca	10.61	5–50	1	[143]
Biomass	112.36	5- 200	1	[144]
Activated carbon				
Green alga Oedogonium Hatei				
Biomass	31	50, 100	2	[144]
Acid-treated	35.2	50, 100	2	[145]
Wheat-residue derived black carbon	21.34	100	1	[145]
Filamentous algae Spirogyra species biomass	14.7	5	2	[146]
Palm shell	20.5	200	3-4	[147]
PEI/activated carbon	12.6	200	3–4	[147]
Activated carbon				
Alga biomass				
Spirulina platensis	188.68	250	1.5	[148]
Chlorella vulgaris	163.93	250		
Algae bloom residue derived activated carbon	155.52	200	1	[108]

Table-12: Different physical characteristic of natural adsorbent [149].

Adsorbent	Surface area (m^2/g)	Moisture content (%)	Point of zero charge	Ash content (%)
Rice straw	1.21	7.26	6.85	9.40
Rice bran	0.12	10.68	6.10	11.72
Rice husk	0.54	9.02	6.05	11.80
Saw dust	3.85	8.63	3.90	12.35
Neem bark	3.47	9.23	4.50	10.62
Hyacinth root	5.78	11.25	6.59	10.74
Neem leaves	0.57	8.33	6.94	13.58
Coconut shell	0.52	6.16	6.62	9.23

Table-13a: Wave number (cm^{-1}) for dominant peaks from FT-IR spectra for Cr (VI) adsorption onto different adsorbents [149].

Functional Group	Rice straw	Cr (VI) loaded rice straw	Rice bran	Cr (VI) loaded rice bran	Rice husk	Cr (VI) loaded husk	Saw dust	Cr (VI) loaded Saw dust
Surface O-H stretching	3348.78	3417.24	3342.03	3328.53	3385.42	3421.10	3335.10	2920.66
Aliphatic C-H stretching	2918.73	2916.81	2924.52	2924.52	2925.48	2925.48	2917.70	X
Aldehyde C-H stretching	X	X	2854.13	2854.52	2854.13	2854.13	X	X
Aliphatic acid C=O stretching	X	X	1709.59	1713.44	X	X	X	X
Unsaturated grouplike alkene	1644.09	1633.41	1655.59	1644.02	1654.62	1638.23	X	1592.88
Amide C-O stretching	X	X	X	X	X	X	1594.04	X
Aromatic C-No_2 stretching	1512.88	1505.17	1546.63	1514.81	1515.77	1509.99	X	X
Carboxylate anion C=O stretching	1321.00	1371.14	X	X	X	X	X	X
Si –O stretching	1072.66	1058.73	1079.94	1055.84	1055.84	1075.12	X	1031.73
Sulphonic acid S=O stretching	X	X	X	X	X	X	1035.60	
Sulphonate S-O stretching	X	X	X	X	X	X	691.28	651.82

X represent absent

Table-13b: Wave number (cm^{-1}) for dominant peaks from FT-IR spectra for Cr (VI) adsorption onto different adsorbents [149].

Functional Group	Neem bark	Cr (VI) loaded neem bark	Hyacinth roots	Cr (VI) loaded hyacinth root	Neem leaves	Cr (VI) loaded neem leaves	Coconut shell	Cr (VI) loaded Coconut shell
Surface O-H stretching	3297.75	3266.82	3328.53	3305.39	X	X	X	X
Aliphatic C-H stretching	X	X	2934.52	2923.88	2920.28	2910.16	X	X
Phosphite ester Group	X	X	X	X	X	X	2353.97	2358.78
Aliphatic acid C=O stretching	X	X	1713.44	1713.44	1715.83	1715.67	1717.73	1715.75
Unsaturated grouplike alkene	X	X	164.02	1633.41	X	X	X	X
Amide C-O stretching	1606.40	1603.52	X	X	X	X	X	X
Aromatic C-No_2 stretching	X	X	1514.81	1505.17	1515.46	1515.80	1507.22	1507.19
Alkane group stretching	X	X	X	X	1455.88	1455.98	1472.91	1456.25
-So_3 stretching	X	X	X	X	X	X	1236.10	1226.83
Suphonyl chlorides stretching	X	X	X	X	1163.39	1162.60	X	X
Sulphonic acid S=O stretching	1032.91	1034.84	1055,84	1035.59	X	X	1031.37	1032.23
Sulphonate S-O stretching	756.92	658.57	X	X	X	X	X	X

X represent absent.

Future Challenges

The review paper so far elucidates the need for the removal of chromium (VI) in the environment, these studies revealed the use of readily available low cost adsorbent as a replacement for the costly activated carbon, since the use of activated carbon in less developed and developing country is unaffordable. There is a need for the search of more materials that can be used as substitute for activated carbon in order to enhance the removal of chromium that is harmful to both human and aquatic organism in the ecosystem. The following issues needs to be looked into in the removal of pollutants such as chromium from water and waste water.

(i) The conditions for the production of low-cost adsorbents after surface modification for higher uptake of chromium need to be optimized. A successful modification process should have a low volume stream containing the contaminant(s) in a concentrated form and a high volume stream containing the decontaminated matrix.

(ii) Cost factor is also a paramount factor and should not be overlooked, the cost of individual adsorbents depends on local availability, processing required, treatment conditions and both recycle and lifetime issues.

(iii) There is need for the achievement of maximum adsorption of chromium depending upon the adsorbent- adsorbate characteristics.

(iv) Selecting and identifying an appropriate low cost adsorbent, solid waste has become one of the society's most vexing problems. This problem is compounded when the waste is contaminated with hazardous chemicals. One solution is recycling where a portion of the remediation cost is recaptured by sale of the recovered substance, If the solid waste can be converted into a low cost adsorbent for the treatment of discharged wastewater that contain toxic metal ion, particularly chromium (vi) the level of pollutant will reduce.

(v) Regeneration studies need to be carried out in details to enhance the economic feasibility of the process. Due to the fact that the regeneration of commercially activated carbon is very expensive to operate, regenerating the low cost adsorbent used will promote the excessive availability and easy accessibility of the adsorbent.

(vi) Much work is necessary to better understand adsorption phenomenon and to demonstrate possible useful technology at a variety of scales for applications at various locations and scales worldwide.

(vii) Adsorbents derived from agricultural wastes and other materials should be tested with real industrial effluents in order to demonstrate its capability on large scale, it efficiency should not be limited to laboratory work alone.

Conclusion

Conclusively, much more dedicated work and further research studies are required; this will ensure the discovery of new or novel effective low cost adsorbents thereby reducing the presence of toxicant chromium pollutant in the environment.

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References

1. D. Park, Y. S. Yun, S. R. Lim and J. M. Park, Kinetic analysis and mathematical modeling of Cr (VI) removal in a differential reactor packed with Ecklonia biomass, *J. Microbiol. Biotechnol.,* **16**, 1720 (2006).
2. R. S. Juang and R. C. Shiau, Metal removal from aqueous solutions using chitosan enhanced membrane filtration, *J. Membr. Sci*., **165**, 159 (2000).
3. G Yan and T. Viraraghvan, Heavy metal removal in a biosorption column by immobilized *M. rouxii* biomass, *Bioresour. Technol*. **78**, 243 (2001).
4. V. Sarin and KK Pant, Removal of chromium from industrial waste by using eucalyptus bark, *Bioresour. Technol.,* **97**, 15 (2006).
5. A. Malik, Metal bioremediation through growing cells, *Environ. Int.* **30**, 261(2004).
6. L. R. Radovic, C. Moreno-Castilla and J. Rivera-Utrilla, *Carbon materials as adsorbents in aqueous solutions, in L R Radovic (Education), Chemistry and Physics of Carbon. Marcel Dekker, Incorporation, New York*. Vol. 27*,* (2000)
7. V. K. Gupta and I. Ali, Adsorbents for water treatment development of low cost alternatives to carbon for the updated Encyclopedia of Surf Colloid sci, Marcel Dekker. pp. 23 (2003).
8. S. Babel and T. A. Kurniawan Low cost adsorbents for heavy metals uptake from contaminated water, a review, *J Hazard. Mater.* 219 (2003).
9. G. Crini, Recent developments in polysaccharide-based materials used as adsorbents in waste water treatment, *Prog. Polym. Sci.* **30**, 38 (2005).
10. S. J. T. Pollard, G.D. Fowler, C. J. Sollars and R. Perry Low cost adsorbents for waste and wastewater treatment, a review, *Sci. Tot. Environ*., **116,** 31 (1992).
11. S. J. Allen, L. Whitten and G. McKay, The production and characterization of activated carbons, a review, Devpt. *Chem. Eng. Min. Process*, **6,** 231(1998).
12. D. Mohan and K. P Singh *Granular activated carbon, in, Lehr J, Keeley J, Lehr J. (Educations.), Water Encyclopedia, Domestic, Municipal, and Industrial Water Supply and Waste Disposal, Wiley/Interscience, New York.* 92 (2005).
13. T. A. Davis, B. Volesky, and A. Mucci, A review of the biochemistry of heavy metal biosorption by brown algae, *Water Res.* **37**, 4311 (2003).
14. A. Kapoor and T. Viraraghavan, Fungal biosorption-an alternative treatment option for heavy metal bearing wastewaters, a review, *Bioresour Technol.,* **53,** 195 (1995).
15. Y. Sag, Biosorption of heavy metals by fungal biomass and modeling of fungal biosorption, a review, *Sep. Sci. Technol.,* **30**, 1 (2001)
16. M. Dinesh, U. Charles and J. Pittman Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. *J Hazard Mater.,* **137**, 762 (2006).
17. V. Sarin and K. K. Pant, Removal of chromium from industrial waste by using eucalyptus bark, *Bioresour. Technol.,* **97**, 15(2006).
18. R. S. Juang and R. C. Shiau Metal removal from aqueous solutions using chitosan enhanced membrane filtration, *J. Membr. Sci*. **21** (10), 1091 (2000).
19. C. D. Gilson and A. Thomas Calcium alginate bead manufacture, with and without immobilized yeast. Drop formation at a two-fluid nozzle. *J. Chem*. *Technol., Biotechnol.,* **62**, 227 (1995).
20. Z. R. Holan, B. Volesky and I. Prasetyo, Biosorption of cadmium by biomass of marine algae, *Biotechnol., Bioeng*., **41**, 819 (1993).
21. N. K. Hamadi, X. D. Chen, M. M. Farid and M. G. Q. Lu. Adsorption kinetics for the removal chromium (VI) from aqueous solution by adsorbents derived from used tyres and sawdust, *Chem Eng J*, **84,** 95 (2001).
22. D. C. Sharma, C. F. Foster A preliminary examination into the adsorption of hexavalent chromium using low cost adsorbents, *Bioresour Technol.,* **47**, 257 (1994).
23. C. P. Huang and M. H. Wu. The removal of chromium (VI) from dilute aqueous solutions by activated carbons, *Water Resour*., **11**, 673 (1977).
24. M. M. Benjamin, PhD Thesis *Effects of competing metals and complexing ligands on trace metal adsorption at the oxide/solution interface,* Standford University. Acta, **60**, 2503 (1978).
25. C. Faur-Brasquet, Z. Reddad, K. Kadirvelu and P.Le-Cloirec Modeling the adsorption of metal ions onto ACCs using surface complexation models, *Appl Surf Sci*. **196**, 356 (2002).

26. K. Selvi, S. Pattabhi, K. Kadirvelu, Removal of Cr (VI) from aqueous solution by adsorption onto activated carbon, *Bioresour Technol.,* **80**, 87 (2001).
27. M. Rao, A. V. Parwate, A. G. Bhole, Removal of Cr(VI) and Ni(II) from aqueous solution using bagasse and fly ash, *Waste Manage.* **22**, 821 (2002).
28. J. P. Chen and M. Lin Surface charge and metal ion adsorption on an H-type activated carbon, experimental observation and modeling simulation by the surface complex formation approach, *Carbon***. 39**, 1491 (2001).
29. S. Yiacoumi and C. Tien, *Kinetics of Metal Ion Adsorption from Aqueous Solutions, Models, Algorithms and Applications*, Kluwer Academic Publishers, pp 221 (1995).
30. A. Sohail, S. I. Ali, N. A. Khan and R. A. K. Rao, Removal of chromium from wastewater by adsorption*, J. Environ Pollut.,* **2**, 27 (1999).
31. S. E. Bailey, T. J. Olin, R. M and Bricka, D. D. Adrian A review on potential low cost sorbent for heavy metal. *Water Res.,* **33**, 2469 (1999).
32. A. Mittal, L. Kurup and V. K. Gupta Use of waste water as potential absorbent for the removal of amamath from aqueous solution, *J. Hazard. Mater*., **117**, 171 (2005).
33. V. K. Gupta, I. Ali and V. K. Saini, Removal of chlorophenol from wastewater using Red mud, an aluminum industry waste. *Environ Sci Technol.,* **38**, 4012 (2004).
34. V. K. Gupta and S. Sharma, Heavy metal removal from waste water, *Ind. Eng. Chem. Res*., **42**, 6619 (2003).
35. V. K. Gupta, C. K. Jain, I. Ali and S. Chandra Removal of indane and malathion from waste water using bagasse fly ash sugar, *Water Res.* **36**, 2483 (2002).
36. V. K. Gupta, S. K. Srivastava and R. Tyagi, Design parameters for the treatment of phenolic wastes by carbon alums (obtained from fertilizer waste industry), *Water Res.* **34**, 1543 (2000).
37. V. K. Gupta, A. Rastogi, M. K. Dwivedi and D. Mohan, process development for the removal of zinc and cadmium from wastewater using slag-A blast furnace waste material, *Sep Sci Technol.,*; **32**, 2883 (1997).
38. M. B. Dinesh and C. U. Pittman Jr. A review on absorption of chromium using low cost adsorbents for remediation of Cr (III) and Cr (VI), *J. Hazard Mater.* B137, 762 (2006).
39. K. R. Cook, *In-situ treatment of soil and groundwater contaminated with chromium*, Technical Resources Guide, United States Environmental Protection Agency, US EPA/625/R-00/005; (2000)
40. N. P. Cheremisinoff, *Hazardous chemical properties entries*. In Handbook of Hazardous Chemical Properties. 1 (2000)**.**
41. H. Gibb and C. Chen, Evaluation of issues relating to the carcinogen risk assessment of chromium*, Sci Total Environ.,* **86**, 181 (1989).
42. P. Suksabye, P. Thiravetyan and W. Nakbanpote, Column study of chromium (VI) adsorption from electroplating industry by coconut coir pith. *J Hazard Mater.* **160**, 56 (2008).
43. Agency for Toxic substances and Diseases Registry (ATSDR), GA, US Department of Health and Human Services, Toxicological Profile for Chromium. Public Health Services Washington, DC (1991).
44. M. Cieslak-Golonka, Toxic and mutagenic effects of chromium (VI) A review, *Polyhedron*., **15**, 3667 (1995).
45. G. A. Cutter Trace elements in estuarine and coastal waters - U.S. studies from 1986-1990.*Review of Geophys Supplement*., 639 (1991).
46. K. K. Krishnani, I. S. Azad, M. Kailasam, A. R. Thirunavukkarasu, B. P. Gupta, K. O. Joseph, M. Murlidhar, and M. Abharam, Acute toxicity of some heavy metals to *Lates calcarifer,* fry with a note on its histopathological manifestations. *J Environ Sci Health,* **38**, 645 (2003).
47. S. L. Brauer, K. E. Wetterhahn Chromium (VI) forms a thiolate complex with glutathione, *J. Ame. Chem Soc***., 113**, 3001 (1991).
48. Z. Kowalski, Treatment of chromic tannery wastes, *J. Hazard. Mater.*; **37**, 137 (1994).
49. I. B. Singh and D. R. Singh, Cr(VI) removal in acidic aqueous solution using iron-bearing industrial solid wastes and their stabilization with cement, *Environ. Technol.,* **23**, 95 (2002).
50. C. P. Huang and M. H. Wu The removal of chromium (VI) from dilute aqueous solutions by activated carbons, *Water Res*., **11**, 673 (1977).
51. D. E. Kimbrough, Y. Cohen, A. M. Winer, L. Creelman and C. A. Mabuni, Critical assessment of chromium in the environment, *Critical Rev. Environ Sci Technol.,* **29**, 1 (1999).
52. J. O. Nriagu and J. M. Pacyna, Quantitative assessment of worldwide contamination of air, water and soils by trace metals, *Nature*, **333**, 134 (1988)
53. M. Jain, V. K. Garga and K. Kadirvelub, Chromium (VI) removal from aqueous system using *Helianthus annuus* (sunflower) stem waste. *J. Hazard Mater.,* **162**, 365 (2009).
54. M. Kobaya Removal of Cr (VI) from aqueous solution by adsorption onto hazelnut shell activated carbon, kinetic and equilibrium studies, *Bioresour. Technol.,* **91**, 317 (2004).

55. M. Dakiky, M. Khamis, A. Manassra and M. Mereb, Selective adsorption of Cr (VI) in industrial wastewater using low cost abundantly available adsorbents, *Adv. Environ. Res*. **6**, 533 (2002).
56. L. Yu, S. Shukla, K. Dorris, A. Shukla, and J. Margrave, Adsorption of Cr from aqueous solution by maple sawdust, *J. Hazard. Mater.* **100**, 53 (2003).
57. Y. Sharma, Cr (VI) removal from industrial effluents by adsorption on an indigenous low cost material, *J. Colloid Surf. A.* **215**, 155 (2003).
58. Y. Orhan and H. Buyukgungor, The removal of heavy metals by using agricultural waste, *Water Sci.Technol.,* **28**, 247 (1993).
59. R. K. Vempati, S. C. Musthyala, Y. A. Molleh and D. L. Cocke, Surface Analyses of Pyrolysed Rice Husk using Scanning Force Microscopy, *Fuel*, **74**, 1722 (1995).
60. K. Srinivasan, N. Balasubramaniam and T. V. Ramakrishna, Studies on Chromium Removal by Rice Husk Carbon, *Indian J. Environ. Health*., **30**, 376 (1998).
61. E. Munaf and R. Zein, The Use of Rice Husk for Removal of Toxic Metals from Wastewater, *Environ*. *Technol.,* **18**, 359 (1997)
62. Y. Guo, S. Qi, S. Yang, K. Yu, Z. Wang and H. Xu, Adsorption of Cr(VI) on Micro- and Mesoporous Rice Husk-Based Active Carbon, *Mater. Chem. Phys***. 78**, 132 (2002).
63. A. A. M Daifullah, B. S. Girgis and H. M. H. Gad, Utilization of Agro-Residues (Rice Husk) in Small Waste Water Treatment Plans, *Mater. Lett.* **57**, 1723 (2003).
64. P. Subramaniam, N. A. Khan and S. Ibrahim, Rice Husk as an Adsorbent for Heavy Metal, Proceedings of International Conference on Water and Wastewater (ASIAWATER), Kuala Lumpur, Malaysia (2004).
65. S. J. Ahmed, M. G. Attar, Parande, Removal of hexavalent chromium Cr (VI)) from industrial wastewater by using biomass adsorbent (rice husk carbone), *Int. J. Adv. Eng. Res. Stud.,* **1**, 2249 (2012).
66. M. A. Hossain and M. Kuita, Optimization of parameters for Cr (VI) adsorption on used black tea leaves, *Adsorption*, **11**, 561 (2005)
67. N. Ahalya, R. D. Kanamadi, T. V. Ramachandra, Biosorption of chromium (VI) from aqueous solutions by the husk of Bengal (Cicer arientinum), *Electron. J. Biotechnol.,* **8**, 258 (2005).
68. N. Fiol, F. Torre, P. Demeyere, A. Florido, I. Villaescusa, Vegetable waste – based sensors for metal in determination, *Sens. Actuator B,* (2006)
69. C. Modrogan, A. R. Miron, O. D. Orbulet C. Costache, M. Anghel, Hexavalent Chromium Removal from Wastewaters, *Bulletin UASVM Agriculture*, **68**, 94 (2011) .
70. A. Ahmadpour, D. D. Do. The preparation of activated carbon from Macademia Nutshell by chemical activation, *Carbon*, **35**,1723 (1997).
71. A. Aygun, S. Y. Karakas, I. Duman, Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties, *Microporous Mesoporous Mater.* **66**, 189 (2003).
72. V. Madhavi, A. V. B. Reddy, K. G. Reddy, G. Madhavi, T. N. K. V Prasad, An Overview on Research Trends in Remediation of Chromium. *Res. J. Recent. Sci.,* **2**, 71 (2013).
73. S. B. Lalvani, T. Wiltowski, A. Hübner, A. Weston, N. Mandich, Removal of hexavalent chromium and metal cations by a selective and novel carbon adsorbent, *Carbon*, **36**, 1219 (1998).
74. D. Erhan, K. Mehmet, S. Elif and O. Tuncay, Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes *Water S. A*., **30**, 533 (2004)
75. N. Renugadevi, G. Anitha and P. Lalitha, Kinetics of the Removal of Hexavalent Chromium Using a Low-Cost Activated Carbon Adsorbent, *Adv. Appl. Sci. Res.,* **1**, 102 (2010).
76. D. N. Renuga, K. Manjusha and P. Lalitha, Removal of Hexavalent Chromium from aqueous solution using an eco-friendly activated carbon adsorbent *Adv. Appl. Sci. Res.,* **1**, 247 (2010).
77. M. P. Candela, J. M. M. Martinez and R. T. Marcia, Chromium(VI) removal with activated carbons. *Water Res*. **29**, 2174 (1995).
78. S. Chand, V. K. Agarwal and C. Pavankumar, Removal of hexavalent chromium from wastewater by adsorption. *Ind. J. Environ. Health*, **36**, 151 (1994).
79. K. Mohanty, M. Jha, B. C. Meikap and M. N. Biswas, Removal of chromium (VI) from dilute aqueous solutions by activated carbon developed from *Terminalia arjuna* nuts activated with zinc chloride, *Chem Eng Sci.* **60**, 3049 (2005).
80. X. S. Wang, Z. Z. Li and S. R. Tao, Removal of chromium (VI) from aqueous solution using walnut hull*, J. Environ. Manage.*, **90**, 721 (2009).
81. Z. A. Zakaria, M. Suratman, N. Mohammed and W. A. Ahmad Chromium (VI) removal from aqueous solution by untreated rubber wood sawdust, *Desalination*, **244**, 109 (2009).

82. T. Karthikeyan, S. Rajgopal and L. R. Miranda, Chromium(VI) adsorption from aqueous solution by *Hevea Brasilinesis* sawdust activated carbon*, J. Hazard. Mater*. *B,* **124**, 192 (2005).
83. M. Sciban, B. Radetic, Z. Kevresan and M. Klasnja, Adsorption of heavy metals from electroplating wastewater by wood sawdust, *Bioresour*. *Technol.,* **98**, 402 (2007).
84. D. Mohan, K. P. Singh and V. K. Singh, Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth, *Ind. Eng. Chem. Res*. **44**, 1027 (2005)
85. N. K. Hamadi, X. D. Chen, M. M. Farid and M. G. Q. Lu, Adsorption kinetics for the removal of chromium (VI) from aqueous solution by adsorbents derived from used tyres and sawdust, *Chem. Eng. J.* **84**, 95 (2001)
86. K. M. S. Sumathi, S. Mahimairaja and R. Naidu, Use of low-cost biological wastes and vermiculite for removal of chromium from tannery effluent, *Biores. Tech*., **96**, 309 (2005).
87. S. S. Baral, N. Surendra and D. P. Rath, Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust, *Biochem. Eng. J.,* **31**, 216 (2006).
88. D. Mohan and C. U. Pittman Jr. Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, *J. Haz. Mater. B*, **137**, 762 (2006)
89. V. K. Gupta, A. Rastogi and A. Nayak Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material. J *Colloid Interface Sci.* **342**, 135 (2010).
90. L. Lakshmanraj, A. Gurusamy, M. B. Gobinath and R. Chandramohan, Studies on the biosorption of hexavalent chromium from aqueous solutions by using boiled mucilaginous seeds of Ocimum americanum, *J Hazard Mater.* **169**, 1141(2009).
91. F. N. Acar and E. Malkoc, The removal of chromium(VI) from aqueous solutions by Fagus orientalis L, *Bioresour Technol.,* **94**, 13 (2004).
92. M. Bansala, D. Singha and V.K. Gargb A comparative study for the removal of hexavalent chromium from aqueous solution by agriculture wastes carbons, *J Hazard Mater.* **171**, 83 (2009).
93. A. Benhammou, A. Yaacoubi, L. Nibou and B. Tanouti, Study of the removal of mercury (II) and chromium (VI) from aqueous solutions by Moroccan stevensite, *J Hazard Mater.* **17**, 243 (2005).
94. K. Csoban and P. Joo, Sorption of Cr (III) on silica and aluminium oxide, experiments and modeling, *Colloids Surf. A: Physicochem. Eng. Aspects,* **15**, 97 (1999).
95. M. Erdem, H. S. Altundogan, M. D. Turan, F and Tumen, Hexavalent chromium removal by ferrochromium slag, *J Hazard Mater. B* **126**, 176 (2005).
96. S. A. Khan, R. U. Rehman and M. A. Khan, Adsorption of chromium (III), chromium(VI) and silver(I) on bentonite, *Waste Manage*, **15**, 271 (1995).
97. M. Lehmann, A. I. Zouboulis and K. A.. Matis, Modeling the sorption of metals from aqueous solutions on goethite fixed-beds, *Environ Pollut*., **113**, 121 (2001).
98. J. H. Potgieter, S. S. Potgieter-Vermaak and P. D. Kalibantonga, Heavy metals removal from solution by palygorskite clay, *Miner Eng*. **19**, 463 (2006).
99. H. Tel, Y. Alta and M. S. Taner, Adsorption characteristics and separation of Cr (III) and Cr (VI) on hydrous titanium(IV) oxide*, J. Hazard Mater*. **112**, 225 (2004).
100. C. S. Uyguner and M. Bekbolet Evaluation of humic acid, chromium (VI) and TiO_2 ternary system in relation to adsorptive interactions, *Appl. Catal B*. 49 (4), 267 (2004).
101. M. G. Da-Fonseca, M. M. de-Oliveira and L. N. H. Arakaki, Removal of cadmium, zinc, manganese and chromium cations from aqueous solution by a clay mineral, *J Hazard Mater. B*, **137**, 288 (2006).
102. N. K. Lazaridis and C. Charalambous, Sorptive removal of trivalent and hexavalent chromium from binary aqueous solutions by composite alginate–goethite beads, *Water Res.* **39**, 4385 (2005).
103. E. Malkoc and Y. Nuhoglu Potential of tea factory waste for chromium (VI) removal from aqueous solutions, Thermodynamic and kinetic studies. *Sep Purif Technol.,* **54**, 291 (2007).
104. G. Arthanareeswaran, P. Thanikaivelan, N. Jaya, D. Mohana and M. Raajenthiren, Removal of chromium from aqueous solution using cellulose acetate and sulfonated poly(ether ether ketone) blend ultrafiltration membranes, *J Hazard Mater*. B, **139**, 44 (2007).
105. Z. Sadaoui, S. Hemidouche, O. Allalou, Removal of hexavalent chromium from aqueous solutions by micellar compounds *Desalination*. **249**, 768 (2009).
106. X. Xu, B. Gao, X. Tan, Q. Y. Yue, Q. Zhong and Q. Li, Characteristics of amine-crosslinked wheat straw and its adsorption mechanisms for phosphate and chromium (VI) removal from aqueous solution, *Carbohydr Polym*., **84**, 1054(2011).

107. A. V. Bankar, A. R. Kumar and S. S. Zinjarde, Removal of chromium (VI) ions from aqueous solution by adsorption onto two marine isolates of Yarrowia lipolytica, *J. Hazard Mater*. **170**, 487 (2009).
108. H. Zhang, Y. Tang, D. Cai, X. Liu, X. Wang, Q. Huang and Z. Yu Hexavalent chromium removal from aqueous solution by algal bloom residue derived activated carbon, Equilibrium and kinetic studies. *J Hazard Mater*. **181**, 801 (2010).
109. Y. T. Wang and H. Shen, Bacterial reduction of hexavalent chromium, *J. Ind. Microbiol*. **14**, 159 (1995).
110. R. Jean-Francios, Visible light-dependent degradation of lipidic phytoplanktonic components during senescence, a review, *Photochemistry* **58**, 187 (2001).
111. G. M. Gadd, Interaction of fungi with toxic metals, New *Phytol*.,**124**, 25 (1993).
112. Z. R. Holan, B. Volesky and I. Prasetyo, Biosorption of cadmium by biomass of marine algae, *Biotechnol. Bioeng*., **41**:819 (1993)
113. R. H. Crist, K. Oberholser, N. Shank and M. Nguyen, Nature of bonding between metallic ions and algal cell walls, *Environ. Sci*. *Technol.,*;**15**, 1212 (1981)
114. L. Deng, H. Wang and N. Deng, Photoreduction of chromium(VI) in the presence of algae, *Chlorella vulgaris, J. Hazard. Mater. B*, **138**, 288 (2006).
115. A. Kapoor and T. Viraraghavan, Fungal biosorption-an alternative treatment option for heavy metal bearing wastewaters, a review, *Bioresour Technol.,* **53**, 195 (1995).
116. Y. Sag Biosorption of heavy metals by fungal biomass and modeling of fungal biosorption, a review, Sep. Sci *Technol.,* **30**, 1 (2001).
117. H. Seki, A. Suzuki and H. Maruyama, Biosorption of chromium (VI) and arsenic (V) onto methylated yeast biomass, *J. Coll. Interf. Sci.* **281**, 261 (2005).
118. R. S. Prakasham, J. S. Merrie, R. Sheela, N. Saswathi and S. V. Ramakrishna, Biosorption of chromium(VI) by free and immobilized Rhizopus arrhizus, *Environ Pollut*., **104**, 421 (1999).
119. Y. Sag and T. Kutsal, Fully competitive biosorption of Cr (VI) and Fe (III) ions from binary metal mixtures by *R. arrhizus*, use of the competitive Langmuir model, *Process Biochem.,* **31**, 573 (1996).
120. S. Deng, Y. P. Ting, Polyethylenimine-modified fungal biomass as a high capacity biosorbent for Cr(VI) anions, sorption capacity and uptake mechanisms, *Environ. Sci. Technol.,* **39**, 8490 (2005).
121. K. C. Sekhar, S. Subramanian, J. M. Modak and K. A. Natarajan. Removal of metal ions using an industrial biomass with reference to environmental control, *Int. J. Min. Process.*, **53**, 107 (1998).
122. M. Y. Arıca and G. Bayramoglu, Cr (VI) biosorption from aqueous solutions using free and immobilized biomass of *Lentinus sajor-caju*, preparation and kinetic characterization, *Colloids Surf. A Physicochem. Eng. Aspects,* **253**, 203 (2005).
123. G. Bayramoglu, G. C. Elik, E. Yalc, M. Yilmaz and M. Y. Arıca, Modification of surface properties of *Lentinus sajor-caju* mycelia by physical and chemical methods, evaluation of their Cr^{6+} removal efficiencies from aqueous medium, *J. Hazard. Mater*. **119**, 219 (2005).
124. R. S. Bai and T. E. Abraham, Studies on chromium (VI) adsorption-desorption using immobilized fungal biomass, *Bioresour Technol.,* **87**, 17 (2003).
125. R. S. Bai and T. E. Abraham, Studies on enhancement of Cr (VI) biosorption by chemically modified biomass of *Rhizopus nigricans*, *Water Res*, **36**, 1224 (2002).
126. R. S. Bai and T. E. Abraham, Biosorption of Cr (VI) from aqueous solution by Rhizopus nigricans, *Bioresour*. *Technol.,* **79**, 73 (2001).
127. S. Tunali, I. Kiran and T. Akar Chromium (VI) biosorption characteristics of *Neurospora crassa* fungal biomass, *Miner Eng.* **18**, 681 (2005).
128. M. Nourbakhsh, Y. Sag, D. O. Zer, Z. Aksu, T. Kutsal and A. C. Aglar A comparative study of various biosorbents for removal of chromium (VI) ions from industrial waste waters, *Process Biochem.,* **29**, 1 (1994).
129. M. N. Nourbakhsh, S. Kilic, S. Ilhan and H. Ozdag, Biosorption of ions in industrial waste water on *Bacillus* specie, *Chem Eng J*, **85**, 351 (2002).
130. M. X. Loukidou, A. I. Zouboulis, T. D. Karapantsios and K. A. Matis, Equilibrium and kinetic modeling of chromium (VI) biosorption by *Aeromonas caviae*, *Colloids Surf. A Physicochem. Eng. Aspects.* **242**, 93 (2004).
131. M. X. Loukidou, T. D. Karapantsios, A. I. Zouboulis and K. A. Matis Diffusion kinetic study of chromium (VI) biosorption by *Aeromonas caviae*, *Ind. Eng. Chem. Res*., **43**, 1748 (2004).
132. Y. S. Ahin and A. Ozturk, Biosorption of chromium(VI) ions from aqueous solution by the bacterium Bacillus thuringiensis, *Process Biochem.,* **40**, 1895 (2005).

133. G. Ozdemir, N. Ceyhan, T. Ozturk, F. Akirmak and T. Cosar, Biosorption of chromium (VI), cadmium (II) and copper (II) by *Pantoea* specie. TEM18, *Chem. Eng. J*. **102**, 249 2004).
134. L. Khezami and R. Capart, Removal of chromium (VI) from aqueous solution using activated carbon, kinetics and equilibrium studies, *J Hazard Mater. B*, **123**, 223 (2005).
135. F. Haghesresht and G. Lu, Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents, *Energy Fuels,* **12**, 1100 (1998).
136. K. Selvi, S. Pattabhi and K. Kadirvelu, Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon, *Bioresour Technol.,* **80**, 87 (2001).
137. G. K. Umesh, M. P. Kaur, V. K. Garg and S. Dhiraj, Removal of hexavalent chromium from aqueous solution*, J. Hazard. Mater*., **140**, 60 (2007).
138. M. Bansal, D. Singh and V. K. Garg, A comparative studies on the removal of hexavalent chromium from aqueous solution using agricultural wastes carbon. *J. Hazard. Mater.,* **171**, 83 (2009).
139. T. Karthikeyan, S. Rajagopal and L. R. Miranda, Cr (VI) adsorption from aqueous solution by Hevea Brasilinesis sawdust activated carbon. *J. Hazard. Mater. B,* **124**, 192 (2005).
140. A. Verma, S. Chakraborty and J. K. Basu, Adsorption study of hexavalent chromium using tamarind-hull based adsorbents, *Sep. Purif. Technol.,* **50**, 336 (2006).
141. J Anandkumar and B. Mandal, Removal of Cr (VI) from aqueous solution using Bael fruit (Aegle marmelos correa) shell as an adsorbent, *J. Hazard. Mater.,* **168**, 633 (2009).
142. R. Gottipati and S. Mishra, Process optimization of adsorption of Cr (VI) on activated carbons prepared from plant precursors by a two level Full Factorial Design, *Chem. Eng. J.* (2010) 160. 1, doi:10.1016/j.cej.(2010) 03.015
143. A. E. Sikaily, A. E. Nemr, A. Khaled and O. Abdelwehab, Removal of toxic chromium from wastewater using green alga Ulva lactuca and its activated carbon, *J. Hazard. Mater.* **148**, 216 (2007).
144. V. K. Gupta and A. Rastogi, Biosorption of hexavalent chromium by raw and acid treated green alga Oedogonium hatei from aqueous solutions, *J. Hazard. Mater*., **163**, 396 (2009).
145. X. S. Wang, L. F. Chen, F. Y. Li, K. L. Chen, W. Y. Wan and Y. J. Tang, Removal of Cr (VI) with wheat-residue derived black carbon, reaction mechanism and adsorption performance, *J. Hazard Mater*., **175**, 816 (2010).
146. V. K. Gupta, A. K. Shrivastava and N. Jain, Biosorption of chromium(VI) from aqueous solutions by green algae spirogyra species, *Water Resour*., **35**, 4079 2001).
147. M. Owlad, M. K. Aroua and W. A. W. Daud, Hexavalent chromium adsorption on impregnated palm shell activated carbon with polyethyleneimine. *Bioresour. Technol.,* **101**, 5098 (2010).
148. S. V. Gokhale, K. K. Jyoti and S. S. Lele, Kinetic and equilibrium modeling of chromium (VI) biosorption on fresh and spent Spirulina platensis/Chlorella vulgaris biomass, *Bioresour. Technol.,* **99**, 3600 (2008).
149. B. Singha, T. K. Naiya, A. K. Bhattacharya and S. K. Das Cr (VI) ions removal from Aqueous solutions using different adsorbent-FTIR studies, *J. Environ. Protect*. **2**, 729 (2011).