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ORIGINAL ARTICLE

Modified agricultural waste biomass with enhanced responsive properties for metal-ion remediation: a green approach

Garima Mahajan · Dhiraj Sud

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Abstract *Dalbergia sissoo* pods, a lignocellulosic nitrogenous waste biomass, was evaluated for sequestering of Cr(VI) from synthetic wastewater. *Dalbergia sissoo* pods (DSP) were used in three different forms, viz. natural (DSPN), impregnated in the form of hydrated beads (DSPB), and in carbonized form (DSPC) for comparative studies. Batch experiments were performed for the removal of hexavalent chromium. Effects of pH adsorbent dose, initial metal-ion concentration, stirring speed, and contact time were investigated. The removal of metal ions was dependent on the physico-chemical characteristics of the adsorbent, adsorbate concentration, and other studied process parameters. Maximum metal removal for Cr(VI) was observed at pH 2.0. The experimental data were analyzed based on Freundlich and Langmuir adsorption isotherms. Kinetic studies indicated that the adsorption of metal ions followed a pseudo-second-order equation.

Keywords Waste water · Biosorption · Kinetics · *Dalbergia sissoo* · Cr(VI)

Introduction

Pollution of surface and ground water supplies with toxic Cr(VI) has been one of the major causes for the deterioration in water quality, as this metal is used in a number of industrial applications including steel production, electroplating, leather tanning, nuclear power plant, textile industries, wood preservation, anodizing of aluminum, water cooling, and chromate preparation (Altundogan 2005). Chromium exists in trivalent and hexavalent forms in aquatic systems. The trivalent form at very low concentration is an essential nutrient (Rojas et al. 2005), but the hexavalent form is toxic, carcinogenic, and mutagenic in nature. It is highly mobile in soil and aquatic systems and also is a strong oxidant capable of being absorbed by the skin (Singh and Singh 2002). The hexavalent form is 500 times more toxic than the trivalent form (Kowalski 1994). Human toxicity includes lung cancer, as well as kidney, liver, and gastric damage (Cieslak-Golonka 1995). 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 the applied chromium, and the rest is usually discharged into wastewaters, causing serious environmental hazards. Chromium ion in liquid tanning wastes occurs mainly in the trivalent form, which gets further oxidized to the hexavalent form. The current drinking water guideline value for Cr(VI) recommended by the world health organization is 0.05 mg/L (Acar and Malkoc 2004). Compliance with this strict standard is expected to be very costly and therefore, treatment efficiency is one of the major concerns for risk management when treating water containing Cr(VI). Numerous treatment methods, such as ion exchange, chemical reduction, chemical precipitation (Acar and Malkoc 2004), membrane separations (Patterson 1977 and Tiravanti et al. 1997), electrochemical precipitation (Dahbi et al. 1999), photo-catalytic reduction (Kapoor et al. 1999), adsorption (Aksu 2001; Zhang et al. 1998; Demirbas 2005) and biosorption (Goel et al. 2005 and Mohanty et al. 2006) have been tested to remove Cr(VI) from effluents to the permissible level. However, due to prohibitive cost, their use is limited in developing countries like India. Hence, there is a need to develop low-cost and easily available

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G. Mahajan (✉) · D. Sud
Department of Chemistry, Sant Longowal Institute of Engineering and Technology, Sangrur, India
e-mail: garima8mahajan@hotmail.com

adsorbents for the removal of heavy metal ions from the aqueous environment. An abundant source of potentially metal-sorbing biomass is lingo-cellulosic agricultural waste materials. These materials could be an inexpensive substitute for the treatment of heavy-metal laden wastewater (Sud et al. 2008). Biomass is widely available, inexhaustible, and inexpensive material that exhibits significant specificity for the heavy metal ions. *Dalbergia sissoo* pods, an agricultural waste material, are generated in large quantities in India. These pods are put in no use and are burned in the open field, dumped in forest areas, or blown into huge piles and left to naturally deteriorate. These pods are very rich in cellulose and hemicelluloses and comprise 80 % of organic matter. They contain many polymeric materials that possess functional moieties that may help for the binding of metal ions. The removal of metal ions from aqueous streams using agricultural materials is based upon metal biosorption (Volesky and Holan 1995). The basic components of the agricultural waste materials biomass include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, starch containing variety of functional groups that facilitates metal complexation which helps for the sequestering of heavy metals (Bailey et al. 1999; Hashem et al. 2005, 2006). The process of biosorption involves a solid phase (sorbent) and a liquid phase (solvent) containing a dissolved species to be sorbed. Due to high affinity of the sorbent for the metal-ion species, the latter is attracted and bound by rather complex process affected by several mechanisms involving chemisorption, complexation, adsorption on surface and pores, ion exchange, chelation, adsorption by physical forces, entrapment in inter and intrafibrillar capillaries and spaces of the structural polysaccharides network as a result of the concentration gradient and diffusion through cell wall and membrane (Bassco et al. 2002; Sarkanen and Ludwig 1971; Qaiser et al. 2007) (Fig. 1) Agricultural waste materials are usually composed of lignin and cellulose as the main constituents. Other components are hemicellulose, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash and many more compounds that contain a variety of functional groups present in the binding process. Cellulose is a crystalline homo-polymer of glucose with $\beta 1 \rightarrow 4$ glycosidic linkage and intramolecular and intermolecular hydrogen bonds (Demirbas 2000a, b). Hemicellulose is a hetropolymer of mainly xylose with $\beta 1 \rightarrow 4$ glycosidic linkage with other substances of acetyl feruoyl and glycouronyl groups (Hashem et al. 2007). Lignin is three-dimensional polymer of aromatic compounds covalently linked with xylans in hardwoods and galactoglucomannans in softwoods (Garg et al. 2007; Sjötröm 1981) The functional groups present in biomass molecules acetamido groups, carbonyl, phenolic, structural polysaccharides, amido, amino, sulphydryl carboxyl groups alcohols and esters (Beveridge and Murray 1980; Gupta et al. 1999). These groups have the affinity for metal complexation. Some biosorbents are non-selective and bind to a wide range of heavy metals with no specific priority, whereas others are specific for certain types of metals depending on their chemical composition. The presence of various functional groups and their complexation with heavy metals during biosorption process has been reported by different research workers using spectroscopic techniques (Ahluwalia and Goyal 2005; Garg et al. 2007; Tarley and Arruda 2004). Various agricultural waste materials have been used, such as rice bran, rice husk, wheat bran, wheat husk, saw dust of various plants, bark of the trees, groundnut shells, coconut shells, black gram husk, hazelnut shells, walnut shells, cotton seed hulls, waste tea leaves, cassia fistula leaves, maize corn cob, jatropha de-oiled cakes, sugarcane bagasse, apple, banana, orange peels, soybean hulls, grapes stalks, water hyacinth, sugar beet pulp, sunflower stalks, coffee beans, arjun nuts, and cotton stalks, etc.(Annadurai et al. 2002; Cimino et al. 2000; Hashem et al. 2005; Macchi et al. 1986; Mohanty et al. 2005; Orhan and Bujukgungor 1993; Reddad et al. 2002; Tee and Khan 1988; Hamadi et al. 2001) A comparison of their adsorption capacities has been given in (Table 1). The present study explores the use of *Dalbergia sissoo* pods as sustainable adsorbent for chromium removal from aqueous systems under different experimental conditions. Experiments were performed in batch mode. *Dalbergia sissoo* pods were taken in three different forms, viz. natural, impregnated in form of hydrated beads, and carbonized forms. The results showed the potential removal of the Cr(VI) metal ion by biomass in matrix mode and carbon form as compared to the natural form under optimized conditions. Equilibrium and kinetic models were investigated and applied to the data to describe the overall adsorption process.

Materials and methods

Preparation of adsorbent

The selected agricultural waste material *Dalbergia sissoo* pods (DSP) was collected from the local area. Hot water treatment was given to them for 1 h to remove the soluble organic components and debris, and the material was dried at 120 °C in hot air oven for 24 h. The material was then ground and sieved (150 MICS). Immobilization of biomass in the form of beads was prepared by mixing sodium alginate (polymer) and biomass in different ratios of 1:1, 1:3, 1:5, 1:7, 1:9, and 1:11 in a pre-calculated amount of

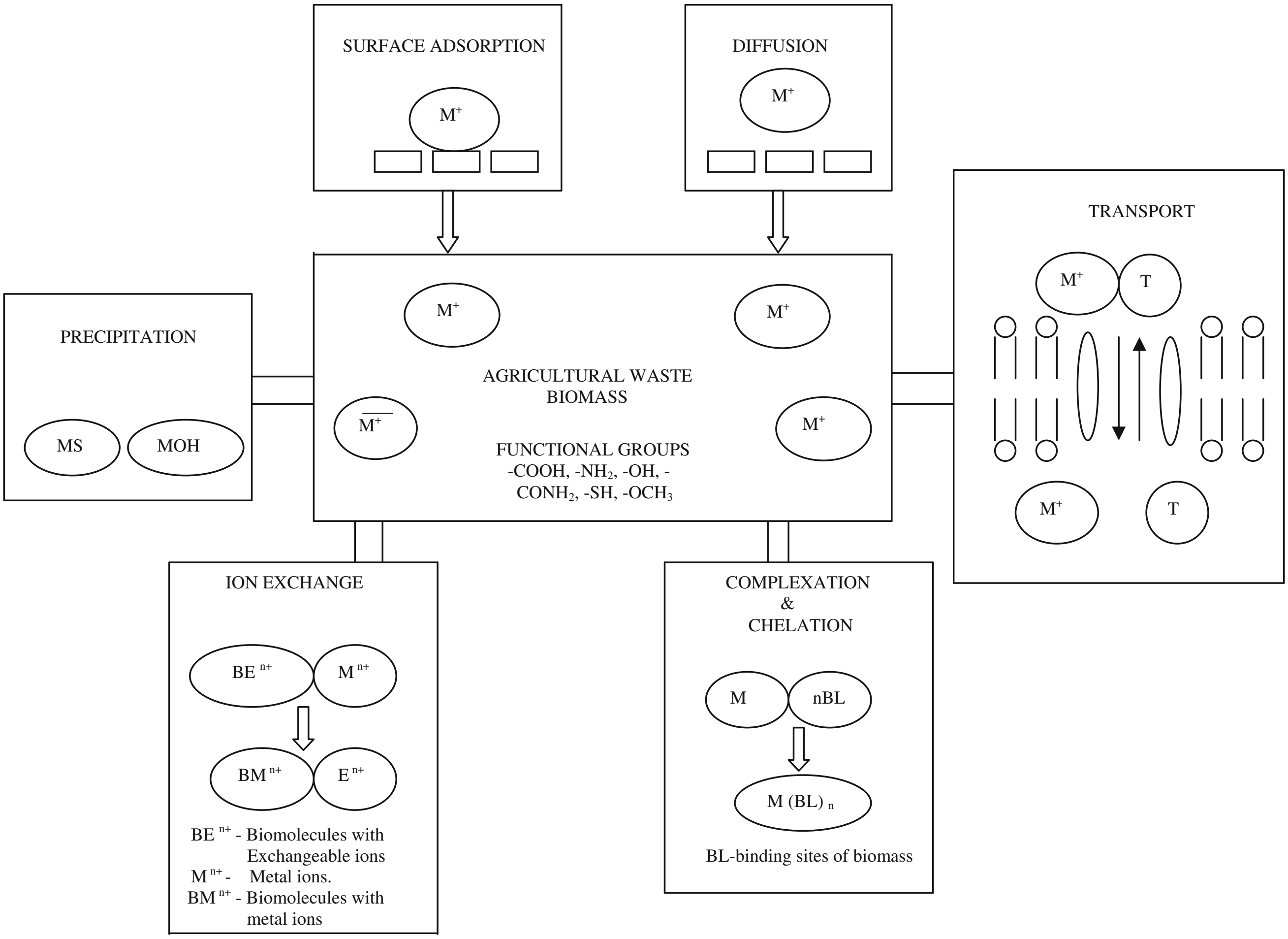

Fig. 1 Plausible mechanism of biosorption

de-ionized water and dropped into a 2 % solution of calcium chloride. The beads thus prepared were stirred in the $CaC1_2$ solution for 24 h for hardening. Beads were then washed three times with de-ionized water and maintained in 2 % $CaC1_2$ solution at 4 °C. The surface area of the beads was found to be 50.2×10^{-3} µm. The carbonized form of the biomass was prepared by heating the powder of biomass in a muffle furnace at 800 °C for 2 h.

Preparation of adsorbate

A stock solution of chromium (VI) (1,000 mg/L) was prepared by dissolving potassium dichromate in double-distilled water. The stock solution was diluted with distilled water to obtain Cr(VI) solutions of the desired concentration range. The pH of the solutions was adjusted using 0.01 M NaOH/0.01 M HCl using an Orion 420A pH meter. The Cr(VI) concentration was determined spectrophotometrically [Double Array UV–Vis Spectrophotometer, Agilent 8453] by the diphenyl-carbazide method (Zhang et al. 1998).

Experimental setup

Adsorption experiments were carried out using 100 mL of chromium solution of the desired concentration (50 mg/L) at an initial pH of 2.0 and with 1.5 g of adsorbent in a 250 mL Erlenmeyer flask at 25 ± 1 °C (stirring speed 250 rpm). At predetermined time intervals (60 min), samples were separated by centrifugation at 4,000 rpm for 10 min. The residual chromium concentration in the supernatant was determined as given earlier. All experiments were replicated three times for all the forms of adsorbents. The removal percentage (*R* %), defined as the ratio of difference in metal concentration before and after adsorption ($C_i - C_e$) to the initial concentration of chromium in the aqueous solution (C_i), was calculated using Eq. 1:

Table 1 Various agricultural products as biosorbents and their sorption potential

Agricultural waste biomass	Percentage of removal (%)	References
Oat biomass	>80	Gardea-Torresdey et al. (2000)
Formaldehyde treated saw dust Indian rosewood	62–86	Garg et al. (2004)
Beech saw dust	100	Acar and Malkoc (2004)
Chemically treated Bagasse	50–60	Krishanani et al. (2004)
Formaldehyde treated rice husk	88.88	Bishnoi et al. (2004)
Bagasse fly ash	96–98	Gupta and Ali (2004)
Wheat bran	>82	Farajzadeh and Monji (2004)
Coconut shell fibers	>80	Mohan et al. (2006)
Commercial granular activated carbon (C2 and C3) and AC of waste from sugar industry (C1)	93–98 C1 > C2 > C3	Fahim et al. (2006)
Eucalyptus bark	Almost 100	Sarin and Pant (2005)
Neem leave powder	>96	Venkateswarlu et al. (2007)
Rubber wood saw dust	60–70	Karthikeyan et al. (2005)
Pretreated bagasse with NaOH and CH_3COOH	90, 67	Rao et al. (2002)
Modified bagasse fly ash	67	Gupta et al. (1999)
Activated carbon from bagasse (carbonization and gasification)	Significant metal uptake	Valix et al. (2006)
Sugarcane bagasse, maize corn cob, jatropha oil cake	Up to 97	Garg et al. (2007)
Raw rice bran	40–50	Oliveira et al. (2005)

Table 2 Structural composition of *Dalbergia sissoo* pods

Structural components	Percentage (%)
Carbon	52.71
Nitrogen	6.23
Hydrogen	5.17
Cellulose	29
Hemi-cellulose	07
Lignin	22
Carbohydrate	16
Crude Protein	14
Fiber	21
Ash	18

Table 3 FT-IT spectra of adsorbent and Cr(VI) treated adsorbent

Adsorbent	Band positions (cm^{-1})				
	O–H	C–H	C=O	OCH_3	Bending vibrations
DSP native	3,083.6	2,922.3	1,739.2	1,055.7	614.5
DSP-Cr(VI)	3,356.8	2,919.2	1,735.8	1,154.2	896.6, 614

$$R(\%) = \frac{C_i - C_o}{C_i} \times 100. \qquad (1)$$

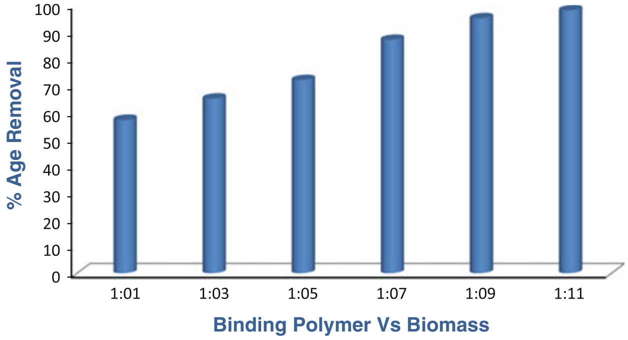

Fig. 2 Binding agent and biomass ratio

Results and discussion

Structural composition

In terms of their structure, *Dalbergia sissoo* pods (DSP) can be regarded as a lingo-cellulosic agricultural waste material containing high amount of proteins and crude fibers (Table 2). The pods are extremely rich in the nitrogenous substances containing various functional moieties for sequestering of heavy metal ions. The mechanism of Cr(VI) removal by lingo-cellulosic biomass is attributed to anionic adsorption or by reduction of Cr(VI) to Cr(III) by ligno-cellulosic biomass. The contributing functional groups such as phenolic methoxyl and hydroxyl groups of lignin are responsible for Cr(VI) reduction and the oxidation of these functional groups gives rise to the formation of carbonyl and carboxyl groups of lingo-cellulosic material. In addition to forming surface complexes, a portion of Cr(III) bound to ligno-cellulosic materials also formed a hydroxide precipitate. FT-IR analysis of the adsorbent before and after sorption of metal ions was performed to determine the vibrational frequency changes in the functional groups of the adsorbent in various forms. The spectra of adsorbents were measured in the range of 500–4,000 cm^{-1} wave number. The FT-IR spectra showed a number of adsorption peaks, indicating the complex nature of the studied adsorbent. In *Dalbergia sissoo* pods (DSP), the sorption peak at 3,083.6 cm^{-1} indicates the existence of free and intermolecular-bonded hydroxyl groups. The peaks observed at 2,922.3 cm^{-1} can be assigned to the stretching vibration of the C–H group. The peaks around 1,739.2 cm^{-1} correspond to the –C=O group. The strong C–O band at 1,055.7 cm^{-1} due to $–OCH_3$ groups also confirms the presence of lignin structures in *Dalbergia sissoo* pods. The C–O absorption peak was observed to shift to 1,154.2 cm^{-1} when DSP was loaded with chromium. It seems that this functional group participates in metal binding. Table 3 presents the fundamental peaks of the adsorbent before and after use. The spectra display a number of absorption peaks indicating the complex nature of the examined adsorbent.

Effect of polymer and biomass ratio

For the formation of beads, biomass was bonded with sodium alginate in the ratio 1:9 of binding agent to biomass. This particular ratio was selected after a series of trials with different ratios of 1:1, 1:3, 1:5, 1:7, 1:9 and 1:11. The adsorption increased with increase in the ratio of biomass to binding agent. Maximum adsorption was achieved with a ratio of 1:9, as compared to 1:11, which was attributed to a lack of stability in the latter; hence, the adsorption experiments were further performed with beads prepared by using the ratio 1:9 (Fig. 2).

Effect of pH

pH is an important controlling parameter in the adsorption process due to its influence on the surface properties of the adsorbent and the ionic form of the metal ion in solution. Adsorption experiments were carried out in the pH range 2–10 (Although it was found that after pH 7, solution gets precipitated, thus studies were limited up to 7 pH only.), while keeping all other parameters constant (chromium concentration = 50 mg/L; stirring speed = 250 rpm; contact time = 60 min, adsorbent dose = 15 g/L, temp. = 25 °C). The pH of the chromium solution was adjusted after adding the adsorbent. The maximum adsorption of chromium was 99, 98, and 92 % for DSPC, DSPB, and DSPN, respectively at pH 2 (Fig. 3). There was a sharp decline in percent adsorption with increase in pH of the aqueous solution. Chromium adsorption by DSPN was decreased from 92 to 25 % as the pH was increased from 2 to 5. Chromium adsorption by DSPB was decreased from 98 to 28 % as pH was increased from 2 to 5. Similarly, chromium adsorption by DSPC was decreased from 99 to 45 % as pH was increased from 2 to 5. Maximum adsorption was observed at pH 2.0, and hence it was taken as the optimal pH value for further adsorption experiments. Our results are consistent with those of other workers (Kapoor et al. 1999; Aksu 2001; Zhang et al. 1998; Goel et al. 2005; Mohanty et al. 2005; Hamadi et al. 2001; Garg et al. 2004) who observed that the removal of Cr(VI) decreases with the increase of pH. The pH dependence of metal adsorption can largely be related to the type and ionic state of the functional groups present on the adsorbent and the metal chemistry in solution (Mohanty et al. 2006). In the pH range of 1.0–6.0, chromium ions co-exist in different forms, such as $Cr_2O_7^{-}$, $HCrO_4^{-}$, $Cr_3O_{10}^{2-}$, and $Cr_4O_{13}^{2-}$, of which $HCrO_4^{-}$ predominates. As the pH of the solution increases, the predominant species become CrO_4^{2-} and $Cr_2O_7^{2-}$. More adsorption at acidic pH suggests that the lower pH results in an increase in H^+ ions associated with the adsorbent surface, resulting in sufficiently strong electrostatic attraction between a positively charged adsorbent surface and negatively charged chromate ions. Lesser adsorption of Cr(VI) at pH values greater than 6.0

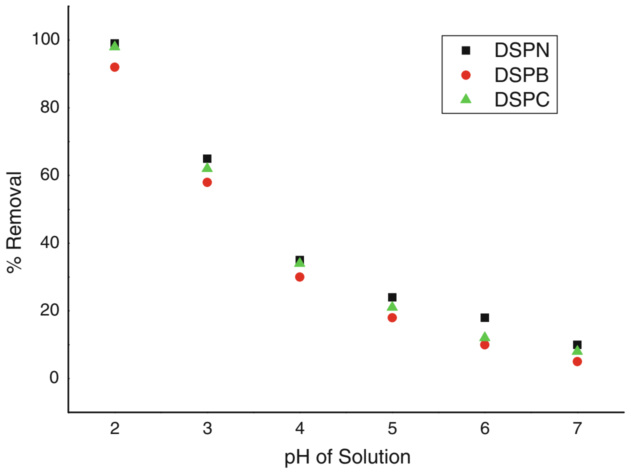

Fig. 3 Effect of pH on chromium removal by different forms of adsorbent (Cr conc. = 50 mg/L; stirring speed = 250 rpm; contact time = 60 and 30 min; adsorbent dose = 15, 12, and 5 g/L (DSPN, DSPB, DSPC)

may be due to the dual competition of both the anions CrO_4^{2-} and OH^- to be adsorbed on the surface of the adsorbent, noting that OH^- adsorption is favored by higher pH. This is in accordance with the earlier studies that have reported the removal of Cr(VI) by different adsorbents (Mohanty et al. 2005).

Adsorption kinetics

Studies comparing the three forms of biosorbents were conducted by varying the contact time from 5 to 120 min at a fixed initial chromium concentration (50 mg/L), stirring speed (250 rpm), temperature (25 °C), and pH (2.0). Maximum chromium was sequestered from the solution within 60 min by the different forms of adsorbent (Fig. 4). The chromium removal was 99 % by DSPC, 98 % by DSPB, and 92 % by DSPN within 60 min of contact time. In the case of DSPC, there was very fast adsorption, so keeping these observations in view, 30 min contact time was chosen for DSPC and 60 min for the DSPB and DSPN forms for further experiments.

Effect of adsorbent dose

The percent adsorption of Cr(VI) on different forms of adsorbent was studied at different adsorbent doses (250,500, 1,000, 1,500 and 2,000 mg/100 mL, respectively), keeping chromium concentration (50 mg/L), stirring speed (250 rpm), pH (2.0), temperature (25 °C), and contact time (30 and 60 min as obtained by kinetic studies) constant. The results showed that with increase in the adsorbent dose, the percentage adsorption of chromium was increased, and the maximum removal was observed with adsorbent dose of 5.0 g/L of DSPC, 12 g/L of DSPB, and 15 g/L of DSPN (Fig. 5). Increase in the percentage adsorption with adsorbent dose may be due to the increase in adsorbent surface area and availability of more adsorption sites (Mohanty et al. 2005). However, unit adsorption was decreased with increase in adsorbent dosage. As the adsorbent dose was increased from 2.5 to 20.0 g/L, the unit adsorption for DSPC, DSPB, and DSPN was decreased significantly. In the case of DSPN, it decreased from 1.74 to 0.30. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles

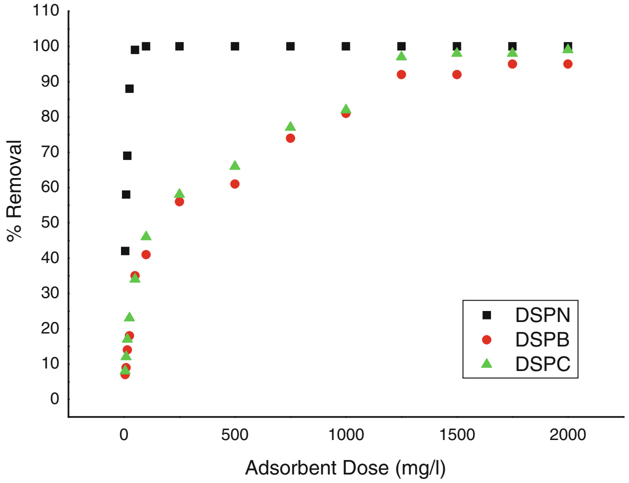

Fig. 5 Effect of adsorbent dose on chromium removal by different forms of adsorbent (chromium conc. = 50 mg/L; stirring speed = 250 rpm; pH 2.0; temperature = 25 °C and contact time = 60 and 30 min)

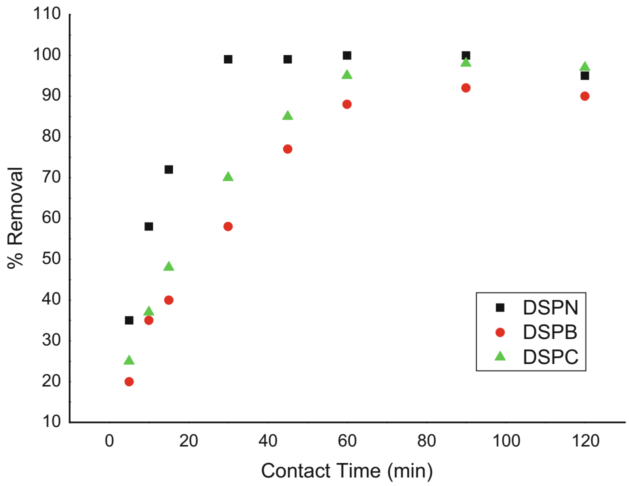

Fig. 4 Effect of contact time (min) of chromium on its removal by different forms of adsorbents (adsorbent dose = 15, 12, 5 g/L) chromium concentration = 50 mg/L, stirring speed = 250 rpm, pH 2.0, and temperature = 25 °C)

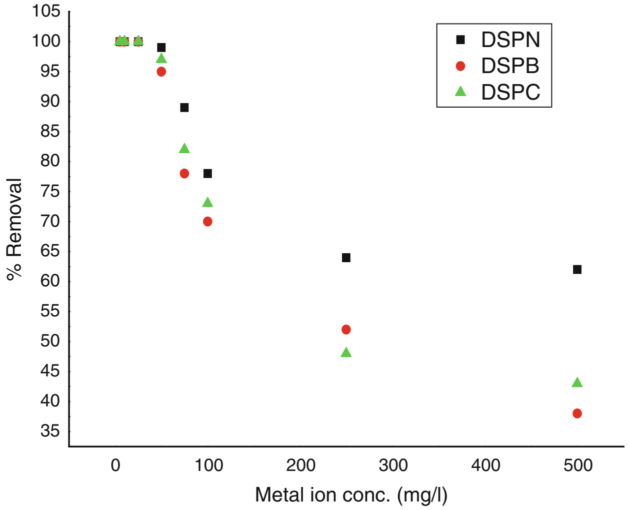

Fig. 6 Effect of initial concentration of chromium on its removal by different forms of adsorbent (adsorbent dose = 20 g/L, stirring speed = 250 rpm, pH 2.0, temperature = 25 °C, and contact time = 60 min)

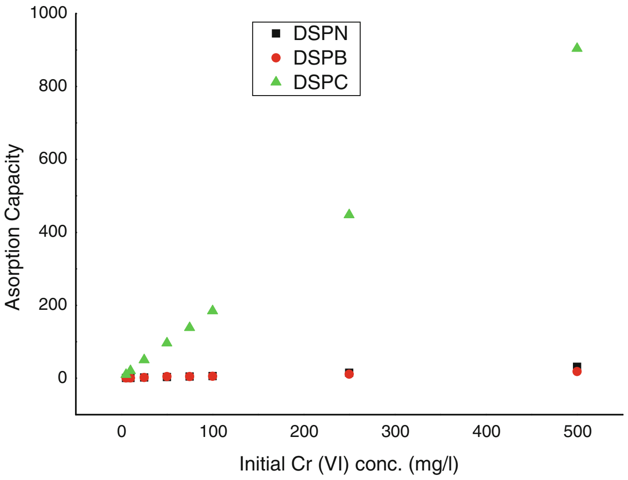

Fig. 7 Effect of adsorption of chromium per unit mass of adsorbent

Table 4 Adsorption capacity of different forms adsorbent at different initial chromium concentration

Initial chromium concentration (mg L^{-1})	DSPN (Q_e) (mg g^{-1})	DSPB (Q_e) (mg g^{1})	DSPC (Q_e) (mg g^{-1})
5	0.412	0.417	12
10	0.758	0.849	21
25	1.921	2.182	54
50	3.62	4.252	97
75	4.69	4.428	142
100	5.85	05.12	188
250	15.27	12.186	452
500	32.42	19.10	912

(Namasivayam et al. 1998). The order of percentage removal of chromium by studied adsorbent forms was: DSPC > DSPB > DSPN.

Effect of initial concentration

The percent adsorption of Cr(VI) with different adsorbents was studied by varying the chromium concentration (5,10, 25, 50, 75, 100, 250, and 500 mg/L), while keeping the adsorbent dose (15 g/L of DSPN, 12 g/L of DSPB, 5 g/L of DSPC), stirring speed (250 rpm), pH (2.0), temperature (25 °C), and contact time (60 and 30 min) constant. Higher concentrations of metal ions were used to study the maximum adsorption capacity of the adsorbents (Mohanty et al. 2006; Karthikeyan et al. 2005; Garg et al. 2007, 2008). The percent chromium adsorption was decreased with increase in initial chromium concentration (Fig. 6). However, the actual amount of chromium adsorbed per unit mass of the adsorbent was increased with increase in chromium concentration in the test solution (Fig. 7). As the chromium concentration in the test solution was increased from 5.0 to 500 mg/L, the unit adsorption of chromium on DSPC, DSPB, and DSPN increased from 12.00 to 912, 0.417 to 19.10, and 0.412 to 32.42 mg g^{-1}, respectively (Table 4). The adsorption capacity of an adsorbent, which is obtained from the mass balance on the sorbate in a system with solution volume V, is often used to acquire the experimental adsorption isotherms. Under the experimental conditions, the adsorption capacities of all the adsorbents for each concentration of chromium (VI) ions at equilibrium were calculated from the following equation (Goel et al. 2005)

$$q_e\left(\mathrm{mg\ g}^{-1}\right) = \left[\frac{C_i - C_e}{M}\right] \times V \tag{2}$$

where C_i is the initial concentration in at equilibrium, V is the volume of solution (in L), and M is the mass of the adsorbent. The order of percentage removal of chromium for different metal-ion concentration was DSPC > DSPB > DSPN.

Adsorption isotherms

The analysis of equilibrium data is important for developing an equation that can be used for design purposes. The simplest adsorption isotherm is based on the assumptions that every adsorption site is equivalent and the ability of a particle to bind is independent of whether or not adjacent sites are occupied. Classical adsorption models, such as the Langmuir and Freundlich models, have been extensively used to describe the equilibrium established between adsorbed metal ions on the biomass (q_e) and metal ions remaining in solution (C_e) at a constant temperature. The experimental results obtained for the adsorption of chromium on DSPC, DSPB, and DSPN at constant temperature (25 ± 1 °C) under pre-defined conditions of pH, adsorbent dose, and stirring speed obeyed the Freundlich adsorption isotherm. The Freundlich isotherm represents the relationship between the amount of metal adsorbed per unit mass of the adsorbent (x/m) and concentration of the metal ion in solution at equilibrium (C_e),

$$\log\frac{x}{m} = \log K_f + \frac{1}{n}\log C_e \tag{3}$$

where K_f (L g^{-1}) is an indicator of adsorption capacity and n (dimensionless) indicates the effect of concentration on the adsorption capacity and represents the adsorption intensity (dimensionless). The plot of log(x/m) versus log C_e for various initial concentrations was linear (figures not given), indicating the applicability of the classical adsorption isotherm to the DSPC-Cr(VI), DSPB-Cr(VI), and DSPN-Cr(VI) systems. The adsorption capacities (K_f) and the Freundlich constant (n) are given in Table 5.

Table 5 Freundlich and Langmuir models regression constants for different forms of adsorbents

Biosorbent	Freundlich Isotherm			Langmuir Isotherm		
	K_f (L g^{-1})	N	R^2	Q_o (mg g^{-1})	b (1 mg^{-1})	R^2
DSPN	0.6852	1.012	0.7262	2.82	0.04255	0.8021
DSPB	0.7218	0.0016	0.9821	3.52	0.0482	0.8912
DSPC	1.1027	0.0017	0.9027	1.47	0.0210	0.9842

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption on to the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is represented by the following equation,

$$\frac{c_e}{q_e} = \frac{1}{Q_0 b} + \frac{c_e}{Q_e} \tag{4}$$

where C_e is the equilibrium concentration (mg/L), q_e the amount adsorbed at equilibrium time (mg g^{-1}) and Q_o and b are the maximum quantity of metal ions per unit weight of biomass to form a complete monolayer on the surface (mg g^{-1}), whereas b is a constant related to the affinity of binding sites with the metal ions (1 mg^{-1}). The plots of $C_e/(x/m)$ versus C_e are linear, which shows that the adsorption of Cr(VI) follows a Langmuir isotherm model. The correlation coefficient (r) values were very high for all the adsorbents (Table 5) which indicates that the data fitted reasonably well to the Langmuir isotherm in the present adsorption studies. Value of slope found to be lesser than unity implied that significant adsorption took place at low metal-ion concentration.

Adsorption kinetics

Pseudo first- and second-order equations

The kinetics of adsorption is important, as it controls the process efficiency. For evaluating the adsorption kinetics of heavy metals, the pseudo-first order equation of Lagergren has been used to test experimental data,

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \tag{5}$$

where Q_e (mg/g) and Q_t (mg/g) are the amount adsorbed of heavy metal ions at equilibrium and at time t, respectively, and K_1 ($\min^{-1}$) is the rate constant of pseudo first-order adsorption. The application of this equation to the data of selected biosorbent (data not shown) indicated the inapplicability of the model.

The pseudo second-order kinetic model is linearly expressed as Ho and Mckay (1998).

$$t/Q_t = 1/K_2 Q_e^2 + t/Q_e \tag{6}$$

where K_2 (g/mg min) is the pseudo second-order rate constant, which can be calculated from the intercept of the straight line obtained from plotting $t/Q_t Vs t$. In addition, the initial sorption rate can be calculated using the relation (Koynucu 2008):

$$K_o = K_2 Q_e^2 \tag{7}$$

The perfect fit of the experimental data of DSP indicates the applicability of model for the adsorption of heavy metal ions on the selected biosorbent.

Film diffusion studies

Mass transfer plays an important role in sequestering of heavy metal from aqueous solution by the sorption process on the solid materials. In the present study, the mass transfer has been studied according to the model (Eq. 8) suggested by Mckay et al. assuming diffusion resistance within the particle to be negligible.

$$\ln\left(\frac{C_t}{C_0} - \frac{1}{1+mk}\right) = \ln\frac{mk}{1+mk} - \frac{1+mk}{mk} \cdot \beta_L \cdot S_S \cdot t \tag{8}$$

where C_t and C_0 (both in mg g^{-1}) are the respective concentrations of Cr(VI) ions at any time t and $t = 0$; k (1 g^{-1}) is the product of Q_0 and b and is known as Langmuir's constant; m (g l^{-1}) is the mass of adsorbent particles per unit volume, and S_s (cm^{-1}) is the outer area of the adsorbent per unit volume. The mass of m and S_s were calculated using Eqs. (9) and (10).

$$m = \frac{W}{V} \tag{9}$$

and

$$S_s = \frac{6m}{d_p \rho p (1 - \varepsilon_p)} \tag{10}$$

where W (g) is the weight of the adsorbent, V is the volume of the particle-free solution; d_p (cm) is the particle diameter, ρ_p is the density of the adsorbent and ε_p is the porosity of the particles. The value of k (1 g^{-1}) in Eq. (8) was calculated using Eq. (11).

$$k = Q^0 b_s \tag{11}$$

where Q_0 and b are the same terms as those used in Langmuir's model; k is also regarded as Langmuir's constant. The curve was found linear up to 60 min; this implies that throughout the process film diffusion plays a significant role in the adsorption of Cr(VI) from aqueous solution onto the studied adsorbents. The mass transfer coefficient β_L was calculated by multiplying the slope and intercept

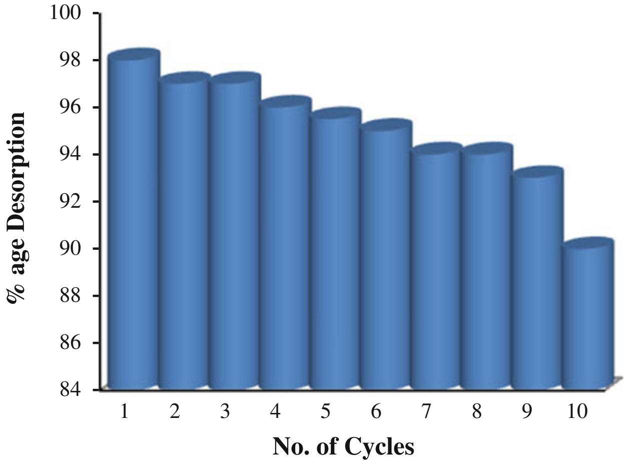

Fig. 8 Reusability of biosorbent with repeated sorption–desorption cycle

of the plot. The β_L at 30 °C was found 0.235 cm s^{-1}, respectively. The values indicate that the velocity of the mass transfer in the system is significant; hence, this process is recommended for industrial application.

Desorption efficiency and reusability

The regeneration of the biosorbent is one of the key factors in assessing of its potential for commercial applications. Two different desorption agents (1 M HCl and 1 M HNO_3) were used to desorbe the Cr(VI) from the biosorbent. The desorption efficiency of Cr(VI) was found to be 98 and 65 % using 1 M HCl and 1 M HNO_3 respectively. Therefore, 1 M HCl solution was selected as desorption agent. The reusability of the biosorbent was also tested in 10 consecutive sorption–desorption cycles. The results showed that the biosorbent offers potential to be used repeatedly in Cr(VI) sequestering process (Fig. 8).

Conclusions

The potential use of *Dalbergia sissoo* pods in its various forms as a biosorbent for sequestering of chromium (VI) was studied. This new biosorbent is able to remove the Cr(VI) ions from aqueous solutions, and the sorption capacity was strongly dependent on the adsorbent nature, the amount used, the initial metal-ion concentration, and the initial pH. The experimental data fitted well to the Freundlich and Langmuir equations, with good correlation coefficients. The experimental data also showed that the process followed a pseudo-second-order equation and both adsorbate and adsorbent were significant in the sorption rate determination. Chromium is adsorbed due to the strong interactions with the active sites of the adsorbent. Further, the utilization of biosorbent impregnated in the form of hydrated beads will also overcome the problem of release of soluble organic materials, while utilizing biomass in its natural form. Moreover, the natural form is not mechanically strong and has a wide size distribution, which can lead to the problems in the operations of reactors by blocking flow lines and clogging filters, while separation of biomass and effluent can be difficult and expensive. Thus, these results can be helpful in designing a wastewater system for the removal of such toxic heavy metal ions. Further work is in progress, in which modifications in the natural form of the biosorbent can lead to the enhanced removal and recovery of the metal ions from aqueous solutions.

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