Removal of hexavalent chromium from aqueous solution by agricultural waste biomass

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Abstract

In the present study adsorption of Cr(VI) from aqueous solutions onto different agricultural wastes, viz., sugarcane bagasse, maize corn cob and Jatropha oil cake under various experimental conditions has been studied. Effects of adsorbent dosage, Cr(VI) concentration, pH and contact time on the adsorption of hexavalent chromium were investigated. The concentration of chromium in the test solution was determined spectrophotometrically. FT-IR spectra of the adsorbents (before use and after exhaustion) were recorded to explore number and position of the functional groups available for the binding of chromium ions on to studied adsorbents. SEMs of the adsorbents were recorded to explore the morphology of the studied adsorbents. Maximum adsorption was observed in the acidic medium at pH 2 with a contact time of 60 min at 250 rpm stirring speed. Jatropha oil cake had better adsorption capacity than sugarcane bagasse and maize corn cob under identical experimental conditions. The applicability of the Langmuir and Freundlich adsorption isotherms was tested. The results showed that studied adsorbents can be an attractive low cost alternative for the treatment of wastewaters in batched or stirred mode reactors containing lower concentrations of chromium.
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Keywords: Adsorbent; Sugarcane bagasse; Maize corncob; Jatropha oil cake; Chromium(VI); FT-IR; SEM; Adsorption isotherms

1. Introduction

Water pollution by chromium is of considerable concern, as this metal is used in a variety of applications including steel production, electroplating, leather tanning, nuclear power plant, textile industries, wood preservation, anodising of aluminium, water-cooling and chromate preparation [1]. Chromium exists in trivalent and hexavalent forms in aqueous systems. The trivalent form is an essential nutrient [2], but hexavalent form is toxic, carcinogenic and mutagenic in nature. It is highly mobile in soil and aquatic system and also is a strong oxidant capable of being adsorbed by the skin [3]. The hexavalent form is 500 times more toxic than the trivalent form [4]. Human toxicity includes lung cancer, as well as kidney, liver, and gastric damage [5,6]. 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. The maximum levels permitted for trivalent chromium in wastewater are 5 mg/l and for hexavalent chromium are 0.05 mg/l [7]. In order to remove Cr(VI) from effluents to the permissible level, chromium is conventionally removed by precipitation [8], ion exchange [9] and adsorption [10] methods.

The commercially available activated carbon in granular or powder form is effective for the removal of various heavy metal ions. However, due to prohibitive cost their use is limited in developing countries like India. So there is a need to develop low cost and easily available adsorbents for the removal of heavy metal ions from the aqueous environment. Several types of biomasses have been investigated for their use in wastewater treatment for heavy metal removal [11–13]. An abundant source of potentially metal-sorbing biomass is cellulosic agricultural wastes. Although their sorption capacity is usually lesser than activated carbons but these materials could be an inexpensive substitute for the heavy metal laden wastewater's treatment

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[1]. Biomass is widely available, inexhaustible, and inexpensive material that exhibit significant specificity for the heavy metal ions.

Sugarcane bagasse, a byproduct of cane sugar processing, is generated in large quantities in India. Bagasse is either used as fuel by sugar mills or a raw material for paper manufacturing. Corncobs are highly voluminous, costless agricultural waste of corn milling process. They have a bulk density of $0.320 \, \text{g/cm}^3$ for a particle size range of 0.85–2.00 mm. Maize corncobs are very rich in cellulose and hemicelluloses which comprises $\approx 80\%$ of the dry matter. They contain many polymeric materials that possess many functional groups. Jatropha crop has recently been introduced in Northern India for biodiesel recovery from its seeds. There is no reported use of the Jatropha oil cake generated in the process of biodiesel recovery from its seeds. Yet no work has been reported on Jatropha oil cake as an adsorbent for the removal of heavy metal ions from the aqueous solutions.

In the present study an attempt has been made to explore the use of sugarcane bagasse, corncobs and Jatropha oil cake as sustainable adsorbents for chromium removal from aqueous systems under different experimental conditions.

2. Experiments

2.1. Materials and reagents

Sugarcane bagasse used in the study was collected from a sugar-mill located in Punjab (India). The collected bagasse was dried under sun and pith was separated manually. Then it was boiled with distilled water for 30 min to make it free from soluble sugars present in it. The material so obtained was dried at 120 °C in hot air oven for 24 h, then the material was grinded and sieved through the sieves of 150 MICS size.

Maize Corncobs were collected from the agricultural fields of a nearby village. The corncobs were boiled with distilled water for 30 min, dried at 120 °C in hot air oven for 24 h, ground and sieved (150 MICS). Jatropha oil cake was collected from a Jatropha processing industry, dried at 120 °C in hot air oven for 24 h, ground and sieved (150 MICS).

Stock solution of chromium (1000 mg/l) was prepared by dissolving potassium dichromate in double distilled water. The stock solution was diluted with distilled water to obtain the Cr(VI) solutions of desired concentration range. pH of the solutions was adjusted using 0.01M NaOH/0.01M HCl using Orion 420A pH meter. The Cr(VI) concentration was determined spectrophotometrically [Double Array UV–vis Spectrophotometer, Agilent 8453] by diphenyl-carbazide method [13]. FT-IR spectra of native and chromium-loaded adsorbents were recorded on Perkin-Elmer-RX 1FT-IR System. The surface morphology of the adsorbents was visualized via SEM (model JSM-840 JEOL microscope of JEOL Techniques LTD, Japan)

2.2. Adsorption experiments

Adsorption experiments were carried out using 100 ml of chromium solution of desired concentration (50 mg/l) at initial pH 2.0 and 2.0 g of adsorbent in 250 ml Erlenmeyer flask at $25 \pm 1 \, °\text{C}$ temperature (agitation speed 250 rpm). At predetermined time intervals (60 min), samples were separated by centrifugation at 4000 rpm for 10 min. The residual chromium concentration in supernatant was determined as given in Section 2.1. All experiments were replicated thrice for all the 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 the below given equation:

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100$$

FT-IR spectra were plotted of native and chromium loaded adsorbents on FT-IR spectrophotometer (Perkins-Elmer) to study the functional groups and binding sites. For the FT-IR study, 5 mg of adsorbent was encapsulated in 400 mg of KBr to prepare the translucent sample disks. From these FT-IR spectra, the presence of functional groups in the adsorbent was confirmed. The surface structure of the adsorbents was analyzed by scanning electronic microscope.

3. Results and discussion

Structurally agricultural materials consist of lignin, cellulose, hemi-cellulose and some proteins which make them effective biosorbents for heavy metal cations. Sugar cane bagasse contained 45% cellulose, 28% hemi-cellulose and 18% lignin [http://www.pakistan.gov.pk/ministries/ContentInfo.jsp?MinID =13&cPath=142_426&ContentID=2595]. Corncobs mainly contained cellulose (52%), hemi-cellulose (32%) and lignin (15.5%) [14]. Where as Jatropha oil cake contained crude fat (38%), carbohydrate (17%), crude protein (18%), fiber (15.5%) and ash content (5.3%) [http://www.jatropha.de/faq].

3.1. Fourier transform infrared analysis of adsorbents

The FT-IR spectra of sugarcane bagasse, maize corncob and Jatropha oil cake before and after sorption of chromium were used to determine the vibrational frequency changes in the functional groups in the adsorbents. The spectra of adsorbents were measured within the range of 500–4000 cm^{-1} wave number. The spectra were plotted using the same scale on the transmittance axis for all the adsorbents before and after adsorption. The FT-IR spectra of the adsorbents display a number of absorption peaks, indicating the complex nature of the studied adsorbents. Table 1 presents the fundamental peaks of the adsorbents before and after use. The spectra display a number of absorption peaks, indicating the complex nature of the examined adsorbents.

In sugarcane bagasse, the absorption peak around 3407.9 cm^{-1} indicates the existence of free and intermolecular bonded hydroxyl groups. The peaks observed at 2922.1 cm^{-1} can be assigned to stretching vibration of the C–H group. The peaks around 1620 cm^{-1} correspond to the C=C stretching that may be attributed to the lignin aromatic groups. The strong C–O band at 1058.2 cm^{-1} due to –OCH$_3$ group, also confirms the presence of lignin structure in sugarcane bagasse (Fig. 1).

Table 1
Some fundamental frequencies of the studied adsorbents (before and after use)

Adsorbent	Band positions (cm^{-1})				
	O–H	C–H	C=O	OCH$_3$	Bending vibrations
SCB native	3407.9	2922.1	1727.6	1051.2	609.8, 832.6
SCB-Cr(VI)	3402.4	2925.3	1727.2	1047.8	665.9, 611.5, 832.7
JOC native	3307.2 (broad)	2925.4	1742.0	1054.5	613.0
JOC-Cr(VI)	3321.2[a]	2926.1	1742.5	1058.0	560.2
MCC native	3403.9	2923.9	1728.5	1043.1	605.9
MCC-Cr(VI)	3345.0	2921.6	1727.7	1043.5	608.9

[a] With shoulder at 3771.4 cm^{-1}.

The additional peak at 609 cm^{-1} can be assigned to bending modes of aromatic compounds. The C–O band absorption peak is observed to shift to 1047 cm^{-1} when SCB are loaded with chromium (Fig. 2). It seems that this functional group participates in metal binding.

In Jatropha oil cake, the broad adsorption band is observed at 3307 cm^{-1} which can be attributed to the bonded –OH groups present in the structure. The other prominent peaks are due to –OCH$_3$ group and aromatic compounds. However in case of Jatropha oil cake—Cr(VI) there is remarkable shift in position and shape of the –OH group indicative of Cr(VI) binding mostly with –OH groups. Similarly the bending modes of aromatics have also shifted, indicative of association with the aromatic ring (Figs. 3 and 4).
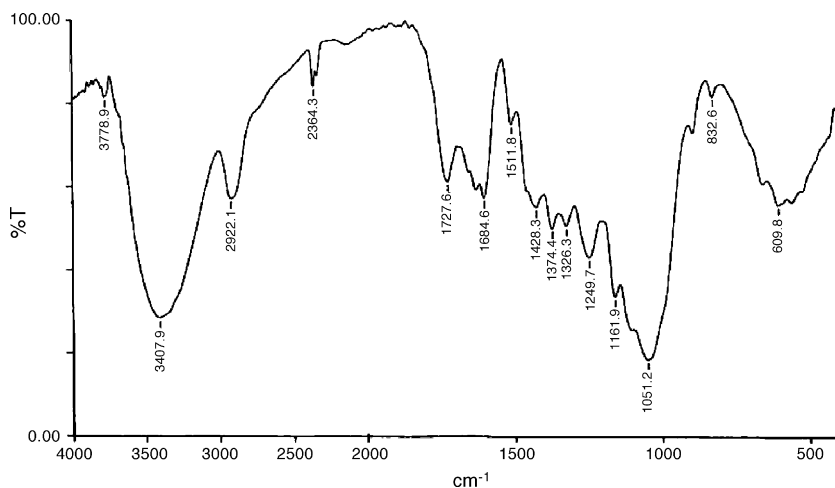

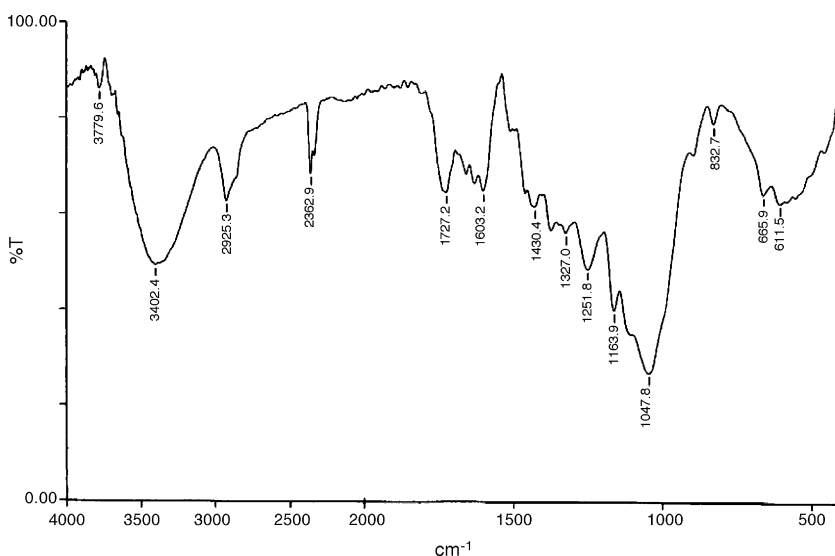Fig. 1. FT-IR spectra of sugarcane bagasse before use.

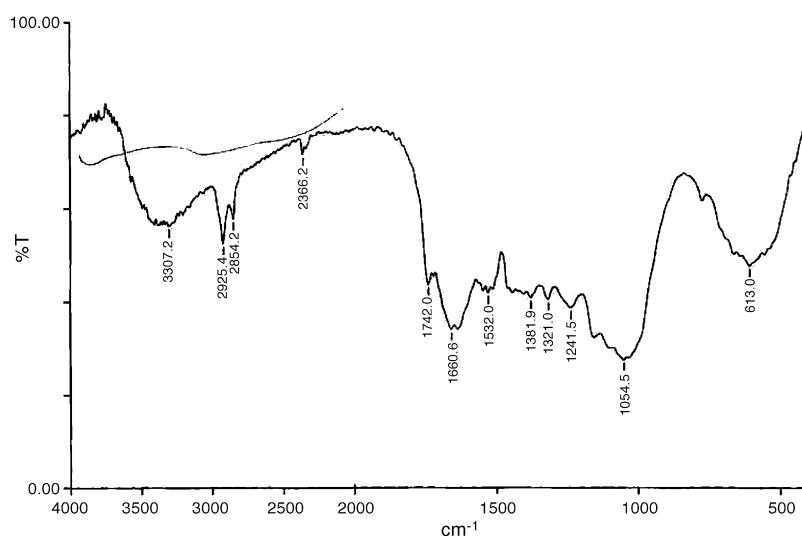Fig. 2. FT-IR spectra of treated sugarcane bagasse after use.

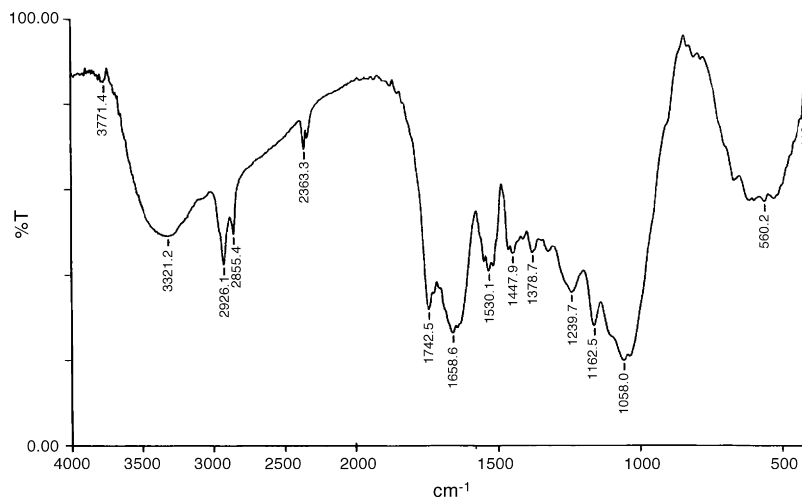Fig. 3. FT-IR spectra of Jatropha oil cake before use.

Fig. 4. FT-IR spectra of treated Jatropha oil cake after use.

In case of maize corncob, the major shift is only of –OH stretching modes from 3403.9 to 3345 cm^{-1} indicative of involvement of –OH groups in binding to chromium (Figs. 5 and 6). These changes in FT-IR spectra confirm the binding of chromium with functional groups present in the adsorbents.

The SEM enables the direct observation of the surface microstructures of different adsorbents. Studies are available which have reported the utilization of the scanning electron microscopy analysis for showing morphology of different adsorbent [15]. It can be observed from Fig. 7a–c that the surface morphology is different of the studied adsorbents.

3.2. Effect of pH

pH is one of the most important parameters while assessing the adsorption capacity of an adsorbent for metal ions sequestering from aqueous solution [11–13]. The pH of the system controls the adsorption capacity due to its influence on the surface properties of the adsorbent and ionic forms of the chromium in solutions. Adsorption experiments were carried out in the pH range of 2–10 keeping all other parameters constant (chromium concentration = 50 mg/l; stirring speed = 250 rpm; contact time = 60 min, adsorbent dose = 20 g/l, temp. = 25 °C). The pH of chromium solution was adjusted after adding the adsorbent. The maximum adsorption of chromium was 92, 97 and 62% for SCB, JOC and MCC, respectively at pH 2 (Fig. 8). There was a sharp decline in per cent adsorption with increase in pH of the aqueous solution. Chromium adsorption by MCC was decreased from 65 to 20% as pH was increased from 2 to 5. Chromium adsorption by JOC was decreased from 97 to 27% as pH was increased from 2 to 5. Similarly chromium adsorption by SCB was decreased from 85 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 other workers
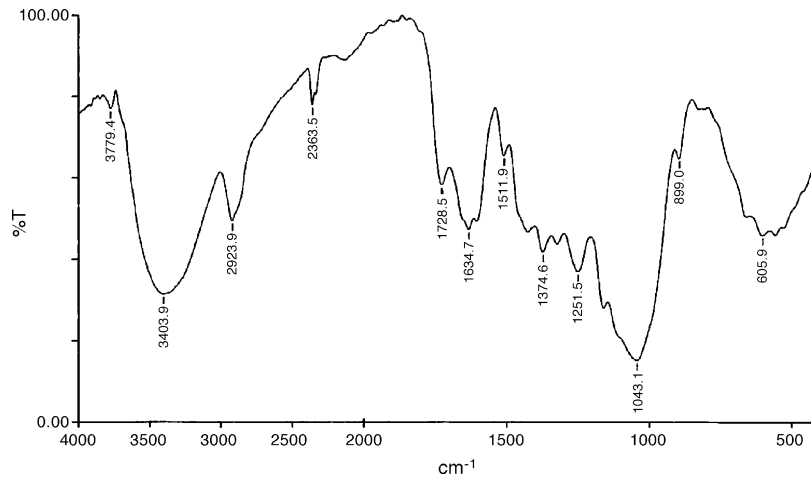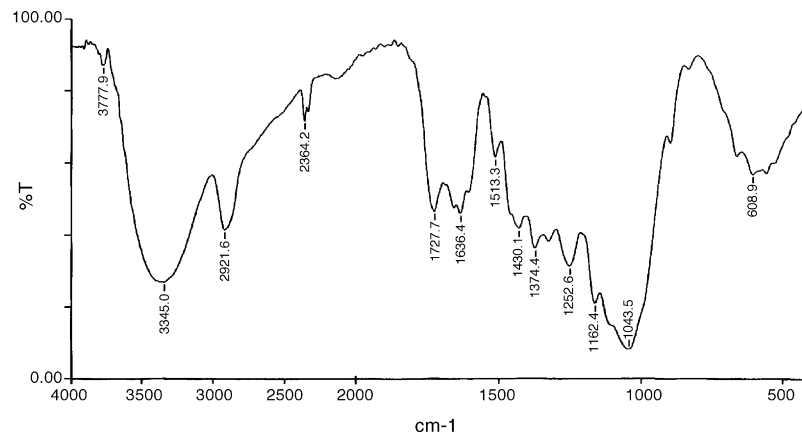
Fig. 5. FT-IR spectra of maize corncob before use.

Fig. 6. FT-IR spectra of treated MCC after use.

[11–13,15,16], that the removal of Cr(VI) decrease with the increase of pH (>5.0). 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 [16]. In the pH range of 1.0–6.0, chromium ions co-exists in different forms, such as $Cr_2O_7^-$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$ of which $HCrO_4^-$ predominates. As pH of the solution increases then the predominant species are CrO_4^{2-} and $Cr_2O_7^{2-}$. More adsorption at acidic pH indicates that the lower pH results in an increase in H^+ ions on the adsorbent surface that results in significantly strong electrostatic attraction between positively charged adsorbent surface and chromate ions. Lesser adsorption of Cr(VI) at pH values greater than 6.0 may be due the dual competition of both the anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent of which OH^- predominates. This is in accordance with the earlier studies that have reported the removal of Cr(VI) by different adsorbents [16–19]. It has also been postulated that under acidic conditions, Cr(VI) could be reduced to Cr(III) in the presence of an adsorbent.

Dichromate ion ($Cr_2O_7^{2-}$) under acidic conditions get reduced to Cr^{3+}

$$Cr_2O_7^{2-} + 14H + 6e^- \rightarrow 2Cr^{3+} + 7H_2O, \qquad E^0 = 1.33\,V$$
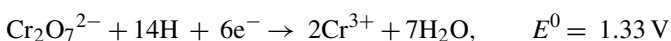
However in basic solutions it is much less oxidizing and exists as $Cr\,(OH)_3$

$$Cr_2O_7^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^-,$$

$$E^0 = -0.13\,V$$
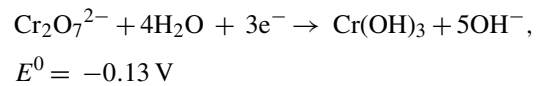
The plausible explanation for higher adsorption in acidic region is that the $Cr_2O_7^{2-}$ ion is oxidized to Cr^{3+}. Being small in size, it gets easily replaced by the positively charged species [17].

3.3. Adsorption kinetics

Studies on all the three biosorbents were conducted by varying the contact time from 5 to 120 min at fixed 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 different adsorbents (Fig. 9). The chromium removal was 92% by SCB, 97% by JOC and 62% by MCC with in 60 min of contact time. In case of MCC there is very little increase in the adsorption after 120 min of contact time (62–67%). So keeping these observations in view, 60 min contact time was opted for further experiments.
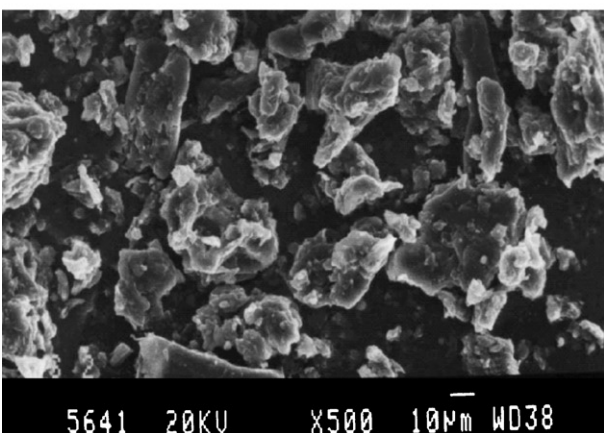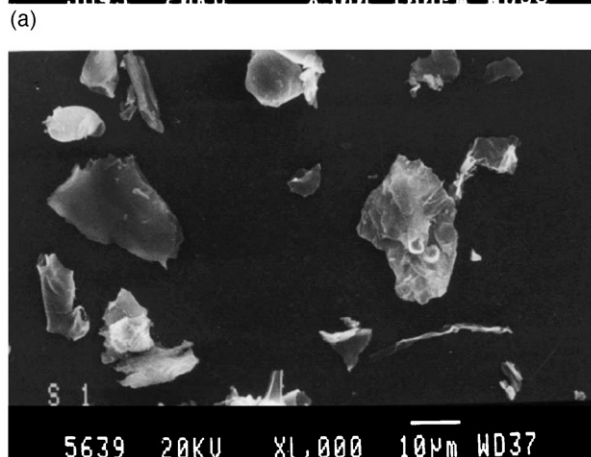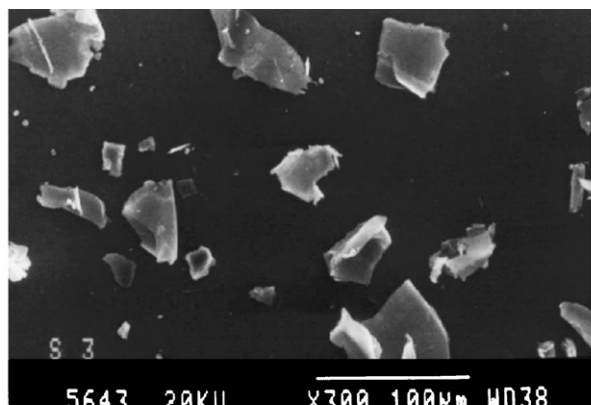
Fig. 7. (a) Scanning electron micrograph (SEM) of sugarcane bagasse, (b) scanning electron micrograph (SEM) of maize corncob, and (c) scanning electron micrograph (SEM) of Jatropha oil cake.

3.4. Effect of adsorbent dose

The per cent adsorption of Cr(VI) on different adsorbents was studied at different adsorbent doses [250,500, 1000, 1500 and 2000 mg/100 ml, respectively] keeping chromium concentration (50 mg/l), stirring speed (250 rpm), pH (2.0), temperature (25 °C) and contact time (60 min) constant. From the kinetic study it has been observed that most of the chromium removal by JOC (97%), SCB (92%) and MCC (62%) was achieved in 60 min (Fig. 9) so these experiments were conducted at 60 min
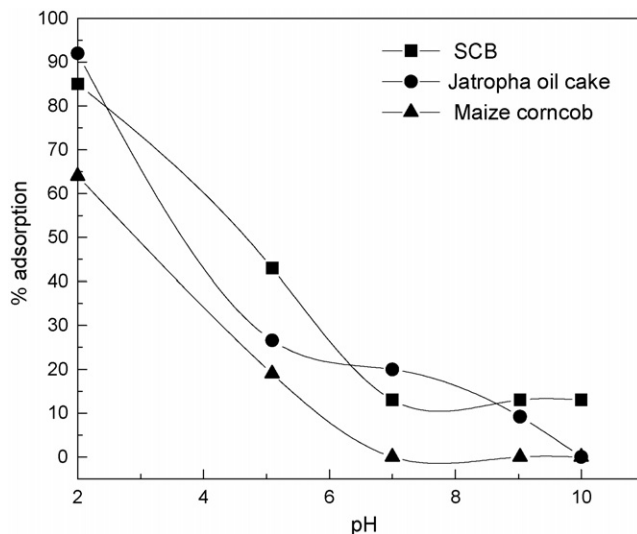

Fig. 8. Effect of pH on chromium removal by different adsorbents [chromium concentration = 50 mg/l; stirring speed = 250 rpm; contact time = 60 min; adsorbent dose = 20 g/l].

contact time. The results showed that with increase in the adsorbent dose, percentage adsorption of chromium was increased and the maximum removal was observed with adsorbent dose of 20 g/l of JOC, SCB and MCC (Fig. 10). Increase in the percentage adsorption with adsorbent dose may be due to the increase in adsorbent surface area and availability of more adsorption sites [20]. But unit adsorption was decreased with increase in adsorbent dosage (Table 2). As the adsorbent dose was increased from 2.5 to 20.0 g/l, the unit adsorption for JOC, SCB and MCC was decreased from 4.76 to 2.30 mg g^{-1}, 4.4 to 2.13 mg g^{-1} and 3.0 to 1.55 mg g^{-1} (Table 2). This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles [21]. The order of percentage removal of chromium by studied adsorbents was: Jatropha oil cake > sugarcane bagasse > maize corncob.
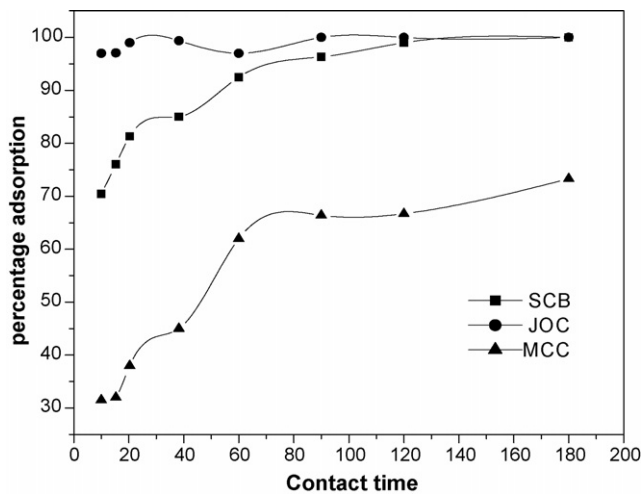

Fig. 9. Effect of contact time (in min) of chromium on its removal by different adsorbents [adsorbent dose = 20 g/l, chromium concentration = 50 mg/l, stirring speed = 250 rpm, pH 2.0, and temperature = 25 °C].
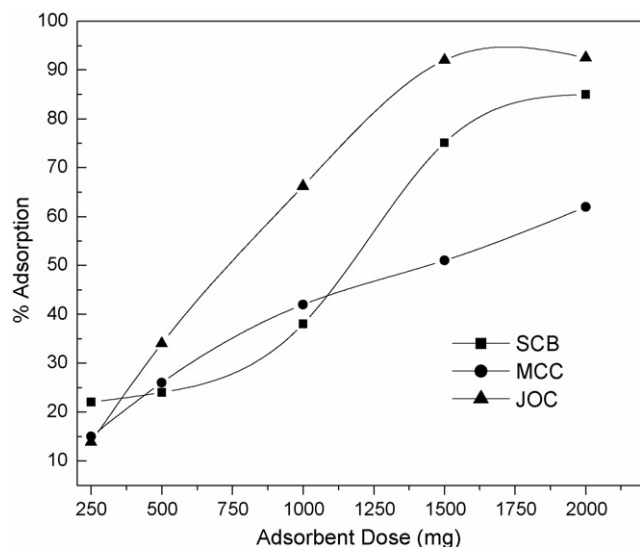
Fig. 10. Effect of adsorbent dose on chromium removal by different adsorbents [chromium conc. = 50 mg/l; stirring speed = 250 rpm; pH 2.0; temperature = 25 °C and contact time = 60 min].
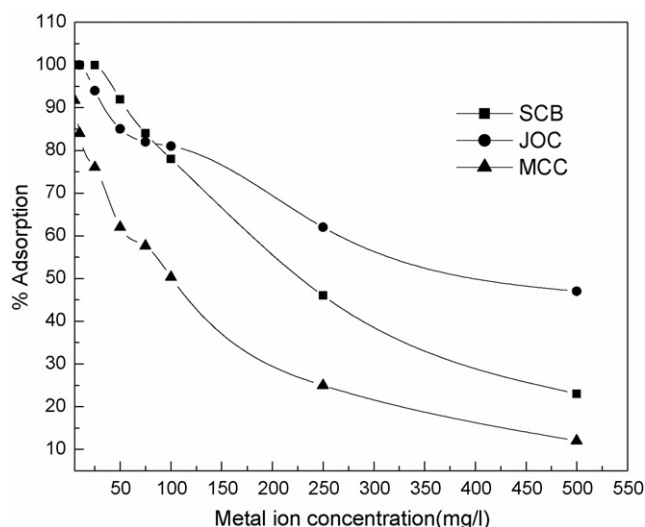

Fig. 11. Effect of initial concentration of chromium on its removal by different adsorbents [adsorbent dose = 20 g/l, stirring speed = 250 rpm), pH 2.0, temperature = 25 °C and contact time = 60 min].

3.5. Effect of initial chromium concentration

The percent adsorption of Cr(VI) with different adsorbents was studied by varying chromium concentration from [5,10, 25, 50, 75, 100, 250 and 500 mg/l] keeping adsorbent dose (20 g/l), stirring speed (250 rpm), pH (2.0), temperature (25 °C) and contact time (60 min) constant. Higher concentrations of metal ion were used to study the maximum adsorption capacity of the adsorbents [16,18]. The per cent chromium adsorption was decreased with increase in initial chromium concentration (Fig. 11). But the actual amount of chromium adsorbed per unit mass of the adsorbent was increased with increase in chromium concentration in the test solution. As the chromium concentration in the test solution was increased from 5.0 to 500 mg/l, the unit adsorption of chromium on JOC, SCB and MCC increased from 0.25 to 11.75 mg g^{-1}, 0.25 to 5.75 mg g^{-1} and 0.23 to 3.0 mg g^{-1}, respectively (Table 3). 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 [15]:

$$q_e(mg/g) = \frac{(C_i - C_e)V}{M}$$

where C_i is the initial concentration in solution, C_e the concentration at equilibrium, V, the volume of solution (in liter) and M is the mass of the adsorbent.

The order of percentage removal of chromium for different metal ion concentration is Jatropha oil cake > sugarcane bagasse > maize corncob.

3.6. Adsorption isotherms

Analysis of equilibrium data is important for developing an equation that can be used for design purposes. 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 sugarcane bagasse, Jatropha oil cake and maize corncob at constant temperature (25 ± 1 °C) under pre-defined conditions of pH, adsorbent dose and stirring speed obeyed the Freundlich adsorption isotherm. Freundlich adsorption isotherm represents

Table 2
Adsorption capacity of different adsorbents at different adsorbent doses

Adsorbent dose (g l^{-1})	SCB (q_e, mg g^{-1})	MCC (q_e, mg g^{-1})	JOC (q_e, mg g^{-1})
2.5	4.40	3.00	4.76
5.0	3.40	2.60	3.40
10.0	2.90	2.10	3.31
15.0	2.50	1.70	2.73
20.0	2.13	1.55	2.30

Table 3
Adsorption capacity of different adsorbents at different initial chromium concentration

Cr(VI) concentration (mg l^{-1})	SCB (q_e) (mg g^{-1})	MCC (q_e) (mg g^{-1})	JOC (q_e) (mg g^{-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

Table 4
Freundlich and Lagmuir models regression constants for different adsorbents

Adsorbent	Freundlich isotherm			Langmuir isotherm		
	K_f $(l\,g^{-1})$	n	R^2	Q_o $(mg\,g^{-1})$	b $(l\,mg^{-1})$	R^2
MCC	0.51	20	0.9954	0.28	1.78	0.8372
JOC	0.51	33.3	0.9955	0.82	2.38	0.9898
SCB	0.15	35	0.9797	0.63	1.51	0.9814

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)

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

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 this sugarcane bagasse-Cr(VI), Jatropha oil cake-Cr(VI) and maize corncob-Cr(VI) system. The adsorption capacities (K_f) and the Freundlich constant (n) are given in Table 4.

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.

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o}$$

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 ($l\,mg^{-1}$) [15]. The plots of $C_e/(x/m)$ versus C_e are linear which shows that the adsorption of Cr(VI) follows Langmuir isotherm model. The correlation coefficient (r) values were very high for all the adsorbents (Table 4) 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.

4. Conclusion

Jatropha oil cake, sugar cane bagasse and maize corncob have been evaluated as possible adsorbents for removal of Cr(VI) from aqueous solutions. This study showed that the maize corncob has lower adsorption efficiency (62%) than the Jatropha oil cake (97%) and sugar cane bagasse (92%) under studied experimental conditions. The chromium removal was highly dependent on pH, initial chromium concentration adsorbent mass and contact time. An initial pH of 2.0 was found to be optimum for maximum Cr(VI) removal by all the adsorbents. Higher chromium removal by JOC and SCB was possible provided the initial chromium concentration was low in the solution. The Cr(VI) ion adsorption on all the adsorbents is described by the Langmuir isotherm model. These all the three adsorbents are readily available in India, so they can be used by small-scale industries having low concentrations of Cr(VI) in wastewater using batched or stirred-tank flow reactors. The kinetic data obtained from the adsorption studies will be useful for fabrication and design of wastewater treatment plants using the, where standard material such as activated carbon were not available.

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