

Removal of Cr(VI) from aqueous solution using Bael fruit (*Aegle marmelos correa*) shell as an adsorbent

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ARTICLE INFO

Article history:

Received 30 October 2008

Received in revised form 29 January 2009

Accepted 12 February 2009

Available online 9 March 2009

Keywords:

Adsorption
Aegle marmelos correa
 Bael fruit shell
 Cr(VI) removal
 Low cost adsorbent

ABSTRACT

In this study, a new activated carbon prepared from non-usable Bael fruit shell (BS) has been used as an efficient low cost adsorbent to remove the Cr(VI) toxic metal from aqueous phase. Batch mode experiments have been performed as a function of initial pH of solution, agitation time, adsorbate concentration and adsorbent dosage. Maximum chromium removal was found at pH 2.0 in an equilibrium time of 240 min by adsorption-coupled reduction. The sorption data fitted satisfactorily with Langmuir as well as Freundlich adsorption model. Evaluation using Langmuir equation gave the monolayer sorption capacity as 17.27 mg/g. Chromium uptake (adsorption-coupled reduction) by Bael fruit shell activated carbon (BSAC) was best described by pseudo-second-order chemisorption model. The progressive changes on surface texture and the confirmation of chromium binding on adsorbent surface at different stages were obtained by the scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectrometer (FT-IR) analysis. Phosphoric acid activation played a significant role to develop the well defined pores on adsorbent surface. The results obtained in this study illustrate that the BSAC is expected to be an effective and economically viable adsorbent for Cr(VI) removal from aqueous system.

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1. Introduction

Advances in water and wastewater treatment technology need spur for the development of technologies that may be more effective and less costly. Nowadays, the contamination of water by toxic heavy metals through the discharge of industrial wastewater is a world wide environmental problem. The term “heavy metal” refers to the metallic elements having density greater than or equal to 6.0 g cm^{-3} [1]. The most familiar metals are cadmium (8.65 g cm^{-3}), chromium (7.19 g cm^{-3}), cobalt (8.90 g cm^{-3}), copper (8.95 g cm^{-3}), lead (11.34 g cm^{-3}), mercury (13.53 g cm^{-3}), nickel (8.91 g cm^{-3}) and zinc (7.14 g cm^{-3}). Among these toxic metals chromium has major impact on environment and it has both beneficial and detrimental properties. In aqueous phase chromium mostly exists in two oxidation states such as trivalent chromium (i.e., Cr^{3+} , $\text{Cr}(\text{OH})_2^{2+}$ or $\text{Cr}(\text{OH})_2^+$, etc.) and hexavalent chromium (i.e., HCrO_4^- , CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$, etc.). Most of the hexavalent compounds are toxic, carcinogenic, and mutagenic and even it can cause lung cancer also [2,3]. Cr(III) is essential for human nutrition (especially in glucose metabolism) and it is relatively innocuous and immobile. Cr(VI) ions mostly exists as H_2CrO_4 form at high acidic medium (pH ≈ 1.0). At

pH 2–6 there is equilibrium between $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- species, if the Cr(VI) concentration is less than 0.02 M, HCrO_4^- is predominant form, when Cr(VI) concentration is greater than 0.02 M the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) is the predominant species and under alkaline condition (pH > 8) it exists as chromate CrO_4^{2-} anion [4]. Chromium and its compounds are widely used in electroplating, leather tanning, cement, dyeing, metal processing, wood preservatives, paint and pigments, textile and steel fabrication industries. These industries produce large quantities of toxic metal wastewater effluents. But the maximum exit Cr(VI) concentration based on US-EPA guidelines for potable water is 0.05 mg/l and the United Nations Food and Agricultural Organization recommended maximum level for irrigation waters is 0.1 mg/l [5].

In general, a wide range of processes have been reported to eliminate the Cr(VI) from water and wastewater such as chemical precipitation, electrochemical reduction, sulphide precipitation, cementation, ion-exchange, reverse osmosis, electro dialysis, solvent extraction and evaporation, etc. [6]. The application of such methods is however cost intensive and is unaffordable for large-scale treatment of wastewater. Hence, more economical means such as adsorption for the removal of toxic metals have been sought for. Therefore, there is a need to search an effective low cost adsorbent for economical wastewater treatment. In recent years, development of surface modified activated carbons using plant biomass is generating a diversity of activated carbon with superior adsorption

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Nomenclature

$1/n$	adsorption intensity (dimensionless)
b	Langmuir isotherm constant (l/g)
C_e	equilibrium chromium concentration (mg/l)
C_f	final residual metal concentration (Cr(VI) and Cr(III)) (mg/l)
C_o	initial chromium concentration (mg/l)
k'	second order rate constant
K	Freundlich isotherm constant (mg/g)
K_{ad}	first order rate constant
q_e	amount of total chromium adsorbed per unit mass of adsorbent (mg/g)
$q_{e, exp}$	experimental value of amount of chromium adsorbed per unit mass of adsorbent (mg/g)
q_t	amount of solute adsorbed at any time (mg/g)
$q_{t, cal}$	calculated value of amount of solute adsorbed at 't' time (mg/g)
Q_o	adsorption capacity (mg/g)
R_L	separation factor or equilibrium constant (dimensionless)
t	agitation time (min)
v	volume of aqueous solution (ml)
w	weight of adsorbent (g)

capacity. That are available in large quantities and it can be disposed of without regeneration due to their lower cost. A variety of natural plant biomass like *Terminalia arjuna* nuts, *Ectodermis* of *Opuntia*, sugar industrial waste, tamarind hull, tea waste, *Azadirachta indica* (neem) leaf powder, pomegranate peel, olive bagasse and *Acacia arabica*, etc. are used in the previous investigations. Literature survey reveals that the plant biomass is capable of reducing Cr(VI) to Cr(III) due to the active participation of its several anionic functional groups like hydroxyl, carbonyl, carboxyl, sulfhydryl and phosphoryl groups [6–9]. For the preparation of activated carbon from plant biomass, many researchers suggested that the optimum temperature required to produce the high quality activated carbon by chemical activation is 500–700 °C [10–12].

In this study, the surface modified Bael fruit shell has been used as a new low cost adsorbent to remove the Cr(VI) from aqueous solution. This waste shells are not put to any use and available at low prices. It helps to reduce the cost of waste disposal and provide an alternative sorbent to the existing commercial activated carbon. The operating parameters that affect the adsorption process such as pH, initial Cr(VI) concentration, agitation time and adsorbent dosage were investigated. Moreover, this is the first attempt to develop an activated carbon from Bael fruit shell biomass. Hence, further investigations required to improve its quality and regeneration capacity for further possible applications including various industrial effluents.

2. Materials and methods

2.1. Preparation of synthetic sample

A stock solution of Cr(VI) (1000 mg/l) was prepared by dissolving appropriate quantity of AR grade $K_2Cr_2O_7$ (Merck India Ltd.) in 1000 ml of Elix water from Millipore® purification unit. The stock solution was further diluted with deionised water to desired concentration for obtaining the test solutions. The initial metal ion concentrations ranged from 50 to 125 mg/l were prepared.

2.2. Preparation of adsorbent

Dry BS's were collected from nearby locality and it was washed with sufficient amount of tap water to remove water-soluble impurities and surface adhered particles. The washed shells were then dried at 110 °C in a hot air oven, shredded using hammer mill and sieved in the size range of 600–860 μm . Chemical activation of BS was done using 88% ortho-phosphoric acid in 1:1 weight ratio (Bael shell:acid) and dried at 110 °C for 2–3 h. The dried material was calcined in a muffle furnace starting from room temperature to 600 °C (time period of 1.5 h) [10,11] and then soaked in 2% NaHCO_3 to remove the residual acid that were left on the adsorbent. Finally, the adsorbent was dried at 110 °C for 2 h and cooled in a dessicator until further use.

2.3. Batch adsorption experiments

Adsorption experiments were carried out in batch mode at ambient temperature. In order to investigate the nature of Cr(VI)–BSAC interaction, initially the effect of pH on percentage removal was carried out and then further experiments on the effect of agitation time, initial concentration and adsorption dosage were conducted by using optimized pH. Only one parameter was changed at a time while others were maintained constant. In the first set of experiment, percentage adsorption was studied at various pH of (1–8) at BSAC of 1 g/100 ml, initial Cr(VI) of 75 mg/l and the predetermined time (240 min) in a rotary shaker at a speed of 160 rpm using series of clean 250 ml conical flasks. Next second set of experiments were conducted with various agitation time, various initial Cr(VI) concentration (from 50 to 125 mg/l) at constant adsorbent (1 g/100 ml) dose and at optimized pH 2.0. In the third set of experiment BSAC dose was varied (0.5–2.0 g/100 ml) while other parameters such as initial Cr(VI) concentration (75 mg/l), optimum time (240 min) and optimum solution pH kept constant. After completion of every set of experiments the supernatant was separated by filtration using Whatman filter paper no. 42 and only 10 ml of each sample was stored for residual chromium analysis. The pH of each solution was adjusted using required quantity of 1N HCl (or) 1N NaOH before mixing the adsorbent. Three replicates per sample were done and the average results are taken for calculation.

2.4. Metal analysis and adsorbent characterisation

Final residual metal (Cr(III) and Cr(VI)) concentration after adsorption was directly measured by flame atomic absorption spectrophotometer (AAS) (Varian spectra, AA 240) with an air–acetylene flame. To estimate the percentage removal of chromium from aqueous solution the following equation was used:

$$\% \text{ Adsorption} = \frac{C_o - C_f}{C_o} \times 100 \quad (1)$$

Metal uptake (q_e) at equilibrium time was calculated by mass balance expression:

$$w(q_e - q_o) = v(C_o - C_e) \quad (2)$$

When $q_o = 0$ Eq. (2) becomes equivalent to

$$q_e = \frac{(C_o - C_e)v}{1000w} \quad (3)$$

where q_e (mg/g) is the amount of chromium adsorbed, C_o is the initial metal concentration (mg/l), C_f and C_e are the final residual concentrations of chromium (mg/l) after adsorption at time 't' and at equilibrium time, respectively, that are directly measured by AAS at 357.9 nm wavelength without any calculation, v is the volume of aqueous solution (ml) and w is the adsorbent weight (g).

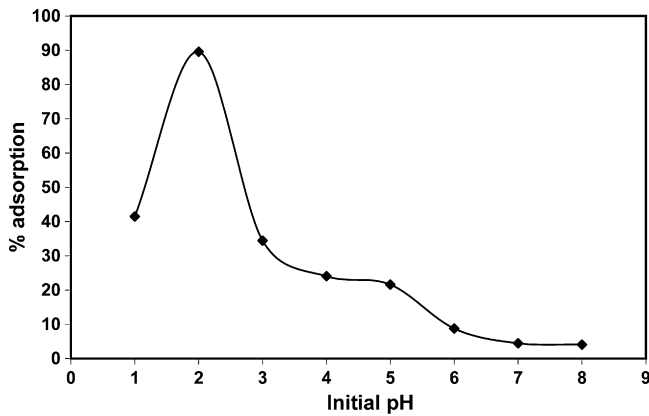


Fig. 1. Effect of pH on percentage adsorption of chromium: ($C_0 = 75$ mg/l, $w = 1$ g, $v = 100$ ml, $t = 240$ min).

Scanning electron microscopy (SEM) (Leo, 1430 vp, Carl Zeiss, German) characterisation was carried out to observe the surface texture and porosity for three states of BS such as BS without activation, BS after activation and BSAC after adsorption. Energy dispersive X-ray spectroscopy (EDS) analysis was employed for further confirmation of chromium adsorption over the surface of the BSAC.

To resolve the functional groups and its wave numbers, spectra analysis was done for BSAC before and after chromium adsorption using Fourier transform infrared spectrometer (FT-IR) (Perkin Elmer, PE-RXI) in the range of $500\text{--}4000\text{ cm}^{-1}$. In this analysis, finely grounded sorbent was encapsulated with KBr in the ratio 1:20 in order to prepare the translucent sample disks.

3. Results and discussion

3.1. Determination of optimum parameters and adsorption studies

Fig. 1 shows the effect of pH on percentage adsorption of chromium. It was observed from Fig. 1 that the adsorption of Cr(VI) decreased with increase in initial pH from 2.0 to 8.0. The maximum removal was occurred at initial pH 2.0 for BSAC. At lower pH the surface area of the adsorbent was more protonated and competitive negative ions adsorption occurred between positive surface and free chromate ion. Adsorption of Cr(VI) at pH 2.0 shows the bind of the negatively charged chromium species (HCrO_4^-) occurred through electrostatic attraction to the positively charged (due to more H^+ ions) surface functional groups of the adsorbent (discussed later in Section 3.4.3). But in highly acidic medium (pH ≈ 1) H_2CrO_4 (neutral form) is the predominant species of Cr(VI) as reported by Agrawal et al. [4]. Hence, at pH 1.0 percentage adsorption decreased due to the involvement of less number of HCrO_4^- anions on the positive surface. At higher pH due to more OH^- ions adsorbent surface carrying net negative charges, which tend to repulse the metal anions (CrO_4^{2-}) [13]. However, there is also some percentage adsorption at pH > 2.0 but the rate of adsorption is reduced. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent or physisorption due to weak undirected Van der Waals forces of attraction [12,14]. When reaction pH increased after 2.0 Cr(III) adsorption also enhanced due to gradual increasing the negative charge on adsorbent. But the adsorption-coupled reduction of Cr(VI) to Cr(III) was less after pH 2.0 due to the less adsorption of HCrO_4^- (discussed later in Section 3.3). At pH ≈ 8.0 CrO_4^{2-} is the predominant form it was repulsed by high negative surface [3].

Fig. 2a depicts the effect of agitation time on Cr(VI) removal at various initial (50–125 mg/l) concentrations. The rate adsorption increased with increase in agitation time before equilibrium (240 min) is reached for all initial concentration. The amount of chromium adsorbed rises sharply with increasing the time for first 30 min, indicating that there are plenty of readily accessible sites available for increasing the rate of adsorption. Eventually, all plots in Fig. 2a reached their maximum level that indicates the saturation level of adsorbent sites. The concentration of solutions did not change after 240 min which are called as equilibrium concentrations (C_e). Further increasing the time after equilibrium shows the rate of adsorption becomes almost constant up to the end of the experiment.

The effect of initial concentration on percentage adsorption can also be seen in Fig. 2a. The percentage adsorption decreased from 91.9% to 85.5% as the initial concentration of Cr(VI) is increased from 50 to 125 mg/l for 1 g/100 ml of adsorbent at equilibrium contact time of 240 min. Interestingly, it has been seen that the adsorption capacity of the unit mass of the adsorbent (1 g) found to be increased from 4.61 to 10.7 mg/g as the Cr(VI) concentration increased from 50 to 125 mg/l. Similar observation has been reported by Garg et al. [15] for Cr(VI) removal using jatropha oil cake, sugarcane bagasse and maize corn cob. This may be due to the fact that the increased Cr(VI) concentrations provide the maximum driving force to overcome all the mass transfer resistances

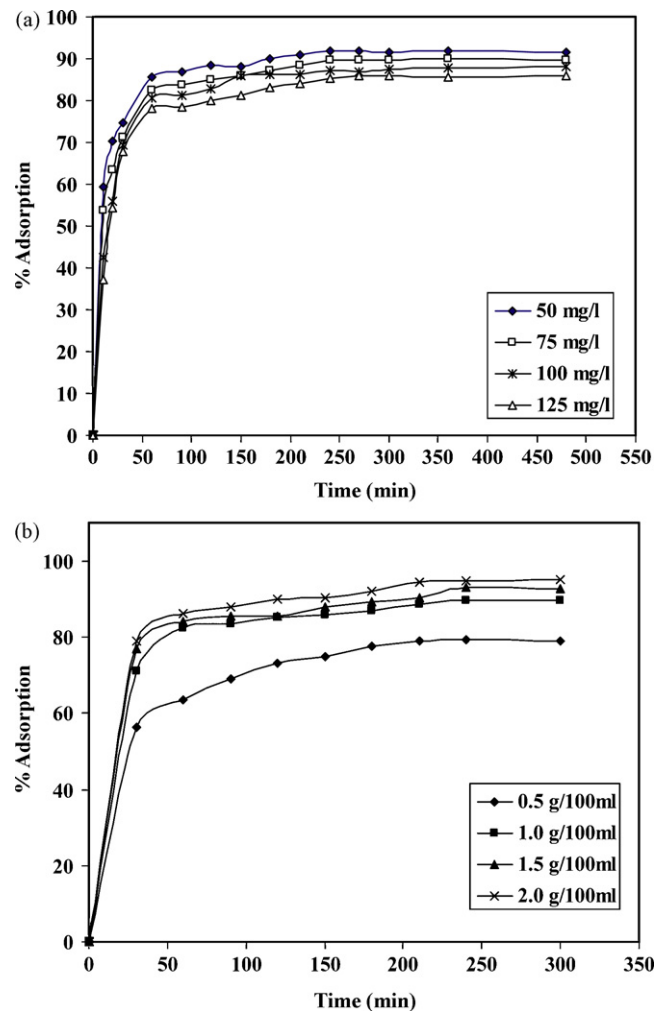


Fig. 2. Effect of agitation time and initial concentration on percentage adsorption of chromium: (pH 2.0, $v = 100$ ml, $w = 1$ g). (b) Effect of adsorbent dose on percent adsorption of chromium: (pH 2.0, $C_0 = 75$ mg/l, $v = 100$ ml, $t = 240$ min).

Table 1
Isotherm constants for adsorption of chromium onto BSAC.

Adsorbent	Langmuir constants			Freundlich constants		
	Q_0 (mg/g)	b (l/mg)	R^2	K (mg/g)	$1/n$	R^2
BSAC	17.27	0.0848	0.9865	2.110	0.5586	0.9996

Table 2
Langmuir separation factor (R_L).

Initial concentration (mg/l)	R_L value
50	0.1908
75	0.1359
100	0.1055
125	0.0862

of metal ions from the aqueous phase to solid phase resulting in higher probability of collision between metal ions and the active sites [14].

The influence of adsorbent dosage on Cr(VI) sorption was studied by varying the amount of adsorbent from 0.5 to 2.0 g. Fig. 2b depicts that the percentage adsorption of chromium increased from 79.4% to 94.9% with increase of adsorbent dosage from 0.5 to 2.0 g/100 ml solution. This trend is obvious because as adsorbent dose increases the number of adsorbent particle also increases, that makes the greater availability of exchangeable sites for adsorption. Similar observation has been reported by other investigators on Cr(VI) sorption [14,15]. However, unit adsorption capacity of BSAC has a reverse trend to the percentage adsorption. It was found to be 11.87 mg/g adsorption capacity at 0.5 g and 3.56 mg/g capacity at 2.0 g adsorbent dosage in an equilibrium time of 240 min. This behaviour is due to adsorption sites remaining unsaturated during adsorption reaction and may be due to the overlapping and aggregation of adsorption sites occurs as a result to overcrowding of adsorbent particles when dose increased from 0.5 to 2.0 g/100 ml [16,17].

3.2. Adsorption isotherm studies

To examine the relationship between adsorbent and adsorbate at equilibrium and the maximum sorption capacity of adsorbent, sorption isotherm models namely the Langmuir and Freundlich isotherm are widely used. Both the isotherm model fittings were analysed in this study for various initial Cr(VI) concentrations ranging from 50 to 125 mg/l at equilibrium time.

The Langmuir equation was chosen to estimate the maximum adsorption capacity corresponding to the complete monolayer coverage on homogenous adsorbent surface without any interaction between adsorbed ions.

Langmuir equation is commonly represented as

$$q_e = \left(\frac{Q_0 b C_e}{1 + b C_e} \right) \quad (4)$$

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_0 b} \right) + \left(\frac{C_e}{Q_0} \right) \quad (\text{linear form}) \quad (5)$$

Table 3
Adsorption kinetic constants for chromium adsorption by BSAC.

Initial concentration (mg/l)	First-order kinetic model				Second-order kinetic model		
	$q_{e, \text{exp}}$ (mg/g)	k_{ad} (l/min)	$q_{e, \text{cal}}$ (mg/g)	R^2	k' (g/mg/min)	$q_{e, \text{cal}}$ (mg/g)	R^2
50	4.595	0.0154	1.3187	0.9410	0.0353	4.661	0.9999
75	6.719	0.0154	2.2480	0.9423	0.0183	6.873	0.9999
100	8.719	0.0200	3.7282	0.9457	0.0119	9.009	0.9999
125	10.682	0.0154	4.3521	0.9287	8.2488×10^{-3}	11.049	0.9997

where q_e is the amount of chromium ions adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of metal ions (mg/l), Q_0 is a measure of adsorption capacity of adsorbent (mg/g), b is the Langmuir constant which is a measure of energy of adsorption (l/mg). The experimental data were fitted into Eq. (5) for linearization by plotting C_e/q_e against C_e (figure not given) and good fit of this equation reflects monolayer adsorption. The values of Q_0 and b (Table 1) obtained in this work were 17.27 mg/g and 0.0848 l/mg, respectively. The separation factor or equilibrium constant (R_L) is represented by:

$$R_L = \left(\frac{1}{1 + b C_0} \right) \quad (6)$$

where C_0 is the initial concentration of Cr(VI) ions (mg/l) and b is the Langmuir constant which indicates the nature of adsorption. The separation factor (R_L) indicates the isotherm shape and whether the adsorption is favourable or not. If $R_L = 0$, adsorption is irreversible; $0 < R_L < 1$, adsorption is favourable; $R_L = 1$ adsorption is linear and $R_L > 1$ adsorption is unfavourable. The R_L factor for various initial concentrations of Cr(VI) sorption on BSAC obtained in this work was in the range of $0 < R_L < 1$ is presented in Table 2. These values are in very good agreement with the reported values in the literature [18,19].

The Freundlich empirical equation was chosen to describe the exponential distribution of active centres, characteristic of heterogeneous surface and infinite surface coverage.

Freundlich equation is commonly represented by:

$$q_e = K C_e^{1/n} \quad (7)$$

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (\text{linear form}) \quad (8)$$

where K is the measure of adsorption capacity and $1/n$ adsorption intensity. The plot of $\log q_e$ against $\log C_e$ shows (figure not given) the isotherm data is well fitted with the Freundlich model ($R^2 = 0.9996$). Slope and intercept give the values of $1/n$ and K . Freundlich constants are also presented in Table 1. The value of $1/n$ is less than 1 indicates a favourability of adsorption. The Freundlich equation frequently gives an adequate description of adsorption data over a restricted range of concentration, even though it is not based on the theoretical background. Apart from homogenous surface, the Freundlich equation is also suitable for a highly heterogeneous surface and an adsorption isotherm lacking a plateau, indicating a multi-layer adsorption.

3.3. Adsorption kinetics

The adsorption kinetics described by the relationship between contact time and metal uptake by BSAC for four various initial Cr(VI) concentrations (50 to 125 mg/l) is discussed below.

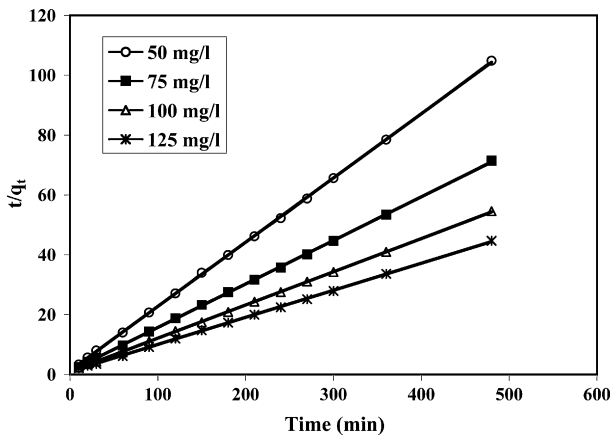


Fig. 3. Pseudo-second-order kinetic plot for adsorption of chromium on BSAC: (pH 2.0, $v=100$ ml, $w=1$ g).

In many investigations, the adsorption kinetics by any plant biomass has been tested for the first order expression given by Lagergren. However, Several investigators have shown that pseudo-second-order kinetics can describe the Cr(VI)-adsorbent interactions very well for plant biomass adsorbents [2,6].

The integral form of Lagergren equation is

$$\log(q_e - q_t) = \log q_e - \frac{K_{ad}}{2.303} t \quad (9)$$

The pseudo-second-order equation is

$$\frac{t}{q_t} = \left(\frac{1}{k'q_e^2} \right) + \frac{t}{q_e} \quad (10)$$

where q_e is the amount of Cr(VI) adsorbed at equilibrium per unit weight of adsorbent (mg/g), q_t is the amount of solute adsorbed at 't' time (mg/g), t is the agitation time (min) and K_{ad} is the adsorption equilibrium rate constant of pseudo-first-order reaction. The slope and intercept of plot of $\log(q_e - q_t)$ against time were used to determine the first-order rate constant K_{ad} , k' is the rate constant of pseudo-second-order adsorption (g/mg/min). It is evident from values of R^2 , $q_{e, cal}$ and $q_{e, exp}$ as presented in Table 3 that experimental data are not fitted well for all Cr(VI) concentrations. Hence, the adsorption mechanism cannot be well described by pseudo-first-order kinetics. The slope and intercept from the plot t/q_t against time (Fig. 3) were used to calculate the (k'). The well fitted linear regressions of various concentrations and their correlation coeffi-

cients (R^2) showed (Table 3) that the pseudo-second order model describes the indication of a chemisorptions mechanism for whole concentration range.

The adsorption mechanism based on ionic equilibrium between Cr(VI) and Cr(III) is complicated for plant biomass adsorbent but it can be related to surface complexation reactions with protonated sites. Recently, Park et al. [8] reported (at pH 2.0) that in Cr(VI) adsorption chromium bound on the surface of 16 adsorbents were mostly or totally in trivalent form with X-ray photoelectron spectroscopy (XPS) confirmation. Two possible mechanisms such as direct and indirect reduction of Cr(VI) to Cr(III) can be suggested in Cr(VI) removal (Fig. 4). In first mechanism, Cr(VI) is directly reduced to Cr(III) by surface electron-donor groups of the adsorbent and the reduced Cr(III) forms complexes with adsorbent or remains in the solution. This Cr(III) is not adsorbed by adsorbent at pH 2.0. But in second mechanism, the adsorption-coupled reduction of Cr(VI) to Cr(III) occurred on the adsorbent sites. It consists of three steps; (i) the binding of anionic ($HCrO_4^-$) Cr(VI) to the positively-charged groups present on the surface of the adsorbent, (ii) the reduction of adsorbed Cr(VI) to Cr(III) taking place by adjacent electron-donor ($C=O$, $O-CH_3$) groups of adsorbed sites and (iii) a part of surface reduced Cr(III) is released into the aqueous solution due electronic repulsion between the positively-charged groups of adsorbent and the surface bound Cr(III). Similar behaviour was observed by Suksabye et al. [20] and Sawalha et al. [21] also, they reported that the most of the chromium bound on the adsorbent was in Cr(III) form and this reduction might be bound with $C=O$ and $O-CH_3$ groups of adsorbents. At pH 2.0 this reduced Cr(III) is in Cr^{3+} form and it cannot be adsorbed by adsorbent [3,22]. When reaction pH was increased further from 2.0 the Cr(VI) adsorption-coupled reduction was less, hence the Cr(III) fraction in the solution decreased steadily. Similar behaviour was observed by Dakiky et al. [23] for both Cr(VI) and Cr(III) removal for seven adsorbents, zero removal of Cr(III) and maximum removal of Cr(VI) were occurred at pH 2.0. Finally, the removal behaviour and the kinetic model of Cr(VI) by BSAC can be described only by adsorption-coupled reduction of Cr(VI) to Cr(III) over the whole range of adsorption at optimum pH 2.0 and no Cr(III) removal is taking place directly at pH 2.0.

3.4. Characterisation of adsorbent

3.4.1. SEM characterisation

It could be observed from Fig. 5a that prior to activation BS having regular plain surface with no pores on it, whereas Fig. 5b (i.e., BS after activation) reveals the progressive changes and well

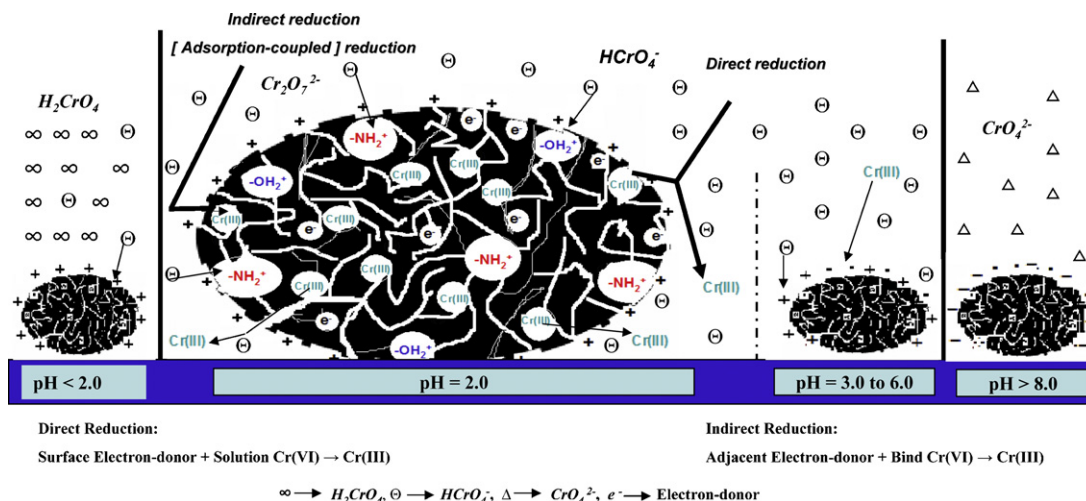


Fig. 4. Mechanism of Cr(VI) adsorption.

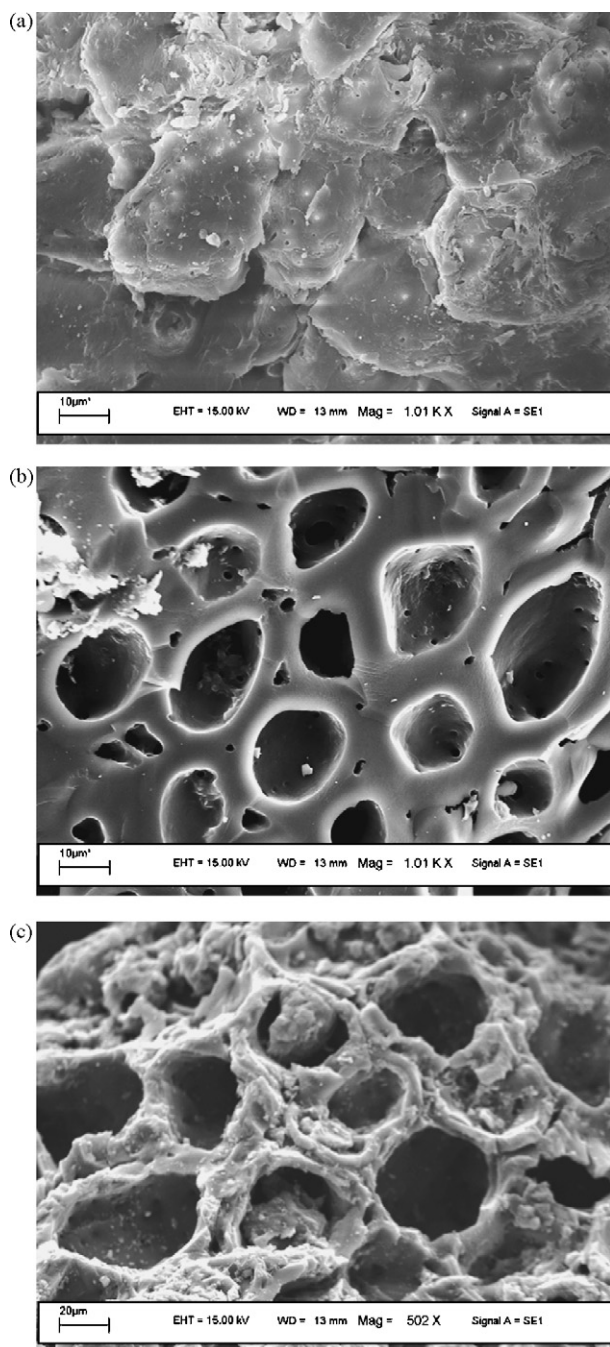


Fig. 5. Scanning electron micrographs of the BS: (a) before activation, (b) after activation and (c) after chromium adsorption.

developed pores on the surface of the BSAC. The pore formation of activated BS is mainly attributed to the addition of phosphoric acid which causes the BS to swell and it opens the surface structure. During activation, phosphoric acid acts as a stabilizer, H_3PO_4 fills up the cavities of the cellulose structure and then due to high temperature during carbonization H_3PO_4 evaporates out of those cavities forming active pores on BS [10–12]. Fig. 5c shows the SEM morphology of BSAC after Cr(VI) adsorption. There is a clear indication of adsorbed chromium on BSAC as a newly bulky coated layer over the surface and some have occupied inside the pores of BSAC.

3.4.2. Energy dispersive X-ray spectroscopy (EDS) analysis

Previous investigations reported that natural adsorbents bear many oxygen surface groups such as acidic character (carboxylic

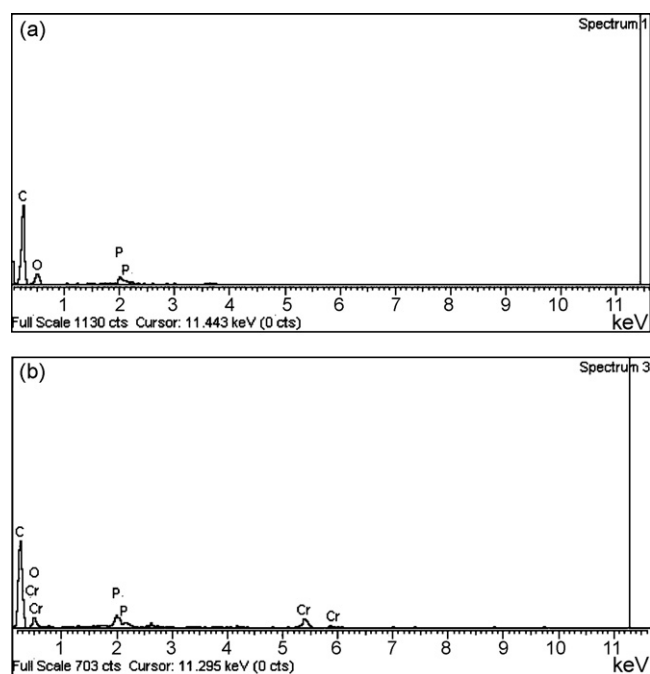
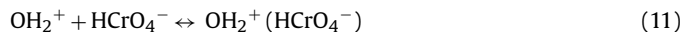


Fig. 6. EDS analysis of (a) BSAC before chromium adsorption and (b) BSAC after chromium adsorption.

and lactonic), non-acidic (ether, quinine and carbonyl), phenol group and anhydride [11]. It has been found from Fig. 6a that BSAC having the carbon, oxygen and phosphorous elements on its surface before interaction with Cr(VI) ions, whereas in Fig. 6b new chromium peak was observed with the surface bearing groups of carbon, oxygen and phosphorous, which confirmed the Cr(VI) adsorption on BSAC.

3.4.3. Fourier transform infrared (FT-IR) analysis

The FT-IR spectra of BSAC before (Fig. 7a) and after chromium adsorption (Fig. 7b) were recorded to acquire the information regarding wave number changes (peak shifting) on the functional groups in the range of $500\text{--}4000\text{ cm}^{-1}$. Table 4 presents some of the basic band frequencies of BSAC before and after metal binding. The band frequency around 3412 cm^{-1} indicates the existence of hydroxyl ($-\text{OH}$) groups and its significant shift from 3412 to 3375 cm^{-1} reveals the chromium binding with ($-\text{OH}$) groups. At low pH (2.0), H^+ ions neutralize (protonation) the surface bearing $-\text{OH}$ groups and then it turns to $-\text{OH}_2^+$ site, it enhanced the negative HCrO_4^- ion adsorption [22,23].



Similar observation has been reported by Mohanty et al. [24] for *Eichhornia crassipes* with chromium binding (peak shifting from 3419 to 3405 cm^{-1}).

The band 2924 and 2913 cm^{-1} is assigned to stretching vibrations of the C–H groups, 1554 and 1528 cm^{-1} is an identification of COO, C=O groups, 1054 and 1043 cm^{-1} is the stretching vibrations of C–O–C, $-\text{OCH}_3$ (lignin structure in BS).

Also, the strong absorption peak at 2850 cm^{-1} is assigned to $-\text{CH}$ stretching [3]. The amino groups (2374 cm^{-1}) that exist ($-\text{NH}_2^+$ and $-\text{NH}^+$) in positive form is predominantly responsible for interaction with anions (HCrO_4^-) in acidic pH 2.0 and that cannot coordinate with reduced Cr(III) [3]. In Fig. 7b there is no stretching vibrations in between 2300 and 2700 cm^{-1} , this might be due to the maximum participation of amino groups on Cr(VI) adsorption. It has also been suggested that the oxidative

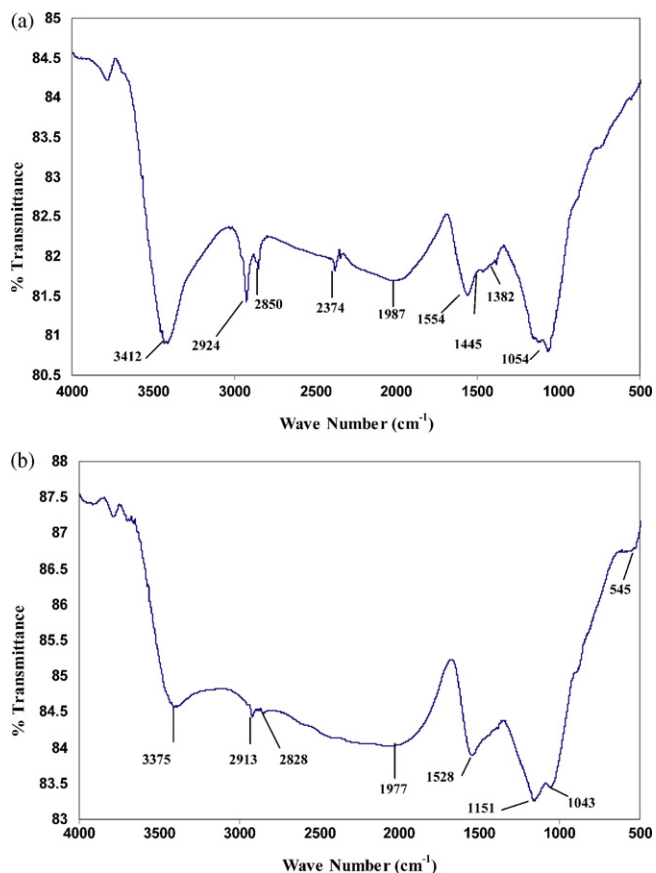
Table 4
Some of the fundamental FT-IR frequencies (a) BSAC (b) BSAC after chromium adsorption.

BS adsorbent	Band position (cm ⁻¹)					Bending vibrations
	O–H	C–H	Amino groups	C=O	C–O	
BSAC before Cr(VI) binding	3412	2924	2374	1554	1382 and 1054	<850
BSAC after chromium binding	3375	2913	–	1528	1043	545

Table 5
Comparison of adsorption capacities of chromium with various adsorbents.

Adsorbents	Adsorption capacity (mg/g)	Initial Cr(VI) concentration (mg/l)	pH	Reference
CSC	2.18	25	6.0	[28]
CAC	4.72		6.0	
Nitric-oxidized CSC	10.88		4.0	
Coconut tree sawdust	3.46	20	3.0	[26]
Olive cake	33.44	100	2.0	[23]
Sawdust	15.82			
Cactus	7.082			
<i>Terminalia arjuna</i> nuts activated carbon	28.4	10–30	1.0	[12]
Sawdust of Sal tree activated carbon	9.55	40	3.5	[14]
Jatropha oil cake	0.82	5–500	2.0	[15]
Maize corn cob	0.28			
Sugarcane bagasse	0.63			
Tamarind hull activated carbon	85.91	25–75	2.0	[27]
GNH – AC	7.0	50	3.0	[25]
SGNH – AC	11.34			
Neem leaf powder	7.43	25–125	7.0	[29]
Bael fruit shell activated carbon	17.27	50–125	2.0	Present study

treatment of adsorbent with H₃PO₄ would introduce more acidic C=O groups on the surface of adsorbent. This would enhance the electrostatic interaction between adsorbent surface groups and HCrO₄⁻.

**Fig. 7.** FT-IR spectra (a) BSAC before chromium adsorption and (b) BSAC after chromium adsorption.

3.5. Comparison with other adsorbents

Recently, the silver impregnated groundnut activated carbon was prepared by using 4:3 ratio of con H₂SO₄ acid, 100:1 ratio of silver nitrate (high cost) and 24 h drying time (high energy) showed only 11.34 mg/g adsorption capacity for Cr(VI) removal. This adsorption capacity is poor compare to our adsorbent, even to spent high cost of materials and energy cost for adsorbent preparation [25]. Similar poor adsorption behaviour was reported for coconut shell charcoal and commercial activated carbon for Cr(VI) removal by Babel and Kurniawan [28]. Besides, there are several adsorbents in literature for arguments. So those are not economically appealing because of its high investment and energy cost to prepare the adsorbents (due to high temperature and inert gas supply). Hence our study depicts, BSAC having better removal capacity (17.27 mg/g) with less preparation cost as compared to the literature reported adsorbents (both cost and capacity) shown in Table 5. Moreover, more investigations required to improve its quality and regeneration capacity for further possible application.

4. Conclusions

The removal of hexavalent chromium from aqueous solution using BSAC has been investigated in batch mode with various operating parameters such as initial pH, agitation time, initial chromium concentration and adsorbent dosage. Moreover, the initial pH of the chromium solution plays a significant role on percentage adsorption of adsorbent towards chromium ions. A decrease in pH (2.0) of aqueous solution led to a significant increase in percentage adsorption. High chromium removal by BSAC was possible by keeping the initial Cr(VI) concentration low at equilibrium time of 240 min. The sorption data of BSAC were well fitted with both the Freundlich and the Langmuir isotherm models. Consequently, Langmuir linear regression data showed the monolayer adsorption capacity of chromium onto BSAC is 17.27 mg/g. It has the better adsorption capacity when compare to the other adsorbents presented in the literature (Table 5). The dimensionless separation factor R_L revealed the favourability of BSAC on Cr(VI) adsorption. Cr(VI) removal by adsorption-coupled reduction is governed by pseudo-second-order

rate equation and this equation is able to provide a realistic description of BSAC adsorption for all concentrations. In this investigation, H_3PO_4 was used for activating the BS and it enhanced the surface property. It was clearly established by SEM micrographs. The FT-IR spectra revealed that the hydroxyl group and amino functional groups were the chromium binding sites at lower pH range and the chromium binding over the surface was confirmed by EDS analysis. Besides that, adsorbent being composed entirely by very low priced agricultural waste and that waste is not put to any other use. It helps to reduce the cost of waste disposal and provide an alternative adsorbent to the existing commercial activated carbon.

Acknowledgement

The authors wish to thank the Central Instrument Facility (CIF), IIT Guwahati for their aid in the SEM and EDS analysis.

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