Removal of Hexavalent Chromium from Aqueous Solutions by Sorption into a Novel Sawdust Anion Exchanger (SAE) Sorbent

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Abstract

This research focuses on removal of Cr(VI) from aqueous solutions using a potential sorbent. The parameters studied include agitation time, co-ion effect, initial chromium ion concentration, pH and temperature. Different kinetic models are studied for two particle sizes, 211 and 84 μm, and the rate is mainly controlled by intraparticle diffusion. Freundlich and Langmuir isotherm models were applied to the equilibrium data at three different temperatures. The adsorption capacity (Q_o) obtained from the Langmuir isotherm plots were 16.83, 20.44, and 23.14 mg g^{-1} respectively at 20, 35, and 50^0C. The temperature variation study showed that the chromium ion adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the pH of the chromium ion solutions. For the particles with diameter 211 and 84 μm, the values of k_{id} were found to be 1.05 and 1.48 mg l^{-1} $min^{-0.5}$. The sorption mean free energy from the Dubinin-Radushkevich isotherm was found to be 10.54 kJ mol^{-1}, indicating the chemical nature of sorption. Various thermodynamic parameters have also been evaluated. Finally, the presence of Cu^{2+} ions in the sorbate was found to decrease the uptake of Cr(VI).

Keywords: Chromium ion, Adsorption isotherms, Thermodynamic parameter, Intraparticle diffusion.

1. Introduction

Rapid industrialization and fast growing population have been responsible for inclusion of heavy metals such as chromium, nickel, arsenic, zinc, and lead into the environment. Heavy metal contamination has gained much attention due to its potential health impact on the public [1]. Among these heavy metals, chromium is considered as highly poisonous, toxic, and carcinogenic [2]. The recommended limit of Cr(VI) in potable water is 0.1 mg l^{-1} [3]. Therefore, removal of this metal from water and wastewater has been a great challenge for environmental scientists [4]. Compounds of Cr(VI) are very mobile, so they readily enter into underground waters and make them poisonous. A huge amount of literature on the various methods that have been applied to aqueous solutions is available. These include reduction followed by chemical precipitation, electrochemical precipitation, ion-exchange, solvent extraction, membrane separation, etc. [5]. However, due to high operation costs, incomplete removal, and problems in disposal of metal sludge, these methods have been confined to laboratory experiments [6]. In order to overcome these problems, attempts have been made to develop low-cost sorbent materials that exhibit fair efficiency in removing toxins from wastewater. In this context, lignocellulosic materials have been most frequently used, as they are not only cheap and easily available, but they also contain a number of OH^- groups that can bind to the metal ions [7]. Apart from using these materials as such, their chemical modification through introduction of desired functionalities has always been the favored strategy for environmental chemists to develop cellulose-based sorbents. In a study by Isa and co-workers [8], sulfuric acid and heat-treated oil palm fibers have been used for removal of Cr(VI) from aqueous solutions. The

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optimal pH was found to be 1.5. The Freundlich isotherm described Cr(VI) adsorption slightly better than the Langmuir isotherm. Similarly, C. Namasivayam and M.V. Sureshkumar [9] modified coconut coir pitch with hexadecyltrimethyl ammonium bromide and applied it as sorbent for Cr(VI) removal. The adsorption capacity of the biosorbent was 76.3 mg g^{-1} at optimum pH 2.0 of sorbate solution. The adsorption kinetics was found to obey second order and Elovich models. P. Alvarez and co-workers [10] prepared activated carbon from a lignocellulosic raw material by thermal treatment at 450 and 650^{0}C in the presence of acid AlCl$_3$, HCl, H$_3$PO$_4$ and H$_2$SO$_4$. These materials were used to obtain optimum experimental conditions for Cr(VI) removal. The adsorption isotherms were best interpreted by the Langmuir model and the sorbents were found to be recovered by filtration with an efficiency of 30%. A novel study used polypyrrole-coated wood sawdust for removal of Cr(VI) [11]. The results showed that the Langmuir isotherm was fairly applicable on the sorption data obtained. In a column system, nearly 99% Cr(VI) was found to be removed by new sorbent material. The successful removal was obtained under acidic or neutral conditions. The husk of *Cajanus cajan* has also been employed for removal of Cr(VI) [12]. The optimal pH for Cr(VI) removal was found to be 2.0. The adsorption data were well fitted with both Langmuir and Freundlich adsorption isotherms. The maximum sorption capacity, Q$_{max}$, was found to be 96.05 mg g^{-1} at pH 2.0. The IR spectral studies revealed that hydroxyl, carboxyl, and amide groups were involved in the Cr(VI) uptake.

In this connection, we hereby report a detailed investigation of Cr(VI) removal from aqueous solutions using sawdust anion exchanger (SAE) as a novel sorbent. This newly developed sorbent has been prepared by treatment of sawdust with epichlorohydrin in a pyridine/DMF medium followed by its reaction with dimethylamine in the presence HCl. The SAE sorbent has been found to be quite effective in removing Cr(VI) from aqueous solutions.

2. Materials and Methods

Sawdust was kindly supplied by a local sawmill. The chemicals epichlorohydrin, dimethylamine, N, N'-dimethylformamide, and pyridine were supplied by HiMedia chemicals Ltd, Mumbai, India, and used as received. Potassium dichromate, sulfuric acid, diphenyl carbazide, and sodium hydroxide were received from E. Merck, Mumbai, India. Double distilled water was used throughout the investigations.

2.1 Preparation of sawdust anion exchanger (SAE)
10 g of completely dry sawdust was allowed to react with epichlorohydrin (100 ml) in 120 ml of N,N'-dimethylformamide(DMF) at 100^{0}C and stirred for 1h. Thereafter, 40 ml of pyridine was added and stirring was

continued for another hour. The reaction product was cooled to room temperature and filtered, and the solid mass was washed with ethanol/water (l:l v/v) at 40^{0}C to remove pyridine and excess epichlorohydrin. Hundred millimeter of 50% (v/v) aqueous solution of dimethylamine was added to the product and stirred for 3h at 100^{0}C. After cooling and filtration, the powder was washed with 2l of 50% aqueous solution of ethanol to remove unreacted dimethylamine followed by extensive washing with dil. HCl, and finally dried at 60^{0}C for 3h. The final product shall be designated as sawdust anion exchanger (SAE) sorbent material. The grinded powder was allowed to pass through standard sieves to give sorbent particles with average diameters of 84 and 211 μm.

2.2 FTIR spectral analysis
The FTIR spectrum of the SAE was recorded on a FTIR spectrophotometer (Shimadzu; Model No 8400S). Samples were prepared in KBr disks (2 mg sample in 200 mg KBr). The scanning range was 400-4,000 cm^{-1} and the resolution was 2 cm^{-1}.

2.3 Cr(VI) uptake studies
The sorbate stock solution was prepared by dissolving a pre-calculated quantity of K$_2$Cr$_2$O$_7$ in double distilled water to give a final concentration of 100 mg l^{-1}. The stock solution was diluted to obtain standard solutions with concentrations in the range of 5 to 30 mg l^{-1}. Fifty milliliters of K$_2$Cr$_2$O$_7$ solution of desired concentration was placed in a 125 ml Erlenmeyer flask containing 0.02 g of sorbent and was agitated in a thermostatic water bath at 50 rpm for 2h. At the end of the experiment, the sorbent was separated by filtration and the supernatant was analyzed spectrophotometrically to determine the remaining concentration of Cr(VI), using the diphenylcarbazide method [13]. This reagent makes a highly colored violet complex with Cr(VI) in 0.1 to 0.2 M H$_2$SO$_4$ (λ = 546 nm). The amount of Cr(VI) sorbed per g of sorbent (i.e., x/m) was calculated using the following formula

$$\frac{x}{m}(\text{mg g}^{-1}) = \frac{(C_o - C_e) \, x \, V}{m \, x \, 100}$$

where C$_o$ = Initial concentration of sorbate solution (mg l^{-1})
C$_e$ = Equilibrium concentration of sorbate solution (mg l^{-1})
V = Volume of sorbate solution taken for sorption study (ml)
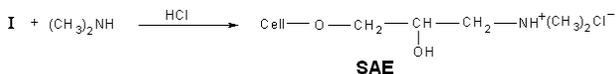m = mass of sorbent (g)

3. Results and Discussion

3.1. Synthetic route to SAE sorbent
Reaction involved in the synthesis of SAE sorbent may be given as below:

In the first step, sawdust is allowed to react with epichlorohydrin
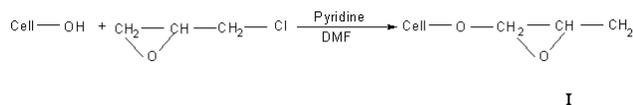
The product I, formed, is now treated with dimethylamine and finally with HCl.

The SAE sorbent is in the form of dark brown powder. Fig. 1 shows a comparative depiction of the physical appearance of (A) sawdust and (B) SAE, respectively.

Figure 1. Photograph of (A) plain and (B) SAE particles.

3.2. FTIR spectroscopy analysis

The FTIR spectra of SAE are shown in Fig. 2. The presence of a strong broad band in the range of 3,000-3,100 cm^{-1} corresponds to stretching vibrations of N-H and hydrogen bonded surface hydroxyls along with chemisorbed water. The 2,721 and 2,800 cm^{-1} refers to the C-H stretching vibration. The band in the region of 1610 cm^{-1} refers to C=O stretching, whereas the peak at 1,364 cm^{-1} refers to C-O stretching of cellulose in sawdust. Finally, the peak in the region of 771 cm^{-1} refers to the aliphatic C-Cl absorption.
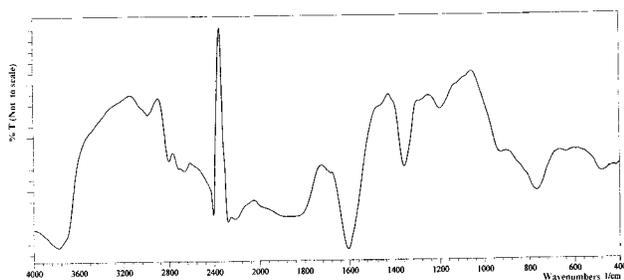

Figure 2. FTIR spectrum of SAE particles.

3.3. Dynamic uptake of Cr(VI)

The sorption kinetics process explains the solute uptake, which in turn governs the residence time of the sorption reaction. In order to understand the kinetic aspects of Cr(VI) uptake on SAE, the sorption study was carried out with sorbent particles of two different sizes, 211 and 84 μm, for the initial sorbate concentration of 20 mg l^{-1} (as shown in Fig. 3). It is clear that the amount of Cr(VI) sorbed increases with time and smaller sized particles exhibit larger chromium uptake. This may simply be attributed to the fact that smaller sized particles have large surface areas, thus providing more binding sites for chromium uptake.
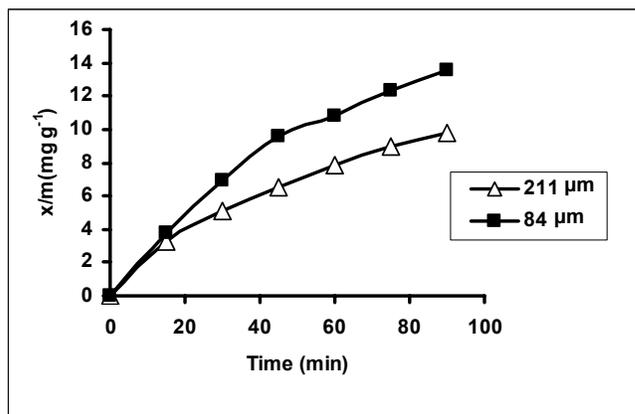

Figure 3. The Kinetic data for Cr(VI) uptake by SAE of two particle sizes.

Using the Cr(VI) uptake kinetic data at room temperature for two particle sizes, 211 and 84 μm (from Fig. 3), we fitted the following kinetic models [14-16].
- Pseudo first-order Lagergren model;
- Pseudo second-order model;
- Simple Elovich model; and
- Power function model.

The estimated models and related kinetic parameters are listed in Table 1. Based on linear regression values, it can be very well seen from Table 1 that the kinetics of Cr(VI) uptake onto SAE can be best described by the 'power function kinetic model' as shown in Fig. 4.

Table 1. Parameters of various kinetics models fitted to experimental data

| S. No.	Kinetic model	Equation*	Parameters with particle size	
			211 μm	84 μm
1.	Pseudo 1st Order Lagergren	$\ln\left(1-\dfrac{q}{q_e}\right)=-K_1 t$	R^2=0.9583 K_1= 0.0316	R^2=0.9774 K_1= 0.0312
2.	Pseudo 2nd Order	$\dfrac{t}{q}=\dfrac{1}{k_2 q^2 e}+\dfrac{1}{q_e}t$	R^2=0.9906 K = 0.0599	R^2 = 0.9853 k = 0.0372
3.	1st Order	$-\ln\left(\dfrac{C}{Co}\right)=kt$	R^2=0.9842 K_1 =- 0.0027	R^2=0.9745 K_1 =-0.0041
4.	2nd Order	$\dfrac{1}{C}\dfrac{1}{Co}=k_2 t$	R^2=0.9926 K_2=3E-05	R^2=0.9849 K_1=0.0001
5.	Simple Elovich	q = a + 2.303 b log t	R^2= 0.9841 a = -2.127 b = 2.629	R^2= 0.9961 a = -5.524 b = 3.555
6.	Power Function	log q = log a +b log t	R^2=0.9974 a = 3.322 b = 0.2346	R^2=0.9825 a = 2.626 b = 0.302

* All notations carry their usual meaning
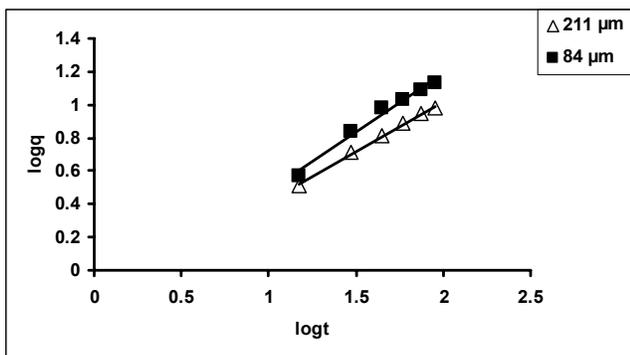
Figure 4. Power Function equation for Cr(VI) uptake by PPCSD.

As mentioned above, the nature of uptake profiles indicated the possibility of intraparticle diffusion of sorbate onto SAE particles. In order to confirm this, curves were plotted between log (% sorption) and log (time) which yielded almost linear plots, as displayed in Fig. 5. This confirmed the occurrence of intraparticle diffusion [17]. An empirically functional relationship common to most adsorption studies is that the uptake varies almost proportionally with $t^{1/2}$, the Weber Morris plot, rather than with the contact time 't' [18]

$$q_t = k_{id}\, t^{0.5}$$

where k_{id} is the intraparticle diffusion rate constant (mg g^{-1} min$^{0.5}$). According to Weber Morris, the linear plot of q_e versus $t^{0.5}$ with zero intercept indicates that intraparticle diffusion alone determines the overall rate of adsorption [18]. On the other hand, the deviation of straight line from the origin indicates that pore diffusion may not be the only 'rate controlling step' in the overall sorption process. The q_t versus $t^{0.5}$ plots, obtained for 211 and 84 μm sized sorbent particles are depicted in Fig. 6. The plots obtained show a fair linearity (with their regression values as 0.9993 and 0.9921 respectively), indicating that the Cr(VI) uptake process is diffusion-controlled. However, the deviation of linear plots from the origin may be attributed to the difference in rate of mass transfer in the initial and final stages of sorption [19]. This also suggests that other mechanisms such as ion-exchange, and physi-sorption may also be partially responsible for the uptake process.
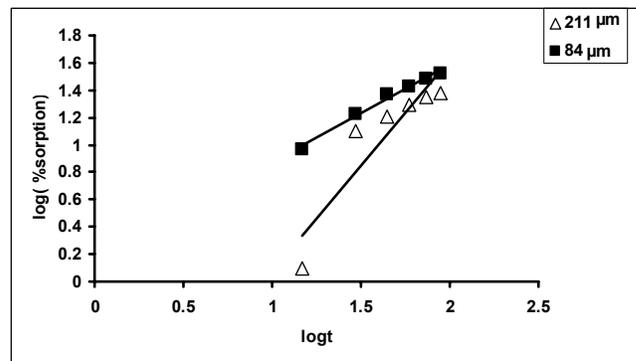

Figure 5. Plot between log (% adsorption) and log (time) to confirm intraparticle diffusion.
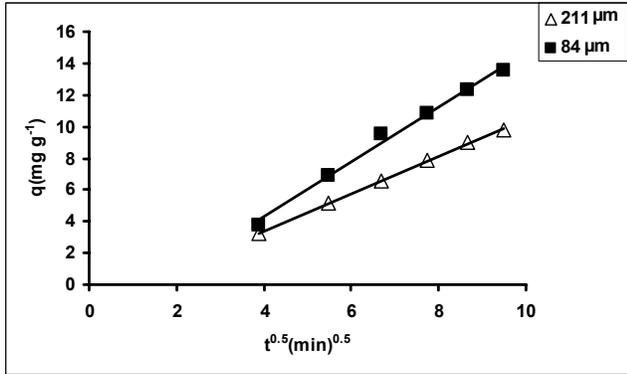
Figure 6. q (mg g^{-1}) versus t$^{0.5}$ plot for determination of k$_{id}$.

Figure 7. Bangham equation showing intraparticle diffusion of Cr(VI) at room temperature for different particle sizes.

The intraparticle diffusion coefficients, as calculated from the slopes of the later linear portion of curves, were found to be 154.3 × 10^{-2} and 70.48 × 10^{-2} mg l^{-1} min$^{0.5}$ for 211 and 84 μm sized particles, respectively. Since increasing the sorbent particle size requires more time to reach equilibrium, this finally results in lowering of k$_{id}$ value for larger particles.

The intraparticle diffusion of sorbate was further confirmed by applying the Bangham equation, as suggested by Ahroni [20] and was applied to the sorption data in the following form:

$$\log \log \frac{Q_o}{Q_o - q_t W} = \log \frac{k_o W}{2.303\, V} + \alpha \log t$$

where Q$_o$ is the initial concentration (g dm^{-3}) of metal ions in the solution, V is the volume of sorbate solution (dm^3), W is the weight (g) of sorbent, q$_t$ is the amount of metal ions sorbed (g g^{-1}) at time t, while α and k$_o$ are constants.

Straight lines with regressions 0.9836 and 0.9258 (see Fig. 7) were obtained by plotting $\log \log \dfrac{Q_o}{Q_o - q_t W}$ against $\log t$ for 211 and 84 μm sized particles, thus indicating the almost fair validity of the Bangham equation. The values of α and K$_o$ for 211 and 84 μm sized particles were calculated from the slopes and intercepts of the plots shown in Fig. 7 and are given in Table 2. Since the values of α and k$_o$ obtained are less than unity, they suggest a diffusion-controlled mechanism of the Cr(VI) uptake process. Almost similar findings have also been reported by Rahman et al. for the sorption of Ni^{2+} ions onto sawdust of *Dalbergia* [21].

The energy of activation was determined from the slope of the Arrhenius plot of lnk$_{ad}$ versus 1/T (Fig. 8) and was found to be 6.40 kJ mol^{-1}. The relatively lower value suggests that Cr(VI) sorption is by an activated or a diffusion-controlled process. In addition, the positive value suggests that sorption is favored by rise in solution temperature.
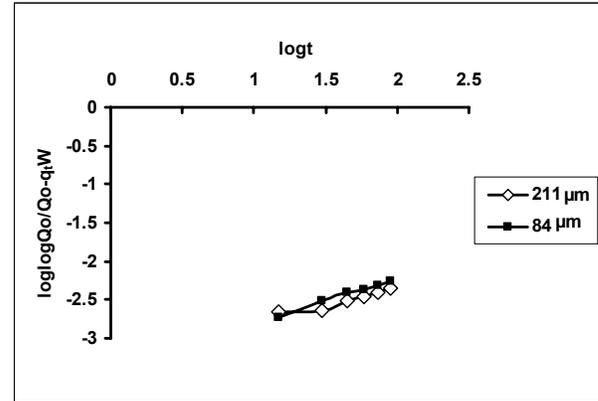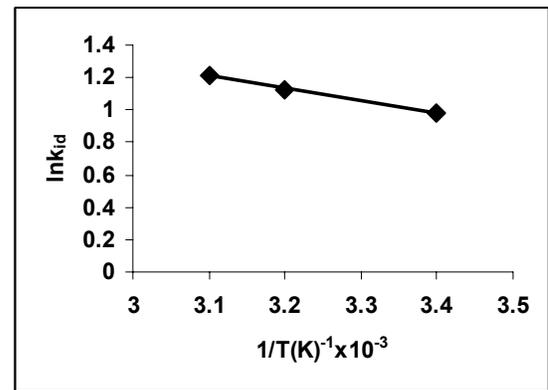

Figure 8. ln k$_{ad}$ versus 1/T plot to evaluate activation energy of sorption process.

Table 2. Kinetic parameters of the Bangham equation for Cr(VI)-uptake onto SAE particles of different size.

Particle size (μm)	α	K$_o$ × 10^3	Correlation coefficient R^2
211	0.4030	7.59	0.8958
84	0.7092	2.98	0.9836

3.4. Adsorption isotherm

Adsorption isotherms are essential for the description of how a metal ion concentration will interact with a sorbent surface, and are useful to optimize the experimental conditions for obtaining maximum metal uptake [22]. The Langmuir model applies to the ion-exchange process with specific assumptions [23], viz, that (i) the maximum exchange depends upon the saturation level of a monolayer

of solute molecules on the sorbent surface, (ii) the sorbent surface is provided with uniform distribution of the exchangeable sites, (iii) each exchanged matter on-site has the same affinity, and (iv) the presence of adsorbed molecules at an adjacent site.

The experimental data was analyzed according to the linear form of the Langmuir [24] isotherms:

$$\frac{C_e}{Q_e} = \frac{1}{Q_o\,b} + \frac{C_e}{Q_m}$$

where C_e (mg l^{-1}) is the equilibrium concentration, Q_e (mg g^{-1}) is the amount adsorbed at equilibrium, b (l mg^{-1}) is the coefficient related to the affinity between sorbent and sorbate, and Q_o (mg g^{-1}) is the maximum sorbate uptake under the given conditions. The isotherms were plotted for 84 μm sized particles at three temperatures, 20, 35, and 50^{0}C, for the different initial sorbate solutions, having concentrations in the range of 5 to 30 mg l^{-1}. The results, as represented by the linearized Langmuir model are shown in Fig. 9. A fair regression value (i.e., > 0.9387) is indicative of fair suitability of the model for Cr(VI) uptake by SAE sorbent particles. The values of Q_0 and b were determined from the slopes and intercept of the linear plots and have been shown in Table 3 along with the corresponding theoretical values obtained by regression analysis. It is quite clear that the experimental values are in fair agreement with those obtained by regression analysis. It is also clear from Table 3 that the maximum sorption capacity Q_0 increases with temperature, thus suggesting that sorption is favored by higher temperature. This may be attributed to the fact that Cr(VI) ions diffuse into sorbate particles at a faster rate with the rise of sorption system temperature. Similar results have also been obtained by Unnithan [25] for the sorption of phosphate ions into iron(III)-loaded carboxylated polyacrylamide-grafted sawdust.
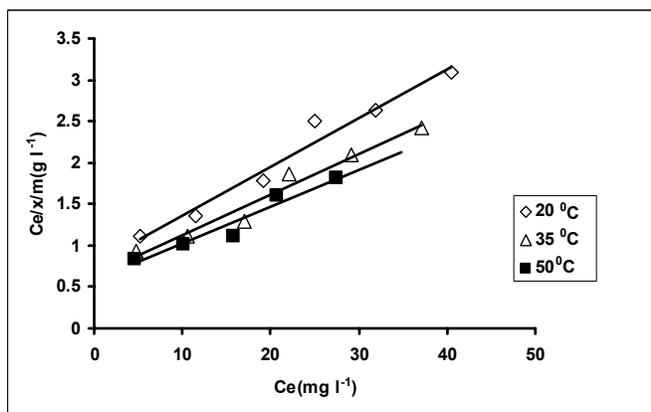

Figure 9. Langmuir isotherms for Cr(VI) uptake at three different temperatures.

Table 3. Values of Q_o and b at different temperatures

Temperature (K)	Graphical values		Regression values	
	Q_o (mg g^{-1})	b (l mg^{-1})	Q_o (mg g^{-1})	b (l mg^{-1})
293	16.86	0.0783	16.86	0.0778
308	20.44	0.0768	20.44	0.0768
323	23.14	0.0727	23.14	0.0726

According to Mohan [26], the essential characteristics of the Langmuir isotherm can be explained in terms of a dimensionless constant separation factor R_L defined as

$$R_L = \frac{1}{1 + bC_o}$$

where b (l mg^{-1}) is the Langmuir constant related to the energy adsorption and C_o (mg l^{-1}) is the initial concentration of Cr(VI) ion. It is clear from Table 4 that R_L values lie between 0 and 1, thus indicating favorable adsorption of Cr(VI) onto SAE.

Table 4. R_L values showing favorable sorption

R_L	C_o (mg l^{-1})
0.56	10
0.390	20
0.299	30
0.242	40
0.20	50
0.176	60

In order to investigate the nature of the sorption process, the sorption data at three different temperatures, 20, 35, and 50^{0}C, were applied to the Dubinin-Radushkevich (D-R) isotherm model. The D-R equation is:

$$C_{ad} = C_m \exp(-B\,\varepsilon^2)$$

where C_{ad} is the amount of Cr(VI) adsorbed on SAE (mol g^{-1}), C_m is the maximum amount of Cr(VI) that can be sorbed (mol g^{-1}) on SAE under optimized experimental conditions, B is a constant with a dimension of energy (kJ mol^{-2}), and Polyanyi potential ε is given as,

$$\varepsilon = RT. \ln (1 + 1/ C_e)$$

where R is the gas constant in kJ mol^{-1} K^{-1}, T is the absolute temperature, and C$_e$ is the equilibrium concentration of Cr(VI) in solution (mol l^{-1}). The obvious linearized form of D-R isotherm is,

$$\ln C_{ad} = \ln C_m - B \, \varepsilon^2.$$

When $\ln C_{ad}$ values were plotted against ε^2, a straight line was obtained (see Fig. 10). The computed value of B for three different temperatures 20, 35, and 50^{0}C, as determined from the slope of linear plots, was found to be 49.0×10^{-4}, 48×10^{-4}, and 45×10^{-4} kJ mol^{-1}. From the calculated value of B, the mean sorption energy E (kJ mol^{-1}) was computed as:

$$E = \frac{1}{\sqrt{-2b}}$$

which is the free energy transfer of one mole of solute from infinity to the surface of magnetite. The numerical value of E is found to be 10.11, 10.20, and 10.54 kJ mol^{-1} which are in the expected range of 8-16 kJ mol^{-1} for ion-exchange chemisorption [27].
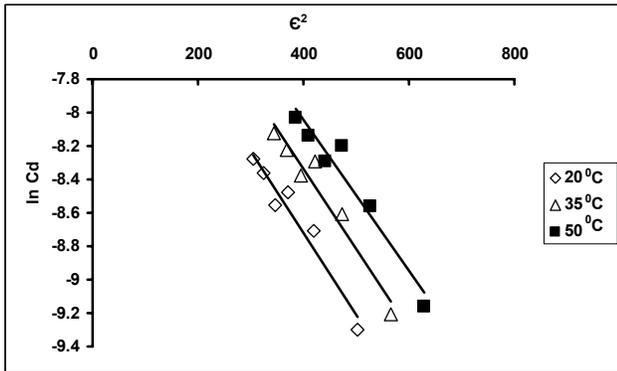

Figure 10. Dubinin-Radushkevich isotherm for evaluation of B at three different temperatures.

3.5. Evaluation of thermodynamic parameters
Thermodynamic parameters were calculated using the following relations:

$$K_c = \frac{C_{ad}}{C_e}$$

where K_c is the equilibrium constant; C_{ad} is the equilibrium concentration of metal on the sorbent (mg l^{-1}), and C$_e$ is the equilibrium concentration of metal on the solution (mg l^{-1}). The change in standard free energy ΔG (kJ mol^{-1}) was calculated as:

$$\Delta G° = - RT \ln K_c$$

Finally, standard enthalpy change $\Delta H°$ (kJ mol^{-1}) and entropy change $\Delta S°$ (JK^{-1} mol^{-1}) were calculated using the slope and intercept of the linear Vant Hoff plot respectively, using the relation:

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{R} \cdot \frac{1}{T}$$
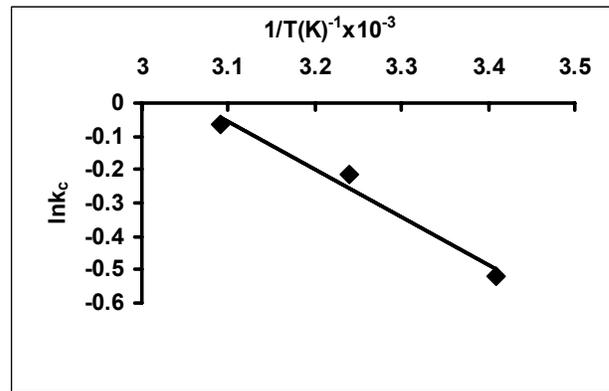
The plot of ln K$_c$ versus 1/T is depicted in Fig. 11.

Figure 11. Plot between lnk$_c$ and 1/T for the evaluation of $\Delta H°$ and $\Delta S°$.

All the values are shown in Table 5. The positive value of $\Delta H°$ supports the endothermic nature of the process. The sorption is found to be more favorable as the free energy of sorption increases. The positive values of $\Delta G°$ and the decrease with rise in temperature indicate that better separation is obtained at a higher temperature. The positive value of $\Delta S°$ also indicates the increased randomness during the uptake of Cr(VI) onto SAE particles.

Table 5. Various thermodynamic parameters for Cr(VI) uptake by SAE particles at different temperatures			
Temperatures (K)	$\Delta G°$ kJ mol^{-1}	ΔH_o kJ mol^{-1}	$\Delta S°$ JK^{-1} mol^{-1}
293	1.259		
308	0.547		
323	0.171	11.83	36.2

3.6. Effect of pH
In order to study the effect of pH of the sorbate solution on Cr(VI) uptake, the pH of the sorbate solutions of fixed concentration was varied in the range 1 to 12 by addition

of H_2SO_4/NaOH, and sorption studies were carried out. The results, as depicted in Fig. 12, reveal that optimum uptake of Cr(VI) occurs in the pH range 2.0 to 4.0 while further change in pH on both sides results in a slight decrease in the amount of chromium sorbed. The effect of pH of the sorbate solution on the sorption capacity of SAE sorbent may be attributed to the predominance of various chromium species existing at different pHs of the solution. In the pH range 2.0 to 6.0, $HCrO_4^-$ and $Cr_2O_4^{2-}$ ions are in equilibrium. At lower pH (pH < 2.0) values, $Cr_3O_{10}^-$ and $Cr_4O_{10}^{3-}$ species are formed [28]. In light of the above facts, the observed change in amount of Cr(VI) at different pH may be explained as follows: when the pH of the sorbate solution lies between 2.0 to 4.0, $HCrO_4^-$ and $Cr_2O_7^-$ species, which are present in dominance, undergo effective ion-exchange with the exchangeable chloride ions present within the SAE particles, resulting in appreciable chromium uptake. However, when the pH is brought below 2.0, the polyanionic species, namely $Cr_3O_{10}^-$ and $Cr_4O_{13}^{2-}$, predominate. However, the relatively slower diffusion of these bulky species into the sorbent particles results in relatively lower metal uptake as is evident from Fig. 12. Moreover, when the pH of the sorbate solution is increased beyond 4.0, the amount of Cr(VI) sorbed continues to decrease with increase in pH of the sorbate solution. The observed decrease may be attributed to the competition between OH^- ions and chromate ions (CrO_4^{2-}) to occupy the active sites within the sorbent particles [29]. This finally results in a slight decrease in chromium uptake. Therefore, it may be concluded that the maximum Cr(VI) uptake of 20.8 mg g^{-1} was obtained in the sorbate solution of pH 4.0.
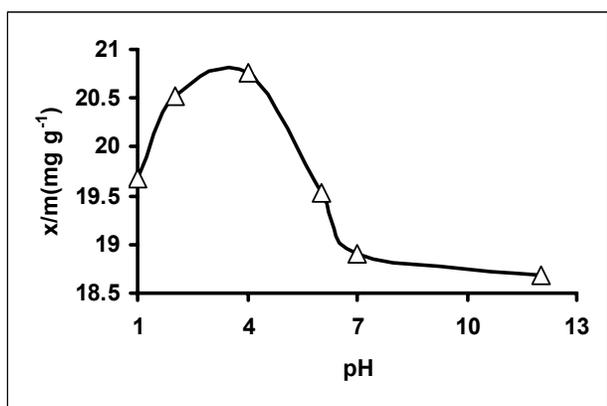

Figure 12. Effect of pH on Cr(VI) uptake by SAE particles.

3.7. Effect of presence of co-ions

It is almost unlikely that only a single type of metal ion [i.e., Cr(VI)] is present in the industrial effluents or domestic water. For example, there are some regions in India where the groundwater contains other metal ions along with chromium. So it may be interesting to see the effect of the presence of co-ions on the Cr(VI) uptake by SAE. Although there may be several types of metal ions present in the groundwater, theoretical justification of results obtained for uptake of a particular metal ion in the presence of more than one type of ion may be difficult because interference of other ions in the mechanism of the key ion will have to be taken into consideration. Therefore, to avoid complexity, the uptake of Cr(VI) was studied only in the presence of Cu^{2+} ions. For this, a Cr(VI) solution initial concentration of 30 mg l^{-1}, and varying amounts of copper chloride were added to yield copper concentrations in the range 2 to 10 mg l^{-1}, and sorption studies were carried out with the same amount of sorbent. The results, depicted in Fig. 13, clearly indicate that there is almost no change in Cr(VI) uptake due to increase in concentration of Cu(II) ions. This may be explained by the fact that uptake of Cr(VI) is governed by its ion exchange with Cl^- ions present within the polymeric sorbent. Hence, presence of Cu^{2+} ions in the sorbent solution does not interfere in the ion-exchange process between Cl^- and $Cr_2O_7^{2-}$ ions, thus causing almost no change in Cr(VI) uptake. In order to further support our argument, a pre-weighed quantity of SAE sorbent was agitated in 25 ml of solution of Cu(II), of known concentration 20 mg l^{-1}. However, it was found that the adsorption of Cu(II) onto the SAE sorbent was almost nil. This confirmed that the presence of Cu(II) did not affect the uptake of Cr(VI) on the SAE sorbent. This also confirms that uptake of Cr(VI) is due to the ion-exchange process.

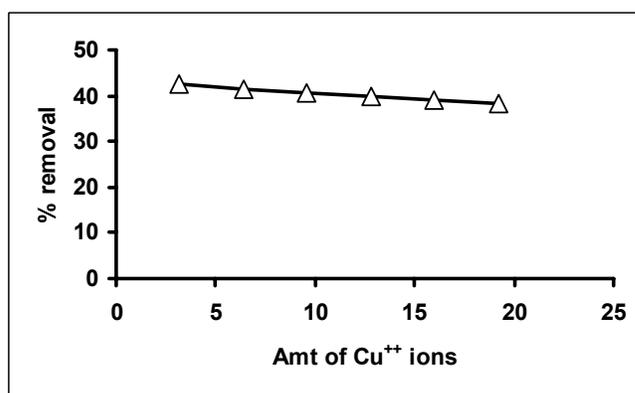Figure 13. Effect of presence of Cu^{2+} ions on Cr(VI) uptake by SAE particles.

3.8. Comparison of SAE with other sorbent

Finally, the adsorption capacity of Cr(VI) onto SAE compared with other adsorbents was reported in the literature and is shown in Table 6. A close look at the values reported clearly reveals that the SAE sorbent has a fair adsorption capacity as compared to the other adsorbents.

Table 6. Comparison of adsorption capacity of Cr(VI) onto SAE and other adsorbents

Adsorbent	Q_o (mg g^{-1})	Reference
Riverbed sand	18.0	[30]
Fireclay	0.23	[31]
Sugar cane bagasse	13.40	[32]
Agave lechguilla biomass	11.31	[33]
Coconut shell carbon	10.88	[34]
Treates sawdust of sal tree	9.55	[29]
Coconut coir	6.30	[35]
Hydrous stannic oxide	3.48	[36]
Aspergillus niger 405	7.20	[37]
Sawdust exchanger	16.86	Present study
PTPS fly ash	0.26	[38]

4. Conclusions

From the above study, we conclude that Cr(VI) undergoes fair sorption onto the newly-developed SAE sorbent. The equilibrium sorption data is well interpreted by the Langmuir isotherm with maximum sorbate values (i.e., Q_o) of 16.86, 20.44, and 23.14 at 20, 35, and 50^{0}C, respectively. We also found that chromium uptake increases with temperature. There is an optimum pH value of 4.0, at which maximum chromium uptake is observed. Out of various kinetic models proposed, the power function seems to fit in experimental data in the best way the sorption seems to govern by chemical forces rather than physical electrostatic interaction. The value of Dubinin-Radushkevich also supports the chemical nature of the sorption process. The presence of Cu^{2+} ions did not affect Cr(VI) uptake. The positive value of ΔH^o indicates endothermic nature of the uptake process. Similarly, positive ΔG^o indicates better separation at higher temperatures and positive ΔS^o indicates increased randomness due to sorption.

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6. References

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