Studies on adsorption behaviour of Cr(VI) onto synthetic hydrous stannic oxide

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Abstract

Hydrous stannic oxide (HSO) was synthesized in the laboratory and its systematic Cr (VI) adsorption behaviour was studied by means of batch experiments. The particle size of HSO used was in the range of 140 to 290 μ m. The variable parameters viz. the effects of pH, concentration of Cr (VI) and time of contact etc. are here reported. The optimum pH and time of contact required for maximum adsorption was found to be 2.0 and nearly 90 min, respectively. The experimental equilibrium adsorption data are tested for the Langmuir, Freundlich, Temkin and Redlich-Peterson equations. Results indicate the following order to fit the isotherms equations: Redlich- Peterson > Temkin > Freundlich > Langmuir. Different kinetic models have been applied to fit the experimental kinetic data. The results are compared, and indicated that the best fit is obtained with the Lagergren or pseudo first-order and the power-function models. A discussion on the adsorption mechanism with respect to the thermodynamic parameters leads to two possible interpretations: One is the exothermic nature of the adsorption process and the other is the ion-ion type electrostatic interaction between the adsorbent and adsorbate ion.

Keywords: Cr (VI), adsorption mechanism, hydrous stannic oxide(HSO), isotherm, kinetics, thermodynamic parameters

Introduction

Chromium, an element of 6th group in the latest IUPAC periodic table, exists in the aqueous environment mainly in +III and +VI states. Cr (III) is non-toxic, and an essential species to mammals that helps the body to control blood-sugar levels in trace concentrations, but toxic to fish when present in water above 5.0 mg/l (Alloway and Ayres, 1997). Cr (VI) is a powerful epithelial irritant, and a confirmed human carcinogen (Porter et al., 1999). Additionally, Cr (VI) is toxic to many plants, aquatic animals and bacteria (Mearns, 1974). Water containing Cr (VI) above 0.05 mg/l is toxic to both mammals and aquatic organisms (Strreth, 1978). Most industries like paint and pigment manufacturing, leather tanning, chrome plating, textile, match, etc. in under-developed countries like India discharge wastewater into the surface water containing Cr (VI) after reduction to the trivalent state. The major drawback of this conventional treatment method is the high cost of chemicals used for the reduction purposes and incomplete reduction of Cr (VI), which may produce toxic sludge due to surface adsorption of Cr (VI) onto the Cr (III) hydroxide precipitate. It is therefore necessary to explore viable technologies for controlling the concentration of Cr (VI) in aqueous discharges/effluents.

Surface adsorption is found to be an important basis for the treatment of toxic element-contaminated water. Numerous adsorbents such as goethite (Mesuere and Fish, 1992), clay (Lazaridis et al., 2001), layered double hydroxides (Goswamee et al., 1998), used tyres and sawdust (Hamadi et al., 2001), activated carbon (Lalvani et al., 1998; Han et al., 2001), zeolite (Tahir et al., 1998; Haggerty and Bowman, 1994), feldspar (Singh et al.,

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1992), hydrotalcite (Lazaridis and Asouhidou, 2003), hydrated zirconium oxide (Ghosh et al., 2001), hydrous titanium oxide (Ghosh et al., 2003), polyacrylamide grafted sawdust (Raji and Anirudhan, 1998), ion-exchange resin (Rengaraj et al., 2001), etc. have been reported in the literature showing Cr(VI) sorptive behaviour and removal from the aqueous solution. A few of them are found to be important for contaminated water treatment but cost-ineffective for 3rd World countries like India. Hydrated stannic oxide (HSO) is a cheap, non-toxic and an insoluble compound showing anion-exchange properties (Amphlett, 1964). Sen et al. (1979) used its anion-exchange property to separate and estimate Cr in some ores and alloys. As the mechanism for the Cr(VI) adsorption onto hydrous metal oxide is not reported earlier, hence hydrous stannic oxide (HSO) is used to investigate the same here.

This study reports the pH effect, contact time and kinetic study on Cr (VI) adsorption. The adsorption data are tested for a number of kinetic and isotherm equations. An evaluation of thermodynamic parameters on Cr (VI) adsorption onto hydrated stannic oxide (HSO) is made. This study will contribute to an understanding of the Cr (VI) adsorption mechanism using hydrous stannic oxide as the adsorbent.

Materials and methods

Reagents

Potassium dichromate (A.R, Glaxo Laboratories India Ltd) was used for the preparation of 1 ℓ of stock Cr (VI) solution (1 000 mg/ ℓ) in distilled water. For pH adjustment throughout the experiment, hydrochloric acid (AR, BDH) and / or sodium hydroxide (Reagent grade, BDH) solutions were used as necessary. A standard (0.25%) diphenyl carbazide (G.R, E.Merck) solution was used for estimation of Cr (VI) spectrophotometrically. Sodium stannate (0.1M) solution was used for the adsorbent synthesis.

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Instruments

A spectrophotometer (Hitachi, model 3210), atomic adsorption spectrophotometer (Perkin Elmer Analyst-100) and pH meter (Elico India, model LI-127) were used for Cr (VI) and pH determination, respectively. The sieves used for separating particles (140 to 290 μ m) of HSO were of BS 52 to BS 100.

Preparation of hydrous stannic oxide (HSO)

Hydrous stannic oxide (HSO) was prepared by treating a 0.1 M sodium stannate solution with 0.1 M hydrochloric acid. The addition of hydrochloric acid solution was continued until the pH of the supernatant liquid was 4.0 to 5.0. The white gel of hydrous stannic oxide so formed was aged as such with mother liquor for 6 d. After decanting the mother liquor, precipitate was washed several times with deionised water to make it free from chloride and alkali. Filtered white mass was dried in an air oven at 50° to 60°C for 72 h. The dried hot mass was treated with cold water, which gave fine crystalline particles. It was sieved to the desired particle size. The HSO particles size ranging from 140 to 290 μ m were used for adsorption experiments after homogenization at a pre-selected pH value at which experiments are to be done.

Adsorption procedure

Batch adsorber tests were carried out by mechanical agitation (agitation speed: 120 to130 r/min) at a temperature $20(\pm 2)^{\circ}$ C, unless stated otherwise. To determine the amount of Cr (VI) adsorption, 0.2 g of HSO was taken into a 100 ml polythene bottle with 50 ml of sorbate solution. The concentrations of Cr (VI) solutions used were in the range of 2.0 to 50.0 mg/l. Ionic strength was not adjusted during adsorption tests. After agitation, all sample solutions were filtered through 0.45 µm membrane filter paper and, the filtrate was analyzed for Cr. The amount of adsorbed Cr (VI) was calculated by the difference of the initial and residual amount in the solution divided by the weight of the adsorbent used. To check the repeatability of the experimental data, each experiment was conducted thrice.

Results and discussion

Effect of pH

The results on Cr (VI) adsorption with increasing pH from 1.0 to 10.0 are shown in Fig.1. It was found that Cr (VI) adsorption capacity (in percentage) of HSO increased from pH 1.0 to 2.0, and decreased from pH 3.0 to 10.0, respectively. The interesting feature of our experimental observation was that the final pH of the solution remained almost the same up to pH 2.0 and, thereafter a notable change in final pH from initial pH \geq 3.0 was observed. This fact can be explained on the basis of surface characteristics (pH_{ZPC} = 4.6 to 6.4) of the adsorbent. In strongly acidic solutions (pH 2.0), HSO surface would be positive and surface positive charge density should decrease with increasing pH. HSO surface should be positively charged up to $pH \le 4.6$, and heterogeneous in the pH range 4.6 to 6.4. Thereafter, it should be negatively charged. Thus, Cr (VI)-sorption can be depicted by the electrostatic phenomenon (Eqs. (1) and (2)) in the pH range below 4.6. Adsorption Eq. (2) is in agreement with the anion-exchange phenomenon (Amphlett, 1964) of HSO.

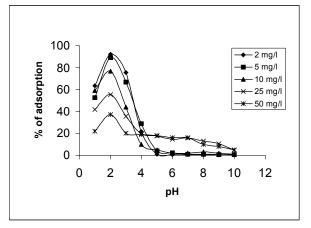


Figure 1 Effect of pH on adsorption of Cr (VI) onto HSO at 20(±2)°C

$$SnOH_{2}^{+} + {}^{\circ}O_{3}Cr O Cr O_{3}^{-} \rightarrow SnOH_{2}^{+} - - {}^{\circ}O_{3}Cr O Cr O_{3}^{-}$$
(outer sphere adsorption) (1)

 $SnOH_{2}^{+} + O_{3}Cr O Cr O_{3}^{-} \rightarrow Sn^{+} - O_{3}Cr O Cr O_{3}^{-} + H_{2}O$ (inner sphere adsorption) (2)

A similar adsorption mechanism was presented by researchers on As(V) sorption onto hydrous metal oxides. An equilibrium between $Cr_2O_7^{-2}$ and $HCr_2O_7^{-}$ exists (Eq. (3)) in strong acidic pH with predominating $HCr_2O_7^{-}$ at pH < 2.0 with concentration dependent some other polymeric species (Greenwood and Earnshaw, 1995).

$$\mathrm{HCr}_{2}\mathrm{O}_{7}^{-} \rightarrow \mathrm{H}^{+} + \mathrm{Cr}_{2}\mathrm{O}_{7}^{-2} \tag{3}$$

Less negative charge on sorbate species might be the cause for less adsorption at pH 1.0. Electrostatic interactions between surface of adsorbent and Cr (VI) are also supported by the determined thermodynamic parameter (negative ΔS value). The decrease in adsorption at $pH \ge 3.0$ is due to the decrease in positive charge density onto the adsorbent surface sites. Thus, adsorption of Cr (VI) at pH \ge 5.0 was found to be negligibly small up to the initial 10 mg/lsolution, whereas a significant adsorption percentage was obtained at high concentrations (25 and 50 mg/ ℓ). At pH \geq 5.0, HSO surface should be negative, where K^+ present (high in concentration) will be adsorbed electrostatically. According to Amphlett (1964), HSO behaves as cation exchanger at and above this pH. Evidence appears from the decrease in final solution pH. Thus, Cr (VI) will be adsorbed in the 2nd adsorption sphere via K⁺-bridge onto the adsorbent surface, and low adsorption percentage has been found.

Effect of contact time

The results of percentage Cr (VI) adsorption at pH 2.0 with increasing contact time are presented in Fig. 2. It was found that the Cr (VI) adsorption percentage increased with increasing contact time. Above 50% of Cr (VI) adsorption occurred in the first 15 to 20 min, and thereafter the rate of adsorption of the adsorbate species onto the adsorbent was found to be slow. The concentration- dependent maximum sorbate sorption capacity of HSO was found to be at nearly 90 min contact time. Very slow sorption was noted later on when determining residual Cr present in equilibrated solution. The time of contact for Cr(VI) adsorption on chemically modified *Acacia arabica*

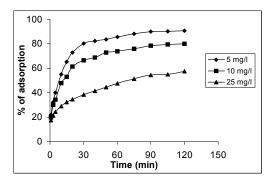


Figure 2 Equilibrium time for adsorption of Cr (VI) onto HSO at 20(±2)°C and at pH 2.0

bark as reported by Singh et al. (1994) was 120 min. Ghosh et al. (2001 and 2003) reported that the contact time required for reaching equilibrium was 90 and 30 min for sorption of Cr(VI) onto hydrated zirconium oxide and hydrated titanium oxide, respectively. Thus, the rate of Cr (VI) adsorption onto HSO is nearly equal to that of hydrated zirconium oxide but slower than that of hydrated titanium oxide.

The initial rapid adsorption is due to the availability of the positively charged surface of the present adsorbent $(pH_{ZPC} = 4.6 \text{ to } 6.4)$ for adsorption of anionic Cr (VI) species present in the solution at pH 2.0. The later slow adsorption is probably due to the electrostatic hindrance between adsorbed negatively charged sorbate species onto the surface of adsorbent and the available anionic sorbate species in solution, and the slow pore diffusion of the solute ion into the bulk of the adsorbent.

However, the contact time required for maximum Cr (VI) adsorption onto HSO was found to be nearly 90 min, which is independent of the sorbate concentration.

Adsorption kinetics

Our time-dependent experimental adsorption data (Fig. 2) are used for kinetic modelling. The model equations used for fitting the data are:

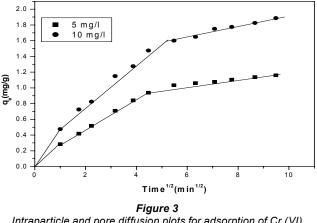
- 1st order equation
- Pseudo 1st order model (Lagergren equation)
- Second order equation
- Pseudo 2nd order equation
- Bhattacharya and Venchobachor model
- Power function equation
- Simple Elovich model.

Lazaridis and Asouhidou (2003) used three kinetic equations (Lagergren, 2nd order and Elovich model equations) to describe Cr (VI)-sorption experimental data onto hydrotalcite, and showed that their adsorption data fit the Lagergren model best. The present Cr (VI)-sorption data of HSO at 20(±2)°C and pH 2.0 are tested for kinetic modelling by linear regression plots. The estimated model and the related statistic parameters are reported in Table 1 (graphs are not shown). Based on linear regression (R²>0.95) values, the kinetics of Cr (VI) adsorption onto HSO can be described well by both Lagergren equation ($R^2 = 0.9723$, 0.9811 and 0.9734) and Power function equation ($R^2 = 0.9592$, 0.9636 and 0.9921). The results clearly indicate that the power function model fits progressively well with increasing sorbate concentration. Moreover, it was found that the experimental data, obtained from 5.0 mg/lof Cr(VI) solution, fit well also to the 2^{nd} order model equation ($R^2 = 0.9785$). Thus, it appears that the pseudo 1st order, 2nd order and power function kinetic models are obeyed well at lowest sorbate concentrations studied. The analyses of different kinetic model parameters show that the fitting of experimental adsorption data deviates largely from one model to the other with increasing initial sorbate concentration.

Macro and micro-pore diffusion

The adsorption mechanism of a sorbate onto the adsorbent follows three steps viz. film diffusion, pore diffusion and intraparticle transport. The slowest of three steps controls the overall rate of the process. Generally, pore diffusion and intraparticle diffusion are often rate-limiting in a batch reactor, while for a continuous flow system film diffusion is more likely the ratelimiting step. Though there is a high possibility for pore diffusion to be the rate-limiting step in a batch process, the adsorp-

TABLE 1Kinetic models and other statistical parameters at 20(\pm 2)°C and at pH 2.0					
Kinetic models and other sta		Concentration of Cr(VI) solution			
Kinetic model	Parameters	5 mg/ℓ	10 mg/ℓ	25 mg/ℓ	
1 st order equation	R ²	0.6721	0.5370	0.4034	
$-\ln(C/C_o) = K_1 t$	K ₁	3.24 x 10 ⁻²	2.21 x 10 ⁻²	1.08 x 10 ⁻²	
2 nd order equation	R ²	0.9785	0.8718	0.5917	
$1/C-1/C_{0} = K_{2}t$	K ₂	2.02 x 10 ⁻²	0.49 x 10 ⁻²	0.06 x 10 ⁻²	
Lagergren equation	R ²	0.9723	0.9811	0.9734	
$\log(q_e-q) = \log q_e - (K_1'/2.303)t$	K ₁ '	4.68 x 10 ⁻²	4.09 x 10 ⁻²	2.97 x 10 ⁻²	
Pseudo second order	R ²	0.6225	0.8968	0.7630	
$1/q_{e}-q = 1/q_{e}+K_{2}'t$	K,'	4.11 x 10 ⁻¹	1.78 x 10 ⁻¹	4.66 x 10 ⁻²	
Bhattacharya-Venkobachor model	R ²	0.9189	0.9095	0.8783	
$ln[1-U(t)] = K_{B}t$ $U(t) = C_{o} - C_{t} / C_{o} - C_{e}$	K _B	5.64 x 10 ⁻²	5.05 x 10 ⁻²	3.77 x 10 ⁻²	
Power function equation	R ²	0.9592	0.9636	0.9921	
Log q = log a + blog t	a	0.3125	0.4936	1.0810	
	b	0.3214	0.3166	0.2536	
Simple Elovich equation	R ²	0.7059	0.7539	0.9305	
q = a + 2.303.b.log t	a	0.5720	0.9073	1.5420	
	b	3.73 x 10 ⁻³	5.99 x 10 ⁻³	0.899x10 ⁻³	



Intraparticle and pore diffusion plots for adsorption of Cr (VI) onto HSO at $20(\pm 2)$ °C and at pH 2.0

tion rate parameter which controls the batch process for most of the contact time is the intraparticle diffusion (Weber and Morris, 1963; Allen et al., 1989). To check this postulation, a plot of Cr(VI) adsorbed at equilibrium $(q_e, mg/g)$ with $t^{0.5}$ (\sqrt{min}) is drawn. Figure 3 shows three separate linear portions for 5.0 and 10.0mg/lof Cr(VI) solutions, respectively. The first part of the curve is attributed to mass transfer effects (slope K₁) (Crank, 1983) taking place with boundary layer diffusion, while the final linear parts indicate intraparticle diffusion (slope K, and K). The diffusion rate parameters K1, K2 and K3 as obtained were shown in Table 2. The values for K_2 and K_3 indicate that the pores are micro-pores and the intraparticle diffusional resistance is due to micro-pores only. The diffusion rate parameters indicate that the intraparticle diffusion controls the sorption rate; which is a slowest step of adsorption. Moreover, pore sorption of Cr(VI) onto HSO is concentration dependent. Increase in sorbate concentration increases the rate of pore diffusion.

Adsorption isotherms

Four isotherms, as described below in Eqs. (4) to (7) (Cooney, 1998), were used for fitting the experimental data obtained at $20(\pm 2)$ °C and at pH 2.0.

Langmuir equation:	$1/q_{e} = 1/(\theta.b.C_{e}) + 1/\theta$	(4)
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Freundlich equation: $\log q_e = \log K + 1/n \log C_e$ (5)

Temkin equation: $q_e = a + 2.303 b \log C_e$ (6)

Redlich-Peterson equation: $C_e/q_e = 1/\alpha + (\beta/\alpha) C_e^{\gamma}$ (7)

where:

 q_a is the amount adsorbed at equilibrium (mg/g)

 C_{a} is the equilibrium Cr(VI) concentration in solution (mg/ ℓ).

The other parameters are different isotherm constants, which can be determined by regression of the experimental data. Due to inconvenience of evaluating three isotherm parameters, the two-isotherm-parameter equations (Langmuir, Freundlich, Temkin equation) are more widely used than the three-isothermparameter equation (Redlich-Peterson equation). Though, the three-isotherm- parameters equations mostly provide a better fit of the isotherm data than a two-isotherm-parameters one. The estimated model parameters with correlation coefficient (R^2) for the different models are shown in Table 3. Our experimental data are found to fit well in the three-parameter model (Eq. (7)), Fig.4a) in terms of R^2 value. A similar inference was also drawn

TABLE 2 Macro- and micro-pore diffusion rate constants				
Adsorbate concentration	Rate constants, intraparticle rate parameter(mg/g·min ^{0.5})			
(mg/ℓ)	K,	K ₂	K ₃	
5	0.267	0.194	5.806 x 10 ⁻²	
10	0.480	0.325	9.032 x 10 ⁻²	

TABLE 3Estimated isotherm parameters for Cr (VI)adsorption at 20(±2) °C and at pH 2.0					
Isotherm models	Estimated isotherm parameters				
Langmuir equation	R ²	θ (mg/g)	b (ℓ/mg)		
$1/q_e = 1/\theta.b.C_e + 1/\theta$	0.9505	3.48	0.941		
Freundlich equation	R ²	K	n		
$\log q_e = \log K + 1/n \log C_e$	0.9790	1.480	3.206		
Temkin equation	R ²	a	b		
$q_e = a + 2.303 b \log C_e$	0.9805	1.5625	0.7170		
Redlich-Peterson equation	R ²	α	β	γ	
$C_e/q_e = 1/\alpha + (\beta/\alpha) C_e^{\gamma}$	0.9990	2.6490	0.7658	0.9500	

by Zeng et al. (2004) for 'Adsorptive removal of phosphate from aqueous solutions using iron oxide tailing'. The Temkin equation fitted the data (Fig.4b) nearly as well as the three-parameter equation. Here the applicability of the two-parameter isotherm models for the present data approximately follows the order: Temkin (Fig.4b) > Freundlich (Fig.4c) > Langmuir (Fig.4d). In the Langmuir equation, θ (mg/g) is the measure of adsorption capacity under the experimental condition and the value is 3.48 mg/g. The essential characteristic of the Langmuir isotherm may be expressed in terms of the dimensionless separation parameter R₁, which is indicative of the isotherm shape that predicts whether an adsorption system is 'favourable' or 'unfavourable'. R₁ is defined (Waber and Chakrobroty, 1974) as:

$$R_{1} = 1/(1 + bC_{0})$$
(8)

where:

 C_0 is the initial concentration of the sorbate (mg/ ℓ) 'b' is the Langmuir constant.

 R_L can be calculated as 0.175, 0.096 and 0.041 for 5, 10 and 25 mg/ ℓ Cr(VI) solution, respectively. In either case, the R_L values for the present experimental data fall between 0 and 1, which is indicative of the favourable adsorption of Cr (VI) on HSO. The R_L values showed that the adsorption of Cr(VI) was more favourable for the higher concentration than the lower one, which is due to the effect of the pore diffusion sorption phenomenon.

Temperature effect and thermodynamic parameters

Cr(VI) adsorption decreases with increasing temperature, showing the exothermic nature of the process. The extent to which the Cr (VI) adsorption capacity decreases with increasing temperature might be attributed to the change in surface properties of the adsorbent, solubility of the adsorbate species and exoor endothermic nature of the adsorption process.

Thermodynamic parameters were evaluated to confirm the adsorption nature of the present study. The thermodynamic constants, free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated to evaluate the thermody-

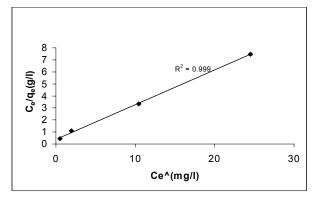


Figure 4a Redlich-Peterson isotherm plots for adsorption of Cr (VI) onto HSO at 20(±2)°C and at pH 2.0

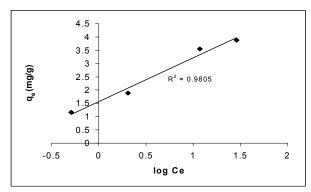


Figure 4b Temkin isotherm plots for adsorption of Cr (VI) onto HSO at $20(\pm 2)^{\circ}$ C and at pH 2.0

namic feasibility of the process and to confirm the nature of the adsorption process. Based on the following literature available equations (Eq. (9) to (11)), the Langmuir constant 'b' can be used for estimation of the said thermodynamic parameters (Gupta, 1998), despite the adsorption data fitting somewhat poorly ($R^2 = 0.9505$).

$$\Delta G^0 = - RT \ln K_0 \tag{9}$$

$$\ln(b_1/b_2) = -\Delta H^0/R (1/T_1 - 1/T_2)$$
(10)

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \tag{11}$$

where:

'b' is a Langmuir constant (l/ mol) at temperature T (K) R is an ideal gas constant (8.314 J/ mol.K) ΔG^0 and ΔH^0 are in J/ mol ΔS^0 in J/ mol.K.

The parameters as calculated are also reported in Table 4. The negative ΔG^0 values confirm the spontaneous nature and feasibility of the sorption process. With the increase of temperature, the ΔG^0 value decreased from 293K to 330K. This indicates that favourable Cr (VI) sorption takes place with decreasing temperature. The negative ΔH^0 values indicate the exothermic nature of Cr (VI) adsorption onto HSO. The negative ΔS^0 values suggest the decrease in adsorbate concentration in solid-solution interface indicating thereby the increase in sorbate concentration onto the solid phase. This is the normal consequence of the physical adsorption phenomenon, which takes place through electrostatic interactions as suggested earlier.

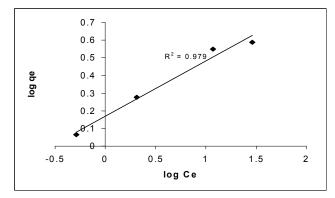


Figure 4c Freundlich isotherm plots for adsorption of Cr (VI) onto HSO at $20(\pm 2)^{\circ}$ C and at pH 2.0

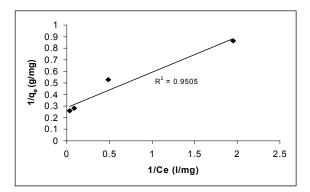


Figure 4d Langmuir isotherm plots for adsorption of Cr (VI) onto HSO at $20(\pm 2)^{\circ}$ C and at pH 2.0

TABLE 4Calculated Langmuir constants and thermody-namic parameters for Cr (VI) adsorption at pH 2.0					
T °K	b ℓ/mg	b ℓ/mole	∆G⁰ KJ/ mole	∆H⁰ KJ/ mole	∆S⁰ KJ/ mole·K
293	0.941	0.4890 x 10 ⁵	-26.303	-28.805	-0.0085
313	0.442	0.2299 x 10 ⁵	-26.134	-29.975	-0.0123
330	0.244	0.1270 x 10 ⁵	-25.925		0.0120

Conclusions

- Optimum pH for highest Cr(VI) sorption is $\cong 2.0$
- The contact time for the maximum adsorption required is nearly 90 min
- The adsorption kinetics for Cr(VI) at pH 2.0 has been well described by the power function and the pseudo 1storder equations in the concentration range studied
- The equilibrium sorption data are satisfactorily fitted in the order: Redlich-Peterson > Temkin > Freundlich > Langmuir.
- The calculated values of the dimensionless separation factor from the Langmuir constant confirm favourable sorption of Cr(VI) onto HSO
- The determined free energy change (ΔG⁰) and enthalpy change (ΔH⁰) indicate the spontaneous and exothermic nature of the adsorption process.

• The adsorption of Cr (VI) onto HSO takes place through electrostatic interaction between adsorbent surface and sorbate species in solution. This is supported by the calculated thermodynamic parameter (negative ΔS^0).

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