Adsorption of Chromium (VI) from Wastewater by Anion Exchange Resin

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Abstract: Strong anion exchange resin (Spectra/Gel IE 1x8) has been investigated as adsorbent for the efficient removal of Cr(VI) ions from synthetic wastewater solutions. Batch experiments were conducted with initial Cr(VI) ions concentration ranging from 25-300 mg/L. Different parameters influencing Cr(VI) adsorption process such as; solution pH, Cr(VI) and adsorbent concentration and contact time were investigated. Results obtained revealed that Cr(VI) was successfully retained by the resin. Equilibrium was established within 30 minutes for initial Cr(VI) concentration up to100 mg/L. The equilibrium data for adsorption of Cr(VI) was fitted with both Langmuir and Freundlich isotherms, however, Langmuir isotherm model was found to be more suitable for the Cr(VI) adsorption and maximum adsorption capacity of the Cr(VI) was found to be 173.8 mg/g. The adsorption process followed second order kinetics. The resin was regenerated by using 4M NaOH as an eluent and retained Cr(VI) adsorption efficiency higher than 83% after three regeneration cycles.

Keywords: Cr(VI) ions, Anion-exchange resin, Wastewater, Removal, Adsorption isotherm, Regeneration.

1. INTRODUCTION

Waste streams from different industries such as; metal-plating facilities, mining processing, tanneries and electronic device manufacturing units, may contain toxic heavy metals in concentrations often exceeding the local discharge limits. The heavy metals contaminants include chromium, lead, mercury, cadmium, arsenic, nickel, and copper which are not easily removed from wastewater without specialized or advanced treatment [1, 2]. Effluents from tannery industry and electroplating are major sources of incorporation of Cr(VI) into the wastewater streams [3]. The presence of high concentration of chromium contaminants in the environment may cause detrimental effects to both human health and ecosystem in the long term [4]. From its various oxidation states, Cr(VI) is environmentally extremely hazardous due to its high toxicity and carcinogenic nature. Due to its mobility in the environment, Cr(VI) can easily penetrate the cell wall and exert its noxious influence. Short-term exposure to above the maximum contaminated level (MCL) of Cr(VI) causes skin and stomach irritation or ulceration. Long-term exposure above MCL can cause dermatitis, damage to liver, kidney ulceration, nerve tissue damage, and death [5, 6]. According to the World Health Organization standards for drinking water, the MCL of chromium is 0.05 mg/L [4]. Therefore, it is necessary to remove chromium from wastewater prior to its final discharge into the environment.

Different treatment technologies such as; chemical precipitation, membrane separation, reverse osmosis, ion-exchange, solvent extraction, and adsorption have been investigated to remove chromium from water and wastewater [1]. Adsorption is an emerging and attractive method which involves a mass transfer process where a substance is transferred from the liquid phase to the surface of a solid and becomes bound to it by physical and/or chemical interactions [4, 7, 8]. The main advantages of this method are low operation cost, reusability of the adsorbent, improved selectivity of certain metal ions of interest and removal of heavy metal ions from effluent. Adsorption using bio-materials, activated carbons, carbon nanotubes and polymer resins has gained considerable attention recently [9-14]. Synthetic polymeric ion-exchange materials have been used for adsorptive removal of heavy metal ions from aqueous solution and wastewater because of their good mechanical strength, diverse structures and easy chemical regeneration capacities [15, 16].

The objective of the present work is to evaluate the effectiveness of the anion exchange resin (Spectra/Gel IE 1x8) for removing Cr(VI) ions from synthetic wastewater solutions over wide range of initial Cr(VI) ions concentrations (close to that of industrial wastewater). Different parameters that affect the adsorption process like solution pH, metal ion

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adsorption capacity, concentration and time have been studied. Kinetic and thermodynamics studies were performed for better understanding the nature of adsorption process.

2. MATERIALS AND METHODS

2.1. Materials

Strong base anion exchange resin Spectra/Gel 1E 1x8 (type 1) with bead size of 75-150 μm was used and evaluated for separation of Cr(VI). The spectra/Gel resins were supplied in chloride form with a trimethylbenzylamonium group as the exchange site. Potassium dichromate ($K_2Cr_2O_7$) purchased from BDH Chemicals Ltd. was used as precursor of Cr(VI). All chemicals used were of technically analytical grade and all solutions were prepared with deionized water.

2.2. Characterization

Surface morphology of the resin before and after Cr (VI) adsorption was studied with SEM Quanta FEG-450, FEI, Amsterdam, Netherland, operating at an accelerating voltage of 20kV after sputtering with a 20nm thick gold layer (JEOL JFC-1600 Auto Fine Coater). For elemental analysis the specimens were analyzed (without coating) by using the energy dispersive analyzer unit (EDAX, Apollo X) to confirm the presence of Cr after adsorption. To obtain the structural information Fourier Transform Infrared (FTIR) Spectra of the Spectra/Gel before and after adsorption were recorded using PerkinElmer Spectrum 100 FTIR Spectrometer, over a wide range of resolution of 650-4000cm^{-1}.

2.3. Adsorption Experiments

The experiments were performed in 100 ml capacity Pyrex flasks. For each run, a specific amount of the resin (adsorbent) was added to 25 ml aqueous Cr(VI) solution of desired concentrations (25-300 mg/L). The mixture was stirred for a predetermined period in a temperature controlled water bath shaker at 200 rpm until equilibrium establishment. For kinetic studies 0.025gm adsorbent was mixed with a series of conical flasks containing 25 ml of Cr(VI) solution of 300 mg/L concentration each at 23, 33 and 43 ^{o}C, respectively. The adsorption capability of Cr(VI) on the Spectra/Gel resin was investigated over a pH range from 2-11. The pH was adjusted with 0.1 M NaOH and 0.1 M HCl and measured with sensION+ pH3 laboratory pH meter (HACH USA). Adsorption isotherm study was carried out with different initial concentrations of Cr(VI) ranging from 25 to 300 mg/L while maintaining the adsorbent

amount of 1g/L. The influence of adsorbent dose on adsorption was also studied by varying adsorbent dose from 0.25 – 2 g/L with Cr (VI) concentration of 50 mg/L at 23 ^{0}C. The concentration of Cr(VI) remaining in the supernatant solutions was determined by Inductively Coupled Argon Plasma (ICP)- Optical Emission Spectrometer (Varian 720-ES). The amount of adsorbed Cr(VI) per unit mass of the adsorbent was calculated using the following equation:

$$q = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where, q is the adsorption capacity in mg/g, C_o is the initial Cr(VI) concentration while C_e denotes equilibrium Cr(VI) concentration in mg/L, v is volume of the solution in L and m is adsorbent mass in grams.

2.4. Desorption and Regeneration Experiments

For desorption studies water, NaOH, NaCl and HCl were used as eluent. 0.025g of Cr(VI) saturated adsorbent was mixed with 25 ml of eluent solution. The effect of various parameters such as eluent concentration, solution pH and temperature were investigated. The regenerated gel was subjected to further adsorption tests under optimum conditions for three adsorption-regeneration cycles while maintaining gel concentration to 1g/L [17].

3. RESULTS AND DISCUSSION

3.1. SEM Characterization

SEM micrograph of the hydrogel at 476 x magnification is given in Figure **1**. It can be seen that the hydrogel particles appear as distinct spherical granules with smooth surface and grain size from 75-150 μm.
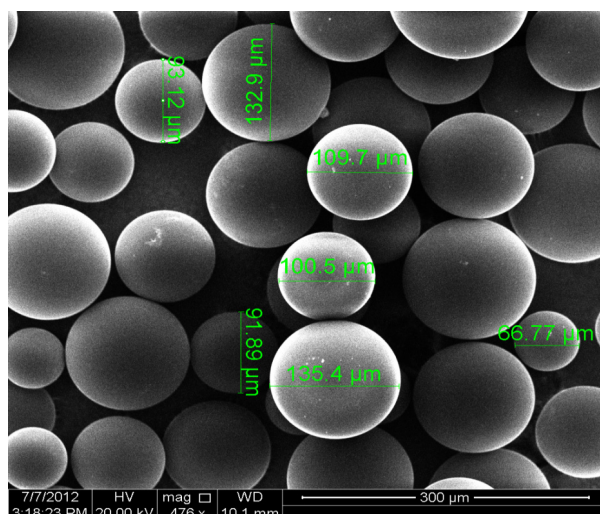

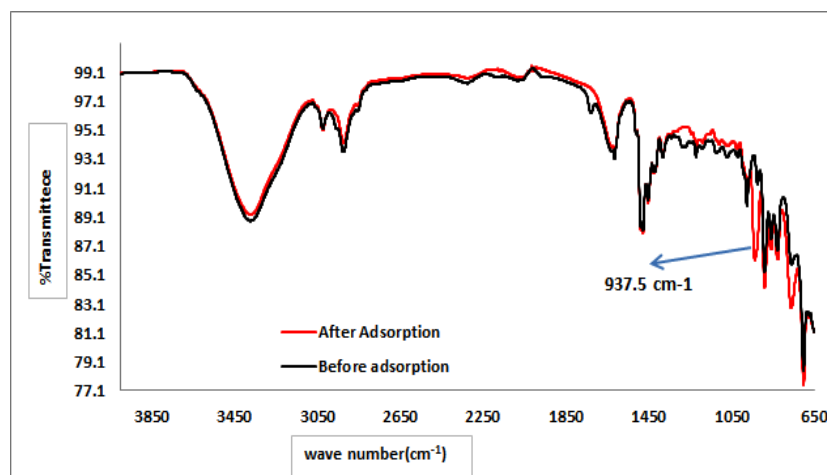**Figure 1**: SEM micrograph of Spectra/Gel adsorbent.

Figure 2: FTIR spectrums of Spectra/Gel adsorbent.

3.2. FTIR Analysis

FTIR analysis of the resin before and after Cr(VI) adsorption was performed to find the interaction between resin and Cr(VI) as shown in Figure **2**. A broad and strong peak appeared at 3376 cm^{-1} corresponding to O-H of moisture as the resin contains about 43% to 48% moisture content. The peak aroused at 2923 cm^{-1} is due to aromatic C-H stretching vibrations. The sharp peak at 1614 and 1477 cm^{-1} may be due to C=C or N-C stretching. A new peak after Cr(VI) adsorption was observed at 937 cm^{-1} due to Cr=O, confirming presence of Cr(VI) on the surface of the adsorbent [18].

3.3. EDAX Analysis

The energy dispersive X-ray spectroscopic analysis of Spectra/Gel after Cr(VI) adsorption is shown in Figure **3**, The plot reveals chromium peaks on the resin surface which confirmed the chromium sorption onto the Spectra/Gel.
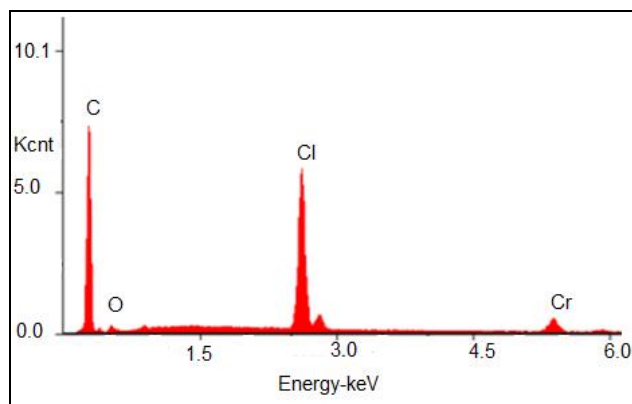

Figure 3: EDX analysis of Spectra/Gel after chromium (VI) adsorption.

3.4. Effect of pH

The pH is one of the important factors that affect the removal of metal ions from aqueous media since pH influences the adsorbent surface properties and ionic forms of chromium in the solution [19]. The influence of pH on the adsorption of Cr(VI) ions is shown in Figure **4**. It was observed that maximum adsorption was achieved at pH 3.0. A gradual decrease in adsorption of Cr(VI) was observed with the increase of the pH values.
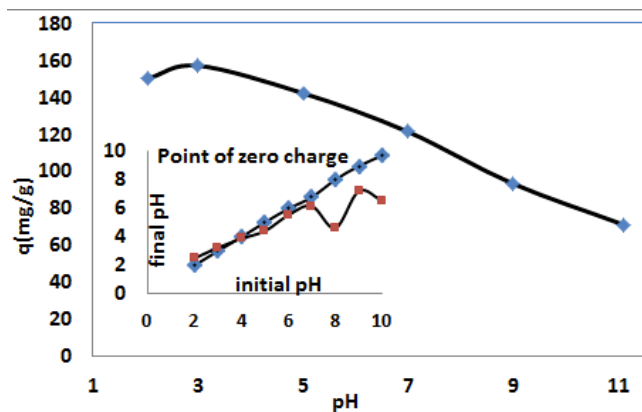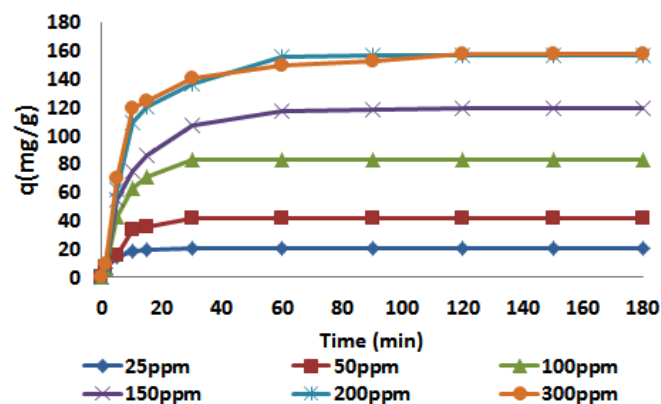

Figure 4: Effect of pH on removal of Cr(VI) from aqueous solution. (Contact Time =30 min, Cr (VI) initial conc. 300 mg L^{-1}, adsorbent = 1g/L). Insect: Point of zero charge study.

The change in adsorption with pH can be explained on the basis of surface charge of the adsorbent and the ionic species of chromium. In aqueous solution, Cr(VI) exists mainly in the form of $Cr_2O_7^{2-}$ and $HCrO_4^-$ in acidic pH (less than 6), while at pH greater than 6 CrO_4^{2-} is the main ionic species. The point of zero charge (pH$_{ZPC}$) of the adsorbent was measured at pH 3.5 At pH lower than the pH$_{ZPC}$, H$^+$ ions are adsorbed by the -

NH- of trimethylbenylamonium groups on the surface of the Spectra/Gel which by electrostatic interactions may form complex with $Cr_2O_7^{2-}$ and $HCrO_4^-$ [20].The, decrease in the adsorption capacity beyond the pH_{ZPC} with strong basic conditions can be associated to the appearance of $Cr(OH)_3$ and anionic $Cr(OH)^{4-}$ species that may have electrostatic repulsion with the deprotonated amine groups [21]. Therefore pH 3 was considered as the optimum for further study of removal of Cr(VI).

3.5. Effect of Time

The influence of contact time on Cr(VI) was studied at 23,33,43 ^{o}C as shown in the Figure **5**. The results reveal that the amount of Cr(VI) adsorbed (mg/g) increased with the contact time and temperature until it gradually approaches the equilibrium state. This can be explained by increase in the pore size of the adsorbent molecules with decrease in the viscosity of the multi atomic layered adsorbent and increase in the velocity of the Cr(VI) ions that facilitates diffusion [22]. The removal efficiency of Cr(VI) steadily increased and reached the maximum within 120 minutes for the entire concentration range. Initially it was observed that the adsorption was fast, possibly because Cr(VI) ions get adsorbed on the vacant adsorbent sites on the surface of the adsorbent [23]. Thereafter, the adsorption occured slowly because the Cr(VI) ions now have to move through the pores of the adsorbent material. Furthermore it was observed that large number of adsorbate species require a short time period to bind them by physical interaction to the adsorbent. Chemical binding of the adsorbate to the adsorbent on the other hand requires a longer contact time to establish equilibrium [24].
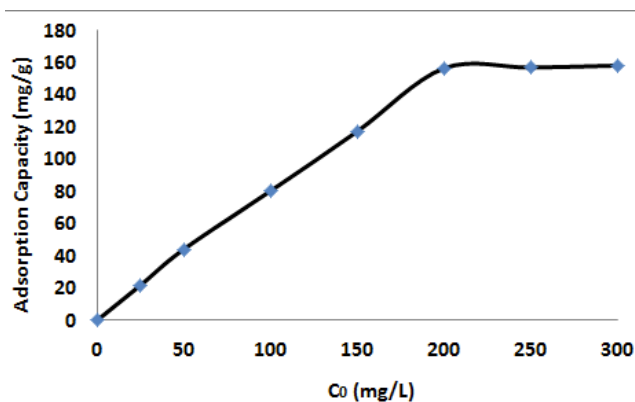
## 3.6. Effect of Metal Ion Concentration

The effect of initial metal ion concentration on the adsorption capacity is shown in Figure **6**. The adsorption capacities were calculated for initial Cr(VI) concentrations varied from 25 to 300 mg/L while other parameters were kept the same. The results showed an increase in Cr(VI) adsorption from 21.8 to 158.1 mg per unit mass of adsorbent. It was also observed that initial Cr(VI) concentrations higher than 200 mg/L showed no further increase in unit adsorption. The decrease in percentage removal can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain initial concentration (1).

3.7. Effect of Adsorbent Dose

The effect of adsorbent amount on removal efficiency of Cr(VI) was evaluated by adding different amounts of the Spectra/Gel adsorbent in the test solution while keeping other parameters constant. The results showed that by increasing the amount of adsorbent in test solution, adsorption capacity of Cr(VI) decreased from 87.7 to 19.07 mg/g for 50 mg/L initial Cr(VI) concentration. Figure **7** shows decrease in unit adsorption with increase in the adsorbent dose. This can be explained by the possible agglomeration of adsorbent particles which decreases the surface area for interaction with Cr(VI) and also results in prolonged diffusion path. On the contrary, the adsorption efficiency increased continuously from 68.3 to 99.06 % with increasing adsorbent dosages from 0.25 to 1 mg in 200 mg/L test solution. Further increase in the amount of adsorbent has insignificant effect on the adsorption efficiency. This may be attributed to reaching maximum adsorption after which the amount of ions bound to the adsorbent and the amount of free ions remains constant [25].

Figure 5: Effect of contact time on removal of Cr(VI) from aqueous solution. (Solution pH =3, Gel dose =1g/L).


Figure 6: Effect of initial concentration on removal of Cr(VI) from aqueous solution. (Solution pH = 3, adsorbent amount = 1g/L, t = 120 min).
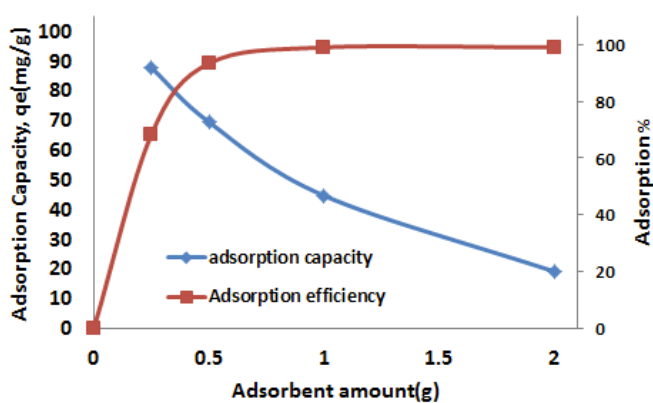
Figure 7: Effect of adsorbent mass on removal of Cr(VI) from aqueous solution. (Solution pH=3, Cr(VI) conc. 50 mg L^{-1}, t = 30 min).

3.8. Adsorbent Regeneration

Cr(VI) was desorbed from the saturated Spectra/Gel adsorbent using water, HCl, NaCl and NaOH solutions. Water and HCl showed no desorption while 14.6% and 37.5% Cr(VI) was recovered with 0.1MNaCl and NaOH respectively. The desorption efficiency increased up to 76.25% with 3.0M NaOH as shown in Figure **8**. The reason behind incomplete desorption may be attributed to the strong chemical interaction between the amine groups and the Cr(VI) ions. Also the inability of the Cr(VI) ions diffusion within the multi-atomic layers of the adsorbent may be responsible for incomplete desorption. The adsorption tests were performed with Cr(VI) concentration of 300 mg/L, pH 3 and adsorbent dosage of 1g/L. After 3 regeneration and adsorption cycles the Spectra/Gel retained its high efficiency and showed 83.5% regeneration efficiency.
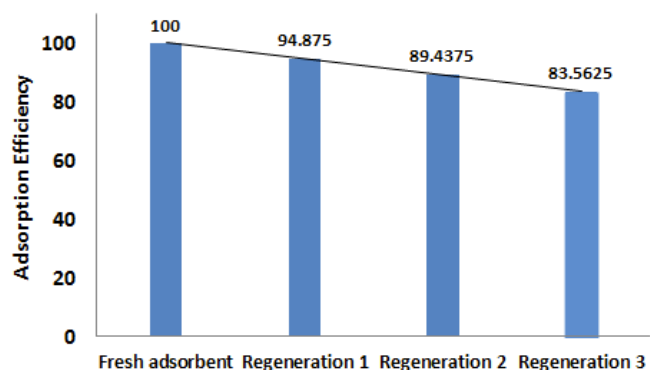
Figure 8: Effect of regeneration on removal of Cr(VI) from aqueous solution. (Cr Conc. =300ppm, pH =3, contact time = 180 min, adsorbent = 1g/L).

3.9. Adsorption Isotherm

To optimize the interaction of the Spectra/Gel adsorbent with the adsorbate, the adsorption equilibrium data was fitted with Langmuir [26] and the Freundlich [27] equilibrium models.

3.9.1. Langmuir Isotherm

The following equation represents the Langmuir isotherm:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m K_L}\right) + \frac{C_e}{q_m} \tag{2}$$

where C_e is initial concentration of Cr(VI) in the solution (mg/L) while q_e is the equilibrium concentration of Cr(VI) adsorbed (mg/g). The adsorption capacity (mg/g) is denoted by q_m and K_L is Langmuir constant (L/mg). The plot of C_e/q_e against C_e over the wide range of Cr(VI) initial concentration showed a linear relationship which suggests that adsorption of Cr(VI) on Spectra/Gel adsorbent followed the Langmuir isotherm (Figure **9**). The Langmuir model represents homogeneous adsorption sites having equal adsorption activation energy and also suggests that adsorbent surface has monolayer adsorption [19]. The values of Langmuir isotherm parameters are given in Table **1**.
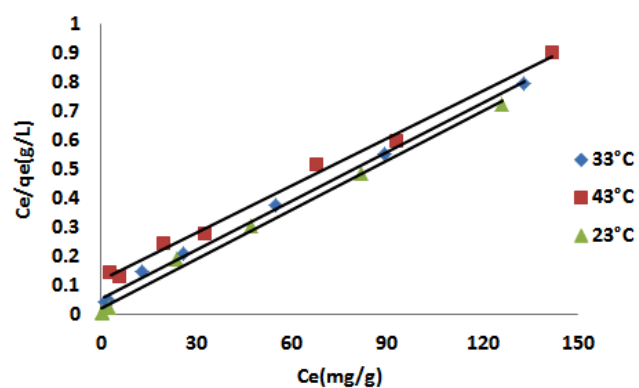
Figure 9: Langmuir isotherm plot for Cr(VI) adsorption onto the adsorbent.

3.9.2. Freundlich Isotherm

The Freundlich isotherm represents heterogeneous surface energy systems and is expressed by the following linearized equation.

$$In q_e = In K_F + \frac{1}{n}\ln C_e \tag{3}$$

where q_e represents Cr(VI) adsorption capacity at equilibrium (mg/g); C_e is the equilibrium solution concentration of Cr(VI) (mg/L); K_F is the Freundlich constant (mg$^{1-1/n}$ L$^{1/n}$ g^{-1}) and 1/n refers to adsorption intensity. Freundlich constants, K_F and n are obtained by plotting the graph between lnq_e versus lnC_e. In general, as the K_F value increases the adsorption

Table 1:   Langmuir Isotherm Parameters for Adsorption of Cr(VI) onto Spectra/Gel Adsorbent

Temperature $°C$	q_m(mg g^{-1})	K_L (L mg^{-1})	R^2	R_L
23	169.4915	0.324176	0.9919	0.01018-0.10984
33	178.5714	0.101083	0.997	0.03192-0.28352
43	185.1852	0.045455	0.9939	0.06832-0.46809

Table 2:   Freundlich Isotherm Paraeters for Adsorption of Cr(VI) onto Spectra/Gel Adsorbent

Temperature °C	N	K_F (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	R^2
23	3.603604	51.68667	0.9022
33	2.54907	29.0349	0.9543
43	1.968892	15.72575	0.9394

capacity of the adsorbent also increases. The obtained result indicates that the equilibrium data is not fitted well with the Freundlich isotherm model. The values of different parameters calculated based on Freundlich model are provided in Table **2**.

3.10. Adsorption Kinetics

For designing and operation of adsorption system for wastewater treatment, study of the kinetic parameters of the adsorption process is very important. In order to understand the kinetics of removal of Cr(VI) using Spectra/Gel as an adsorbent, pseudo first-order equation, pseudo second-order equation and intraparticle diffusion kinetic model were tested with the experimental data.

3.10.1. Pseudo First-Order Kinetics

The equation for the pseudo-first-order kinetic model has the following differential form [28].

$$In\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{4}$$

where q_e and q_t denote the amount of adsorbed Cr(VI) (mg/g) at equilibrium and at time t(min) respectively, while k_1 is the pseudo-first order adsorption rate constant (min^{-1}). A straight line obtained from the plot of ln(q_e-q_t) versus t represents the pseudo first-order kinetics for the removal of Cr(VI). The values of k_1 and lnq_e were calculated from the slope and intercept of the plots respectively. The predicted values of different parameters of pseudo-first-order kinetic model are given in Table **3**.

3.10.2. Pseudo-Second-Order Kinetics

The kinetics for adsorption of Cr(VI) is tested with the second-order kinetic model. Following equation corresponds to the pseudo-second-order kinetics [29].

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \frac{t}{q_e} \tag{5}$$

where k_2 is equilibrium rate constant of the pseudo second-order adsorption (g/mg min) and q_t is the equilibrium adsorption capacity (mg/ g). Application of second order kinetics by plotting t/q_t vs. t (Figure **10**)

Table 3:   Values of Pseudo-First-Order Parameters for Cr(VI) Adsorption on Spectra/Gel Adsorbent

Initial Cr(VI) Conc. (mg L^{-1})	k_1(min^{-1})	q_e (mg g^{-1})	R^2
25	0.1521	14.86486	0.9539
50	0.1406	42.19914	0.9364
100	0.1368	82.2283	0.994
150	0.0665	91.57882	0.9906
200	0.0682	120.2533	0.9788
300	0.0335	76.79196	0.8605

yielded the second-order rate constant, k_2. Calculated equilibrium capacity q_e, and regression coefficient for the initial Cr(VI) concentration ranging from 25 – 300 mg/L are reported in Table **4**.
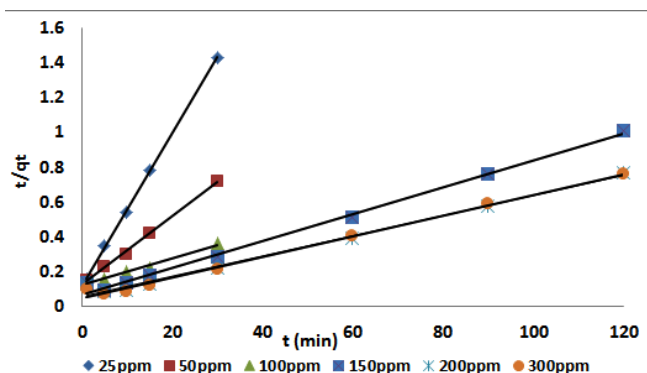
Figure 10: Pseudo-second-order kinetic model for Cr(VI) adsorption onto theSpectra/Gel sorbent.

The calculated q_e values show good agreement with the experimental values and the obtained values for regression correlation coefficients are close to 0.999, which indicates that the second order kinetic model can be applied for the removal of Cr(VI) using Spectra/Gel as an adsorbent.

3.10.3. Intraparticle Diffusion Kinetic Model

Pseudo first and second order kinetic models do not provide information about the intraparticle diffusion of Cr(VI) ions, so the Weber-Morris intraparticle diffusion model [30] was used to determine the transport of Cr(VI) ions within the porous structure of the adsorbent. Intraparticle diffusion model assumes that the film diffusion is negligible and intraparticle diffusion is the only rate-controlling step, which is usually true for well-mixed solutions. In most adsorption processes the adsorbate uptake varies proportionally with $t^{1/2}$ rather than with the contact time t [23].

$$q_t = k_d t^{\frac{1}{2}} + C \qquad (6)$$

where k_id represents intraparticle diffusion rate constant (g/(mg min)). For intraparticle diffusion a plot of q_t versus $t^{1/2}$ should give a straight line. Values of K_d and C are given by slope and intercept of the straight line plot. Values of intercept give an idea about the thickness of boundary layer, *i.e.*, larger the intercept greater is the boundary layer effect. As seen in Table **5**, the experimental data do not well agree with the intraparticle diffusion kinetic model.

From the three kinetic models applied to the experimental data, pseudo-second-order kinetic model gives the best fit for the investigated adsorption system at wide range of initial Cr(VI) concentrations (25- 300 mg/L) with regression coefficients values $R_2 > 0.9992$. The calculated q_e values were also in good agreement

Table 4: Values of Pseudo-Second-Order Parameters for Cr(VI) Adsorption on Spectra/Gel Adsorbent

Initial Cr(VI) Conc. (mg L^{-1})	q_m (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
25	22.83105	0.016581	0.9994
50	50.76142	0.003199	0.996
100	128.2051	0.000509	0.978
150	129.8701	0.000864	0.9935
200	172.4138	0.000585	0.9882
300	169.4915	0.000741	0.9934

Table 5: Values of Intraparticle Diffusion Parameters for Cr(VI) Adsorption on Spectra/Gel Adsorbent

Initial Cr(VI) Conc. (mg L^{-1})	K_d (mg g^{-1}min$^{-1/2}$)	R^2
25	3.143	0.8433
50	7.8222	0.8946
100	17.339	0.9668
150	9.5953	0.7608
200	12.723	0.7335
300	11.775	0.6795

with the experimental results. This suggests that the pseudo-second-order model is potentially a generalized kinetic model for the adsorption of Cr(VI) on to the Spectra/Gel adsorbent. Better fitting with pseudo-second-order kinetics also suggests that the rate-limiting step for this study may be chemisorption [31]. This confirmed that adsorption of Cr(VI) takes place probably via surface exchange reactions until the surface functional sites are fully occupied; thereafter chromate molecules diffuse into the adsorbent network for further interactions.

4. CONCLUSIONS

Cr(VI) ions were efficiently removed from synthetic wastewater solutions by using Strong anion exchange resin (Spectra/Gel IE 1x8). Equilibrium was established within 30 minutes for initial Cr(VI) concentration up to100 mg/L. Maximum adsorption capacity of the Cr(VI) was found to be 173.8 mg/g with an adsorbent dose of 1 mg/L. The kinetic data fitted very well with the pseudo-second-order kinetic model. The results showed better fits with Langmuir isotherm than the Freundlich isotherm. The calculated isotherm parameters confirmed the favorable adsorption of Cr(VI) on the Spectra/Gel sorbent.

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CONFLICT OF INTERESTS

The authors of the manuscript reported that they do not have a direct financial relation with the commercial identities mentioned in the paper that might lead to a conflict of interest for any of the authors.

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