

REMOVAL OF CHROMIUM (VI) FROM SYNTHETIC WASTEWATER USING SPECTRA/GEL ION-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 to 100 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 with 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. Effluents from tannery industry and electroplating are major sources of incorporation of Cr(VI) into the wastewater streams. 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. According to the World Health Organization standards for drinking water, the MCL of chromium is 0.05 mg/L (Witek-Krowiak et al. 2010). Therefore, it is necessary to remove chromium from wastewater prior to its final discharge into the environment. 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 (Rafati et al. 2010). 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 (Witek-Krowiak et al. 2010; Samani et al. 2010). Adsorption using bio-materials, activated carbons, carbon nanotubes and polymer resins has gained considerable attention

recently (Rodriguez et al. 2012). 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 (Pan et al. 2009). 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).

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 trimethylbenzylammonium group as the exchange site. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) purchased from BDH Chemicals Ltd. was used as precursor of Cr(VI).

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 650-4000 cm^{-1} .

2.3. Adsorption Experiments

The experiments were performed in 100 ml capacity Pyrex flasks. 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 $^{\circ}\text{C}$, respectively. 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:

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

where, q is the adsorption capacity in mg/g, C_0 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.

3. RESULTS AND DISCUSSION

3.1. SEM characterization

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

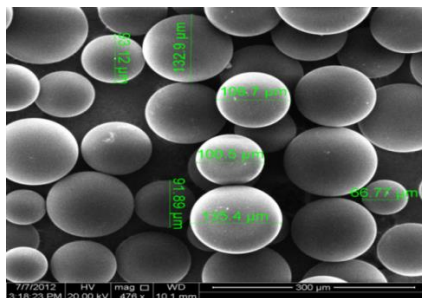


Figure 1. SEM micrograph of Spectra/Gel adsorbent

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 **Fig. 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 (Gandhi et al. 2010).

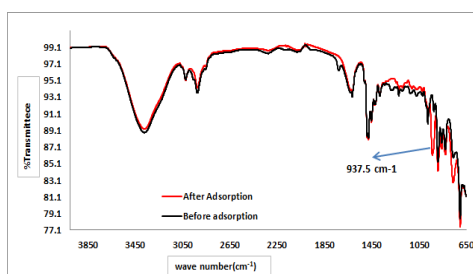


Figure 2. FTIR spectrums of Spectra/Gel adsorbent

3.4. Effect of pH

The pH influences the adsorbent surface properties and ionic forms of chromium in the solution (Crini 2008). The influence of pH on the adsorption of Cr(VI) ions is shown in **Fig.4**. In aqueous solution, Cr(VI) exists mainly in the form of $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- in acidic pH (less than 6), while at pH greater than 6 CrO_4^{2-} is the main ionic species. At pH lower than the pH_{ZPC} (3.5; inset), H^+ ions are adsorbed by the -NH- of trimethylbenzylammonium groups on the surface of the Spectra/Gel which by electrostatic interactions may form complex with $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- (Cui et al. 2013). The decrease in the adsorption capacity beyond the pH_{ZPC} with strong basic conditions can be associated to the appearance of $\text{Cr}(\text{OH})_3$ and anionic $\text{Cr}(\text{OH})_4^-$ species that may have electrostatic repulsion with the deprotonated amine groups.

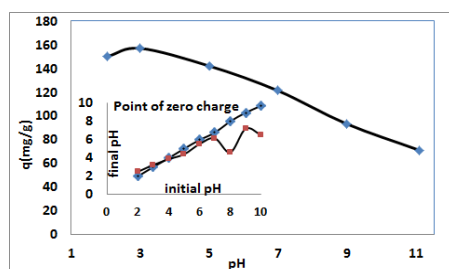


Figure 4. Effect of pH on removal of Cr(VI) from aqueous solution;
Inset: Point of zero charge study
(Contact Time =30 min, Cr (VI) initial conc. 300 mg L^{-1} , adsorbent = 1 g/L)

3.5. Effect of contact time

As shown in the **Fig.5** it was observed that the amount of Cr(VI) adsorbed (mg/g) increased with the contact time 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 (Lu et al. 2006). 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. Thereafter, the adsorption occurred slowly because the Cr(VI) ions now have to move through the pores of the adsorbent material. Chemical binding of the adsorbate to the adsorbent on the other hand requires a longer contact time to establish equilibrium.

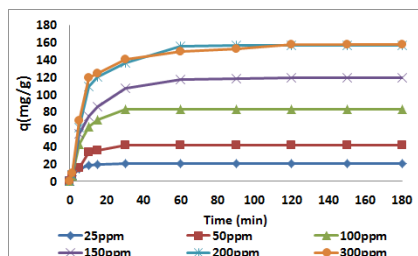


Figure 5. Effect of contact time on removal of Cr(VI) from aqueous solution
(Solution pH =3, Gel dose =1g/L)

3.6. 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 **Fig. 6**. The reason behind incomplete desorption may be attributed to the strong chemical interaction between the amine groups and the Cr(VI) ions. After 3 regeneration and adsorption cycles the Spectra/Gel showed 83.5% regeneration efficiency.

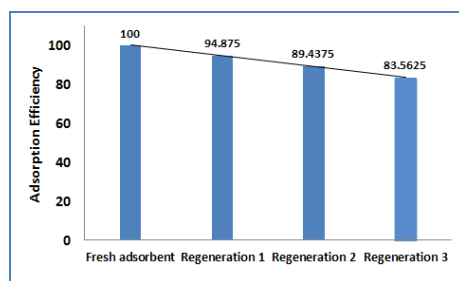


Figure 6. Effect of regeneration on removal of Cr(VI) from aqueous solution
(Cr Conc. =300ppm, pH =3, contact time = 180 min, adsorbent = 1g/L)

3.7. Langmuir Isotherm

To optimize the interaction of the Spectra/Gel adsorbent with the adsorbate, the adsorption equilibrium data was fitted with Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1907) equilibrium models. The following equation represents the Langmuir isotherm:

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

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 results suggests that adsorption of Cr(VI) on Spectra/Gel adsorbent followed the Langmuir isotherm (Fig. 7).

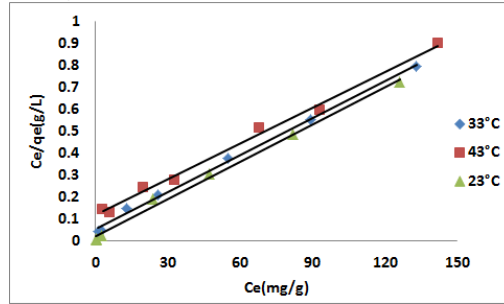


Figure 7. Langmuir isotherm plot for Cr(VI) adsorption onto the adsorbent.

The Langmuir model represents homogeneous adsorption sites having equal adsorption activation energy and also suggests that adsorbent surface has monolayer adsorption. The values of Langmuir isotherm parameters are given in Table 1.

Table 1. Langmuir isotherm parameters for adsorption of Cr(VI) onto Spectra/Gel adsorbent.

Temperature °C	$q_m(\text{mg g}^{-1})$	$K_L(\text{L mg}^{-1})$	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

3.8. Adsorption Kinetics

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.

3.8.1 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 (Ho and McKay 1998).

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

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 (Fig. 8) yielded the second-order rate constant, k_2 .

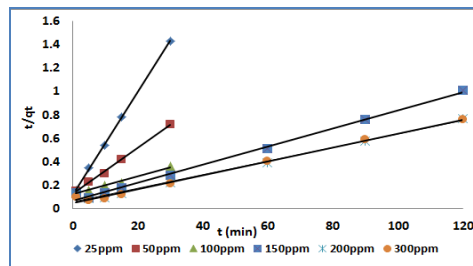


Figure 8. Pseudo-second-order kinetic model for Cr(VI) adsorption

Calculated equilibrium capacity q_e , and regression coefficient for the initial Cr(VI) concentration ranging from 25 – 300 mg/L are reported in Table 2.

Table 2. 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

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.

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 to 100 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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