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Adsorption kinetics and adsorption isotherm studies of chromium from aqueous solutions by HPAM-chitosan gel beads

Wei Kuang[a,b,*], Yebang Tan[a,*], Lihong Fu[b]

[a]*School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, PR China*
[b]*School of Chemistry and Pharmaceutical Engineering, Shandong Polytechnic University, Jinan 250353, PR China*
Tel. +86 531 89631208; Fax: +86 531 88564464; emails: kkwei261@yahoo.com.cn (Wei Kuang), *ybtan@sdu.edu.cn* (Yebang Tan)

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ABSTRACT

HPAM-chitosan gel beads were utilized as an adsorbent in removing Cr(VI) and Cr(III) from aqueous media. The high percentage of removal for Cr(VI)—82.9% and Cr(III)—67.6% suggests the great potential for HPAM-chitosan gel beads as an adsorbent for the removal of chromium (Cr) ion from aqueous solution. The kinetic data has been tested in the process of adsorption for Cr(III) and Cr(VI), and proved that it follows the pseudo-second-order rate equation. Both Langmuir equations and Freundlich equations were used for explaining the experimental data of adsorption isotherm, which demonstrated a better fit to the Lagmuir model. Thus, it suggests a monolayer adsorption process onto the gel beads. Moreover, Chromium adsorption profile onto HPAM-chitosan gel beads is suggested through the schematic representation.

Keywords: Adsorption; Kinetics; Isotherms; Chromium; Gel beads; Hydrolyzed polyacrylamide

1. Introduction

During the past decade, the use of chromium(Cr) chemicals in several industrial processes (leather tanning, mining of chrome ore, production of steel and alloys, dyes and pigment manufacturing, cement industries, wood preservation, textile industry, metal cleaning, plating and electroplating, etc.) has caused natural water contamination mainly due to improper disposal methods [1]. Chromium exists in aqueous environment mainly in the form of Cr(VI) and Cr(III) oxidation states. On the one hand Cr(III) at low concentrations can help the body control blood sugar levels less toxic and soluble [2], on the other hand under certain circumstances Cr(III) may be oxidized to Cr(VI) [3], however, Cr(VI) is a powerful epithelial irritant and a confirmed human carcinogen [4]. Recently, more than 5000 tons of chromium compound waste was dumped illegally by two truck drivers in rural areas near Qujing city in China from the end of April to June, 2011. The discharge of effluents containing Cr(VI) and Cr(III) into groundwater caused livestock death and pollution for soil and water.

Although inorganic contaminants such as Cr(III) and Cr(VI) cannot be chemically destroyed, many different technologies such as chemical precipitation [5], sedimentation [6] electrochemical processes [7,8], ion exchange [9], and biological operations [10], etc., are available to remove Cr(III) and Cr(VI) from wastewater. The most common conventional method for Cr(VI) removal is reduction of Cr(III) to pH 2.0 and precipitation of $Cr(OH)_3$ by increasing pH to 9–10 using lime. However, an alternative way of decreasing their harmful effects is adsorption process, which seems to be most

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*Corresponding authors.

versatile and effective. For example, adsorption with activated carbon, which provides an active surface and a porous structure, is an efficient but expensive alternative. Furthermore, this adsorbent has a limited recycling as a result of loss during the recovery process [11–13]. Therefore, cost-effective alternative technologies or adsorbents for the removal of these heavy metal ions are needed.

In the present work, we propose to use HPAM-chitosan gel beads as a potential alternative adsorbent for removal of several heavy metal ions such as Cr(VI) and Cr(III) from aqueous solutions, and the objective of our investigation is to develop a safe disposal of chromium effluents. As a result, the adsorption kinetics and adsorption isotherms of heavy metal ions mentioned earlier were performed to demonstrate the efficiencies of HPAM-chitosan gel beads.

2. Experiments

2.1. Materials

HPAM aqueous solution (1 wt%) (HPAM average M_W 4.3×10^6 g mol^{-1} and the hydrolysis degree of it was 46%.) was extruded dropwise through a syringe into $AlCl_3$ solution (0.2 mol l^{-1}), and the generated HPAM-Al gel beads were washed with distilled water for three times and immersed into chitosan solution (CS, average M_W 9.1×10^5 g mol^{-1}; degree of deacetylation 71%) for 24 h. These gel beads were dried under reduced pressure at 50° for 48 h and were labeled HPAM-chitosan gel beads [14,15].

In the adsorption tests, standard solutions of Cr(VI) and Cr(III) were prepared to use either potassium dichromate ($K_2\ Cr_2\ O_7$) or $CrCl_3 \cdot 6H_2O$, respectively. Other materials were analytical reagent and used as received from Kermel.

2.2. Adsorption experiments

Stock solution of Cr(VI) and Cr(III) with a concentration of 1000 mg l^{-1} was prepared by ($K_2\ Cr_2\ O_7$) and $CrCl_3 \cdot 6H_2O$ respectively, which were diluted for preparation of standard and test solutions. All adsorption flasks were kept in a temperature controlled batch. For each experimental run, 40 ml of Cr(VI) or Cr(III) solution of known concentration, which contained only one kind of metal ion, was taken from a 100 ml stoppered reagent bottle. The solution was stirred by a magnetic stirrer continuously during the adsorption experiment. The metal ion concentration of solution was determined by atomic adsorption spectrophotometer (Varian Spectra HP 3510).

For kinetic studies of known concentration Cr ion solution, a known amount of adsorbent was kept in 100 ml flask in a water bath, maintained at a desired temperature, and the mixture was mechanically agitated. After a definite interval of time, the solution in the flasks was filtered and each filtrate was analyzed for the uptake of Cr ion.

Adsorption isotherm experiments were also performed by agitating 0.4 g of the gel beads with 40 ml of Cr ion of varying concentrations from 200.0 to 1000.0 mg l^{-1} in a 100 ml stoppered reagent bottle. The pH of the solution and the contact time were adjusted to an optimum pH and an established time respectively. The adsorption studies were also performed under different temperatures.

2.3. Desorption experiments

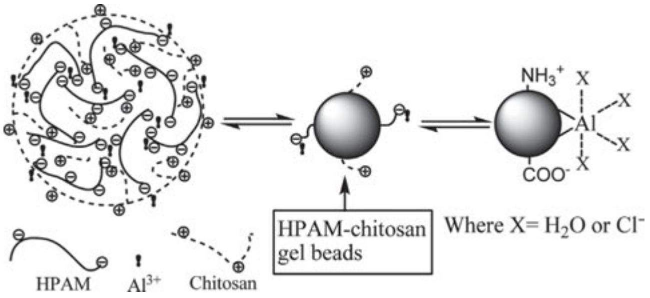
To evaluate the possibility of regeneration of the adsorbents, desorption and regeneration studies were also carried out. After immersed into chromium ion solution at pH 4.2 for 4 h, the gel beads were taken out from the metal ion solution, then the adsorbent was separated from solution by centrifugation and washed gently with water to remove any unadsorbed Cr. The adsorbed Cr ions in gel beads were removed by stirring in 40 ml of HCl (0.1mol l^{-1}) solution for 30 min, followed by centrifugation for separation. The spent gel beads thus regenerated were reused for adsorption purpose. The adsorption-dead-sorption test of the gel beads was repeated for six consecutive times.

3. Results and discussion

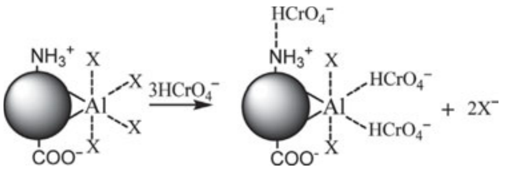
3.1. Schematic representation of the formation of the HPAM-chitosan gel beads and chromium adsorption profile onto gel beads

When the HPAM-Al gel beads are immersed into a chitosan solution for a long time, these possibilities of interaction based on the electrostatic attraction between -COO$^-$(HPAM) and -NH_3^+ (chitosan) or aluminium ion(Al^{3+}) can form the skeleton structure presented as gel beads, which provides large electrical charges and coordination bond. A schematic representation of the formation of the gel beads is shown in Scheme 1.

The chromium(VI) adsorption can be considered to be ligand exchange reaction between coordinated Cl^- ion (or H_2O) and $HCrO_4^-$ species. Also it has the possibility to interact on the chitosan (-NH^{3+}) surface of gel beads with Cr(VI) ($HCrO_4^-$). So the pH increased beyond 4.2, the hydrogen ions from the chitosan (-NH^{3+}) on the surface of gel beads reduced and the removal of Cr(VI) adsorbed were decreased through favorable electrostatic attraction. The reactions can be schematically represented as Scheme 2(a):



Scheme 1 The schematic representation of the formation of the HPAM-chitosan gel beads.



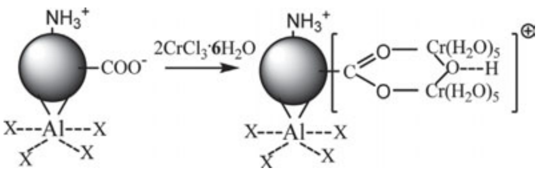
Scheme 2(a) Chromium(VI) adsorption profile onto HPAM-chitosan gel beads.

Generally the negative charge(-COO$^-$) remained on HPAM-chitosan gel beads will be attracted toward the positively charge chromium (III) (CrCl3·6H2O), and major species of Cr(III) presented as hydroxo group with H2O were bound on the gel beads through the peripheral oxygen atoms from carboxyl group. The favorable adsorption of Cr(III) onto -COO$^-$ (HPAM) is shown in proposed Scheme 2(b):

3.2. *Effect of pH on Cr removal*

Aqueous phase pH values play a critical role in the speciation of Cr and the dissociation of active functional sites on the gel beads. In the present work, adsorption can not be performed beyond pH 5.0 due to precipitation of $Cr(OH)_3$ and, therefore, the experiments of pH effects on Cr were also done within the pH range of 0.5–5.0. Removal of adsorption for chromium as a function of solution pH values is shown in Fig. 1.

Results of Cr(VI) adsorption experiments show that the removal efficiency increased from 7.14% to 82.96% as function of pH at the range of 0.5–5.0 in the solution, and the maximum adsorption was observed at pH 4.2, which indicated that the reduction of Cr(VI) was favored in the weak acid solutions. For Cr(III) species, there was hardly any adsorption at pH below 1.5 and the amount of absorbed Cr(III) exhibited a sharp increase with pH (from 2 to 4) while there appeared a similar plateau at 4.0≈5.0 , until the maximum Cr(III) removal yield was obtained at pH 5.0 in this case.



Scheme 2(b) Chromium(III) adsorption profile onto HPAM-chitosan gel beads.

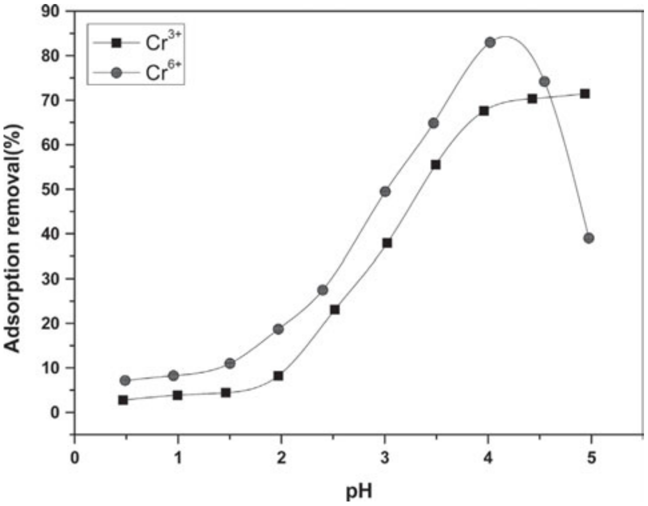


Fig. 1. Effect of pH on the adsorption removal of chromium species with 0.1 g of HPAM-chitosan gel beads placed in 40 ml of 50 mg l^{-1} chromium solution for 4 h.

From the above results, pH 4.2 was selected as the most suitable for all subsequent studies on Cr removal by gel beads.

3.3. *Adsorption kinetics*

The adsorption kinetic studies are fundamental in determining the adsorption capacity of Cr onto the gel beads. In order to calculate an effective and applicable adsorption model, kinetics of the adsorption process was monitored by observing the effects of contact time on adsorption of Cr.

The amount of chromium ion q_e (mg g^{-1}) adsorbed by the gel beads is determined by the following equation:

$$q_e = \frac{(C_0 - C_t)\times V}{m} \tag{1}$$

where C_0 is the initial adsorbate concentration (mg l^{-1}), C_t is the equilibrium concentration in solution at time t (mg l^{-1}). V is the volume of solution (l), and m is the mass (g) of the adsorbents used.

The kinetic data has been tested by the pseudo-second-order rate equation shown below as Eq. (2)[16,17]:

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

where K is the pseudo-second-order rate constant of adsorption (g (mg min)$^{-1}$); q_t and q_e are the uptake (mg g^{-1}) of chromium ion at time t and at equilibrium, respectively.

The contact time for the chromium removal by gel beads is an important parameter for designing adsorption systems and the optimum operating time is required for the following batch processes. A compared adsorption between Cr(VI) and Cr(III) on gel beads at 100 mg/l of initial Cr concentration is illustrated in Figs. 2(a) and (b). The results indicated that the gel beads have a good performance on the removal of Cr ion, and as compared with Cr(III) ion, the uptake of absorbed Cr(VI) ion remains at a higher level. It is also observed that a sharp increase of adsorption of Cr(VI) and Cr(III) was obtained during the first 100 min of contact time, followed by a slow increase until an equilibrium state was reached.

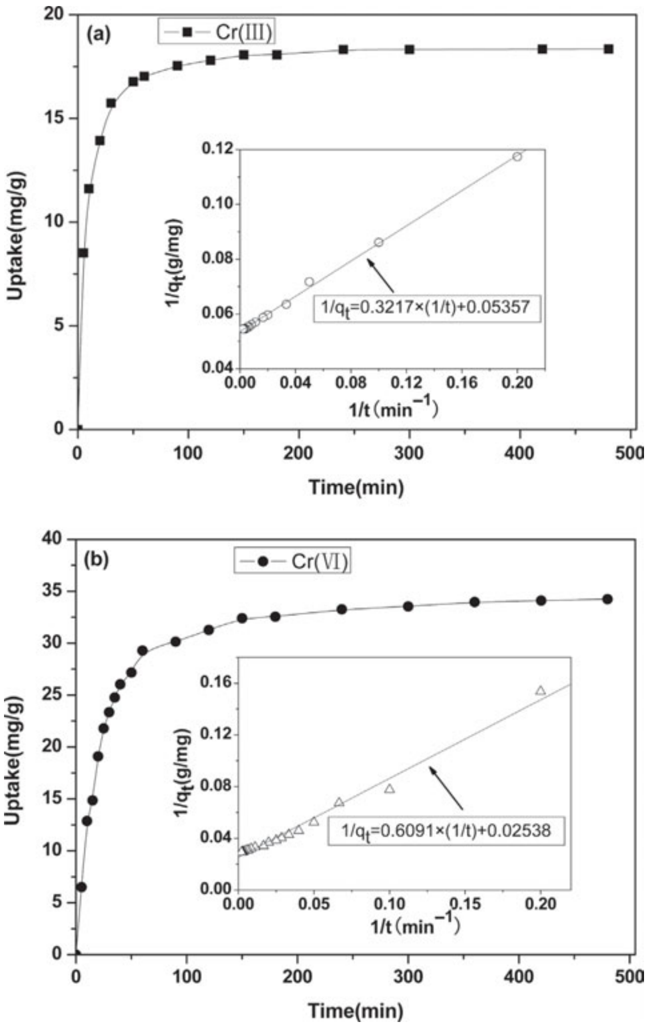


Fig. 2. Adsorption kinetics of Cr(III) (a) and Cr(VI) (b) by HPAM-chitosan gel beads (35°C, pH 4.2; initial metal concentration 100 mg l^{-1}).

The kinetic model of Cr ion adsorption can be observed and the values of $1/q_t$ versus $1/t$ were calculated through the investigation of the uptake of Cr ion versus the contact time. Kinetic parameters of the pseudo-second-order rate equation were used widely for evaluating the adsorption of solute from a liquid solution at different Cr concentrations, which were calculated from the slope and intercepts of the linear plots in Figs. 2(a) and (b), given in Table 1. Obviously, from the result of Table 1, the value of q_e for Cr(VI) increased from 9.95 to 66.12 mg g^{-1}, higher than the q_e value of Cr(III) at the corresponding initial concentration, which increased from 25 to 200 mg l^{-1}. It indicated that a more efficient utilization of the sorptive capacities of the sorbent is expected due to a greater driving force by the higher initial Cr ion concentrations [16]. The data also showed that a very high correlation between the experimental data and the pseudo-second-order model (R^2 > 0.968) was obtained in our experiment.

3.4. Adsorption isotherm

The isotherms were evaluated by Langmuir and Freundlich models, which have been used commonly to fit experimental data when the solute uptake occurs by a monolayer sorption, which suggests a monolayer adsorption occurred on homogeneous surface [18]. The Langmuir sorption isotherm equation is given below:

$$\frac{1}{q_e}=\left(\frac{1}{bq_{\max}}\right)\times\frac{1}{C_e}+\frac{1}{q_{\max}} \tag{3}$$

where q_e and C_e are the amount of adsorbed chromium ions per unit weight of adsorbent and unadsorbed chromium ion concentration in solution at equilibrium, respectively. $q_{\max}$ signifies the adsorption capacity and b is related to the energy of adsorption.

The Freundlich sorption isotherm equation can be used to estimate the adsorption intensity of the adsorbent towards the adsorbate and is expressed in the linear form as:

$$\ln q_e=\ln K_F+\frac{1}{n}\ln C_e \tag{4}$$

where K_F (mg^{1-n}L^{n} g^{-1}) and n are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity [19]. Freundlich

Table 1
Kinetic parameters of the pseudo-second-order rate equation for Cr ion onto HPAM-chitosan gel beads

Initial Cr ion concentration (mg l^{-1})	Parameters of the pseudo-second-order rate equation for Cr(III)			Parameters of the pseudo-second-order rate equation for Cr(VI)		
	K (g (mg min)$^{-1}$)	q_e	R^2	K(g (mg min)$^{-1}$)	q_e	R^2
25	9.69×10^{-2}	6.85	0.977	4.01×10^{-2}	9.95	0.996
50	3.12×10^{-2}	11.28	0.996	7.52×10^{-3}	19.78	0.988
100	8.92×10^{-3}	18.67	0.987	1.06×10^{-3}	39.40	0.973
200	2.40×10^{-3}	31.15	0.968	4.40×10^{-4}	66.12	0.975

isotherm equation is widely used in heterogeneous systems and indicates adsorption in many layers [20].

The adsorption isotherm of Cr ion onto gel beads was obtained at the three chosen temperatures (25°C, 35°C, and 45°C), by varying the initial Cr concentration in the range of 200 to 1000 mg l^{-1}. Langmuir and Freundlich adsorption models were also used to describe the adsorption system. Experimental data from the adsorption isotherms shown in Fig. 3 fit to Langmuir and Freundlich models. Values of the Langmuir constants and Freundlich constants evaluated from the slope and intercept of the graphs are given in Table 2.

In the case of Cr(VI) adsorption, Langmuir and Freundlich adsorption models were also used to describe the adsorption system. The experimental adsorption isotherm determined at different temperatures is depicted

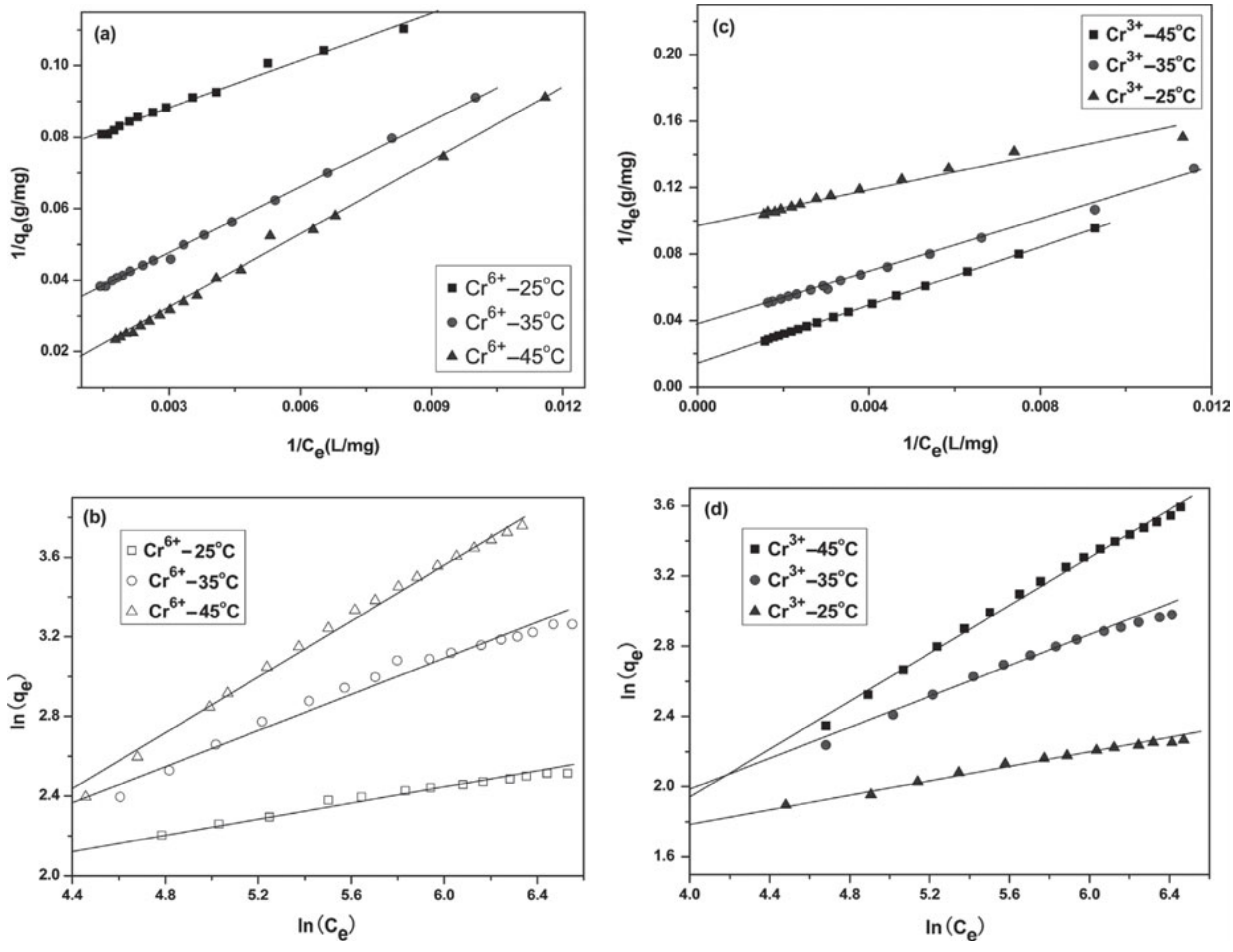


Fig. 3. Adsorption isotherms for Cr ion removal by HPAM-chitosan gel beads; Conditions:initial Cr ion concentration 200–1000 mg l^{-1}, mass of gel beads 0.4 g, contact time 4 h, pH 4.2, V 40 ml. (a) Langmuir models of Cr(VI); (b) Freundlich models of Cr(VI); (c) Langmuir models of Cr(III); (d) Freundlich models of Cr(III).

Table 2
Langmuir and Freundlich constants and correlation coefficients for chromium removal by HPAM-chitosan gel beads

Initial Cr ion	T (°C)	Langmuir constants			Freundlich constants		
		$q_{\max}$ (mg g^{-1})	b (l mg^{-1})	R^2	K_F(mg g^{-1})	n	R^2
Cr(III)	25	10.32	0.018	0.977	2.59	4.82	0.993
	35	26.48	0.0048	0.998	1.24	2.26	0.993
	45	71.48	0.0016	0.999	0.45	1.46	0.998
Cr(VI)	25	13.34	0.017	0.994	3.43	4.96	0.989
	35	34.18	0.0048	0.999	1.44	2.21	0.986
	45	84.89	0.0017	0.998	0.52	1.43	0.997

in Figs. 3(a) and (b). By observing the Cr(VI) adsorption shown in the pictures, the Langmuir model fitted better than the Freundlich model to the experimental data, which suggests the presence of homogeneous surface sites and an adsorption process of Cr(VI) through monolayer formation. Comparison of Freundlich isotherms constants in Table 2 shows that Cr(VI) on the gel beads exhibits higher K compared to Cr(III) on the adsorbent.

This indicates that the gel beads is more effective for the removal of Cr(VI) from water. In addition, for both Cr(III) and Cr(VI) the gel bead is a strong adsorbent for chromium since $n > 1$, the adsorption is favorable [21]. This means that the adsorbent can be practical and has potential industrial significance for water treatment. The results in Table 2 also show that an increase of temperature from 25°C to 45°C will enhance the maximum adsorptive capacity of gel beads, which indicates the endothermic nature of chromium-removal process by adsorption onto gel beads.

3.5. Desorption

Desorption is an important requirement for commercial adsorbents, which will help to regenerate the adsorbents which can be reused in water treatment. Acid regeneration was tested since it was known to be a suitable eluent for most cation exchangers [22,23].

In the present work, according to the preliminary investigations in the desorption of Cr on gel beads, 0.1 M HCl was selected as better eluent for conducting regeneration studies. The results of regeneration indicated that there was a noticeable loss of adsorption capacity after the first reuse cycle and the adsorption capacities of gel beads for Cr(III) and Cr(VI) decreased from 67.6% to 54.8%, 82.9% to 72.3% respectively. However, the adsorption capacities of gel beads did not show obvious decrease after the second reuse cycle. After the sixth reuse cycle, the highest efficiency of desorption (67.6%) was obtained with Cr(VI), followed by Cr(III) (48.8%).

4. Conclusions

Batch studies of adsorption by HPAM-chitosan gel beads demonstrated that the maximum percentage of removal for chromium(Cr) ion from its aqueous solutions at pH 4.2 was found to be 82.9% for Cr(VI) and 67.6% for Cr(III) respectively. Moreover the adsorption kinetics and adsorption isotherms of chromium ions were performed to demonstrate the efficiencies of HPAM-chitosan gel beads. Statistical analysis revealed that the process of adsorption for Cr(III) or Cr(VI) follows a pseudo-second-order kinetics and is endothermic in nature. The equilibrium data can be well fitted with a Langmuir isotherm and Freundlich isotherm at 25°C, 35°C, and 45°C. The adsorbed Cr(III) or Cr(VI) desorbed quantitatively by 0.1 M HCl solution and the adsorbent can be reused for six cycles consecutively. The research performed in the present work clearly suggests that HPAM-chitosan gel beads as a biosorbent for the removal of chromium(Cr) ion from aqueous solution is feasible, and there is a great potential for the adsorbent in developing a safe disposal of chromium effluents.

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