Adsorption of Cr(VI) using Fe-crosslinked chitosan complex (Ch-Fe)

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ABSTRACT

In the present investigation, Fe-chitosan crosslinked is used as adsorbent for the removal of chromium from aqueous solutions. The influence of pH, temperature and other ions was evaluated. pH 2.0 was found to be the optimum pH for adsorption of Cr(VI) onto Ch-Fe. Coordination of unsaturated sites for the iron(III) complex of polymer were considered to be the adsorption sites for Cr(VI) species, the predominant species being $HCrO_4^-$. The Langmuir and Langmuir–Freundlich adsorption isotherm models were applied to describe the isotherm parameter for Cr(VI) adsorption. The results indicate that the Langmuir–Freundlich adsorption model and maximum adsorption capacity was calculated as 295 mg/g at 25 °C, with pH 4.7. Cr(VI) uptake on the adsorbent decreased from 295 mg/g at 25 °C to 209 mg/g at 65 °C. Rate constants as a function of temperature were evaluated with the help of a proposed second order kinetic model. The other coexisting ions, nitrate, chlorides and sulphate influenced Cr(VI) adsorption.

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1. Introduction

Cr(VI) is a contaminant commonly found in wastewater produced by several industries, including the dye, stainless steel, photography, leather tanning, and wood preservative industries. Chromium occurs in aqueous systems in trivalent and hexavalent forms, but the latter form is of particular concern due to its greater toxicity. When chromium enters the gastric system, epigastric pain, nausea, vomiting, severe diarrhea, corrosion of skin, respiratory tract and lungs carcinoma may occur [1–4]. The discharge limit of chromium from industries is <100 μg/L. Chromium is hazardous to health when its limit in drinking water exceeds 50 μg/L [5].

Several methods for removal of Cr(VI) from wastewater have been reported, including chemical precipitation [6], oxidation [7], ion exchange [8], reverse osmosis [9] and solvent extraction [10].

Adsorption is a simple technique that has been reported for removal of Cr(VI) using a variety of materials, such as active carbon [11,12], magnetic beads [13] and modified silica-gel [14]. Biosorption processes have advantages over other processes, including the lower cost of materials, such as, microalgal [15], plant leaves [16] and waste biomass [17] and its ease of operation. Many biopolymers such as, chitosan [18,19], alginate [20], and chitin [21] are known to bind metals strongly, and the use of biopolymers as adsor-

bents for the recovery of valuable metals for the removal of toxic metal contaminants has been studied.

Various reports have already been published involving Fe-crosslinked chitosan complex (Ch-Fe) as adsorbent of oxianions, such as phosphate [22], arsenate [23] and chromium (VI) [24] and the results have demonstrate that Ch-Fe could be a stronger adsorbent of oxianions.

In this study Ch-Fe was used to remove Cr(VI) under a wide range of conditions, such as, initial pH, temperature, Cr(VI) ion concentration and competing ions. The adsorption capacity was determined using the Langmuir and Langmuir–Freundlich isotherm equation models. The kinetics adsorption was evaluated by the pseudo-first order and pseudo-second order models.

2. Materials and methods

2.1. Materials

The procedure for the preparation and characterization of the Fe-crosslinked chitosan complex (Ch-Fe) was the same as that reported in literature [25]. The quantity of iron in the sample was determined by calorimetric methods using 1.10 phenantroline and a Spectrovision DB 2500 spectrophotometer, and was found to be 80.6 mg/g. The zero-point charge (pH_{zpc}) was determined using a potentiometric titration [26] and was found to be 8.9. All the reagents used in this study were of analytical grade. An aqueous solution of Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ (VETEC, São Paulo, Brazil) in distilled water. A stock solution with a concentration of 1000 mg/L of Cr(VI) was prepared and subsequently diluted.

2.2. Isotherm

The equilibrium isotherm was determined using batch studies. In the experiments, 0.025 g of Ch-Fe samples was added to 20 mL solution of Cr(VI) concentration between 50 mg/L and 300 mg/L, pH 4.8, in an isothermal shaker, for 60 min, at 25 °C, 35 °C, 45 °C, 55 °C and 65 °C. After adsorption, the solution was filtered and the amount of unabsorbed Cr(VI) was determined.

2.3. pH effect

The effect of pH on Cr(VI) adsorption was investigated in initial pH range 2–8. The pH of the solution was adjusted using NaOH 1.0 M, and HCl 1.0 M. Ch-Fe 0.025 g was added to 20 mL of the Cr(VI) solution (initial concentration of 600 mg/L). The solution was stirred for 60 min, at 25 °C, then the solutions were filtered and the Cr(VI) concentrations determined.

2.4. Kinetics study

Pseudo-first and pseudo-second order rate equations were used to model the kinetics of Cr(VI) adsorption. The experiments were conduced at 25 °C, 45 °C and 65 °C to investigate the adsorption kinetic parameter. 0.025 g of the Ch-Fe was added to 20 mL of the Cr(VI) solution (600 mg/L). The solution was stirred, and samples (0.5 mL) were removed at different time intervals to determine the concentration of Cr(VI).

2.5. Salt effect

Experiments were carried out to study the effect of salt on adsorption of Cr(VI) by the Ch-Fe. In the experiment, 0.025 g was added to 20 mL of the Cr(VI) solution (initial concentration of 600 mg/L) and stirred for 60 min at 25 °C. The salts used for the test were: Na_2SO_4, $NaNO_3$, $NaCl$, at a concentration of 0.1 M. Simultaneously, experiments were conduced with NaCl, varying the concentration at 0.01 M, 0025 M, 0.05 M, 0.1 M and 0.5 M. After 60 min, the samples were filtered and the remaining Cr(VI) in the solution was determined. All the adsorption experiments were conduced without controlling the pH of the solution, in order to prevent influence by the buffer ions on the adsorption.

2.6. Cr(VI) analysis

The Cr(VI) analysis was carried out spectrophotometrically at 540 nm in a spectrophotometer (Spectrovision DB 2500), using diphenylcarbazide as the complexing agent. The amount of Cr(VI) adsorbed was calculated based on the difference in their initial and final concentrations [16].

3. Results and discussion

3.1. pH effect

pH is an important factor for controlling the adsorption process, as it affects the surface charge of the adsorbents, the degree of ionization, and the species of adsorbate. The ion adsorption of Cr(VI) on the surface of ChFe is strongly influenced by the pH of the solution, as shown in Fig. 1. It was found that maximum adsorption occurs at pH 2, where the adsorbed quantity is 325 mg/g and decreases to 125 mg/g when pH was increased to 8.0. In aqueous solutions from pH 1 to 8 Cr(VI) exists in ionic form as CrO_4^{2-}, $Cr_2O_7^{2-}$, $HCrO_4^-$, $HCr_2O_7^-$ depending on the Cr(VI) concentration. Under the conditions used, concentration of Cr(VI) 0.001 M and pH 4.8, the relative abundance observed for the ionic species $HCrO_4^-$ is around 97%, therefore chromium uptake in the pH range 2.0–5.0 occurs via
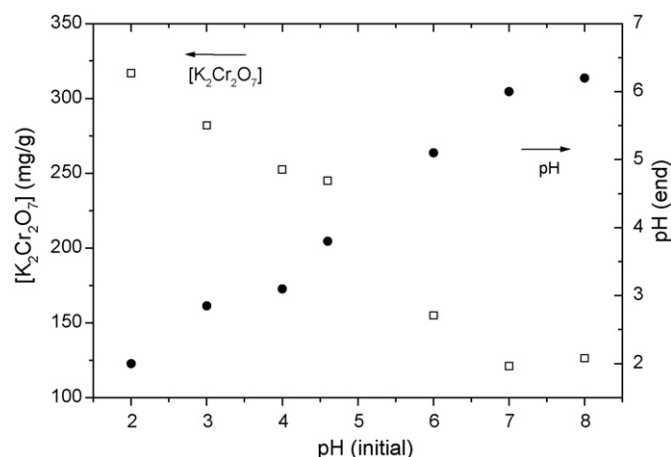

Fig. 1. Effect of pH on adsorption of Cr(VI) (initial Cr(VI) concentration 600 mg/L; volume of Cr(VI) solution 20 mL; amount of ChFe 25 mg; temperature 25 °C).

the ligand-exchange mechanism. The adsorption of $HCrO_4^-$ can be considered as a ligand-exchange reaction between the coordinated nitrate and $HCrO_4^-$ ions. This reaction can be represented as shown in Fig. 2.

The decrease in adsorption of Cr(VI) at higher pH values can be attributed to several factors: first, the higher concentration of OH^- ions present in the solution, which compete with Cr(VI) species for the adsorption sites (the end-pH was lower than the initial pH), Fig. 2; second, in basic medium the only significant specie is CrO_4^{2-} which is not absorbed by Ch-Fe [27]; finally, the pH_{zpc} of ChFe is 8.9 and with an increase in pH, the net surface charge on the adsorbent becomes less positive. At $pH > pH_{zpc}$, the net surface charge becomes negative, resulting in repulsive forces between Ch-Fe and Cr(VI).

The maximum removal of chromium (42 mg/g) was reported at a pH value of 2.0 for waste biomass [17]. With chitosan beads as adsorbent [17], the maximum uptake capacity (58 mg/g) was noted at a pH of 3.5. The magnetic beads [13] removed 108 mg/g at a pH of 2.0. The maximum removal of chromium (108 mg/g) was reported at a pH of 2 with activated carbon [11].

3.2. Isotherm study

The amount of Cr(VI) adsorbed by Ch-Fe, q_{eq} (mg/g) was correlated with concentration at equilibrium c_e (μg/L) using the Langmuir and Langmuir–Freundlich adsorption isotherm models. The experimental values of the isotherms were used in this nonlinear form of Langmuir equation (1). This equation is valid for monolayer adsorption. The model contains a limited number of sites and predicts a homogeneous distribution of adsorption energies [28]:

$$q_{eq} = \frac{K_L q_m c_e}{1 + K_L c_e} \tag{1}$$

where q_e is the amount of Cr(VI) adsorbed at the equilibrium (mg/g); c_e is the equilibrium solution concentration (mg/L); K_L is the Langmuir adsorption constant (L/mg); q_m is the maximum amount of Cr(VI) adsorbed onto 1 g of adsorbent.

The Langmuir and Freundlich models can be combined to give the composite Langmuir–Freundlich equation (2):

$$q_{eq} = \frac{K_{L-F} q_m c_e^c}{1 + K_{L-F} c_e^c} \tag{2}$$

where K_{L-F} is the Langmuir–Freundlich adsorption constant (L/mg); c is the heterogeneity parameter. As the equation has three fitting constants, it describes the adsorption much better. For independent
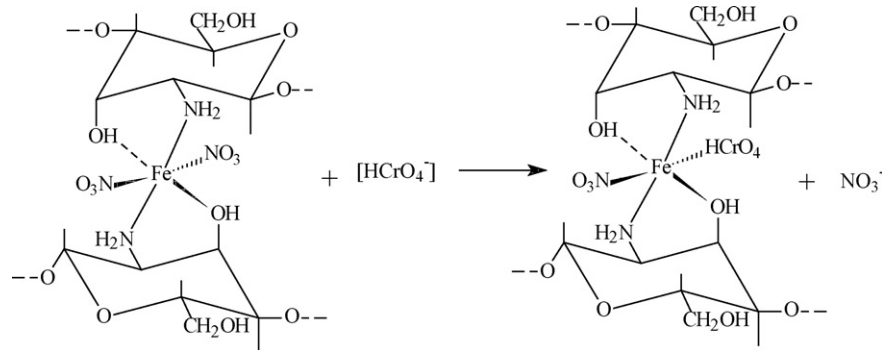
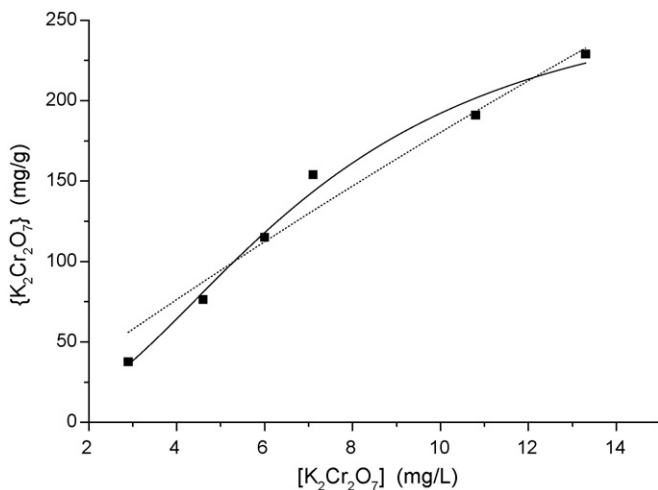**Fig. 2.** A schematic reaction between Ch-Fe and Cr(VI) ion.

Fig. 3. Adsorption isotherm for adsorption of Cr(VI) on ChFe: Langmuir isotherm plot (...) and Langmuir–Freundlich isotherm plot (---) (Cr(VI) concentration 50–300 mg/L; volume of Cr(VI) solution 20 mL; amount of Ch-Fe 25 mg; temperature 25 °C; pH 4.8; contact time 60 min).

non-interacting adsorption sites corresponding to the Langmuir model, c is 1. When $c > 1$, positive cooperativity is assumed, and when $0 < c < 1$, negative adsorption cooperativity is expected.

Fig. 3 shows the experimental equilibrium data and predicted theoretical isotherm for adsorption of Cr(VI) onto Ch-Fe. The values of the constants of the two models, along with the regression coefficient, are listed in Table 1. The value of the parameters was evaluated from a non-linear plot. Between the two types of adsorption isotherm models used, that of Langmuir–Freundlich gives a relatively better representation than the Langmuir isotherm. This indicates that the adsorption of Cr(VI) onto Ch-Fe does not occur through the monolayer coverage of Cr(VI) on the surface of Fe-Ch. This behavior can be attributed to the presence of other adsorption sites, non-specific such as NH or OH found in chitosan.

The maximum adsorption capacity of Cr(VI) on the Ch-Fe (295 mg/g), calculated by the Langmuir–Freundlich isotherm

model, at 25 °C and pH 4.6, is approximately 2.5 times higher than that adsorbed in Fe^{3+}-coordinated amino functionalized mesopourus-silica [14], 58 times higher than $Fe(OH)_3$ immobilized in sugar bagasse [5] and 2.7 times higher on magnetic particles (Fe_3O_4) immobilized onto PEI/acrylate beads [13]. Adsorption of Cr(VI) is also considerably higher than in a study previously reported for chitosan powder 1.9 time [27], chitin powder 4 times [21], chitosan beads 3.8 times [18] and chitosan flake 39.3 times [19].

3.3. Thermodynamic parameter

The thermodynamic parameters, including the Gibbs free energy change ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$), were determined using the following equations and represented as van't Hoff equations:

$$\ln K_{L-F} = \frac{\Delta S°}{R} + \frac{\Delta H°}{RT} \tag{3}$$

$$\Delta G° = -RT \ln K_{L-F} \tag{4}$$

where K_{L-F} is the equilibrium constant obtained from the Langmuir–Freundlich isotherm model; R is the gas constant (8.314 J mol^{-1} K^{-1}); T is the absolute solution temperature (K).

The plot of $\ln K_{L-F}$ vs $1/T$ was found to be linear, Fig. 4. The negative value of $\Delta H°$ (−499 kJ/mol) suggests the exothermic nature of the process. The negative values of ΔG^0 at various temperatures (−12.3 kJ/mol, −10.8 kJ/mol and −10.6 kJ/mol to 298 K, 308 K and 328 K, respectively) indicate that the adsorption process is spontaneous in nature. The adsorption is exothermic; hence, the amount adsorbed at equilibrium must decrease with increasing temperature, because $\Delta G°$ decreases with increasing temperature of the solution. Similar results from $\Delta G°$ to $\Delta H°$ have been reported for Cr(VI) adsorption by iron (III) hydroxide-loaded sugar beet pulp Altungodan [5]. The negative value $\Delta S°$ (−1.69 kJ/mol K) of Cr(VI) adsorption corresponds to a decrease in randomness at the solid/liquid interface during the adsorption of Cr(VI) on Ch-Fe. The results are in agreement with those reported by Zubair et al. [17] for adsorption of Cr(VI) by waste biomass.

Table 1
Langmuir and Langmuir–Freundlich isotherm constant for Cr(VI) on ChFe (Cr(VI) concentration 50–300 mg/L; volume of Cr(VI) solution 20 mL; amount of ChFe 25 mg; pH 4.8; contact time 60 min).

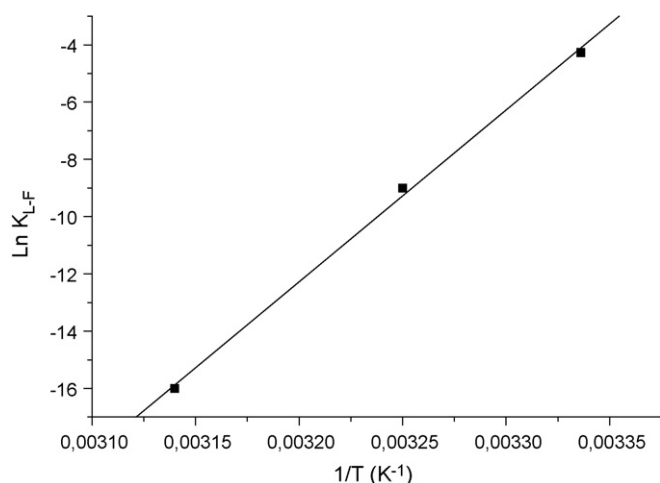| Temp.	Langmuir			Langmuir–Freundlich			
	K_L (L/mg)	q_m (mg/g)	R^2	K_{L-F} (L/mg)	q_m (mg/g)	β	R^2
25	0.034	512	0.991	2.7×10^{-2}	295	1.5	0.996
35	0.050	377	0.854	1.8×10^{-6}	212	5.6	0.999
45	0.010	960	0.980	1.4×10^{-2}	273	2.2	0.994
55	0.011	715	0.925	1.2×10^{-4}	240	4.0	0.994
65	0.080	373	0.871	1.0×10^{-7}	209	3.8	0.983

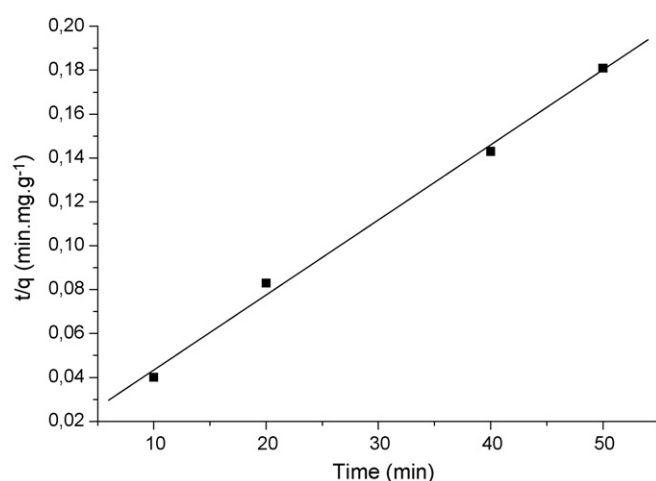**Fig. 4.** van'Hoff plot for adsorption of Cr(VI) on Ch-Fe.

Fig. 5. Pseudo-second order kinetics plot for the removal of Cr(VI) (initial Cr(VI) concentration 600 mg/L; volume of Cr(VI) solution 20 mL; amount of Ch-Fe 25 mg; temperature 25 °C, pH 4.8).

3.4. Kinetic study

From an economic point of view, the contact time between the sorbate molecules and the sorbent is of significant importance in wastewater treatment by sorption. The adsorption equilibrium time is defined as the time required for a heavy metal concentration to reach a constant value. The equilibrium time for Cr(VI) adsorption was 90 min at a constant pH of 4.6, Ch-Fe dosage 2.5 g/L, initial chromium concentration 600 mg/L and temperature of 25 °C. A further increase in contact time did not show an increase in adsorption. Different equilibrium agitation times are reported in the literature for the removal of chromium. With the *Citrus reticulata* waste biomass the equilibrium agitation time is found to be 6 h [17]. This time is 12 h with the thermally activated weed *Salvinea cucullata* [12], 69 h with the microalga *Chorella miniata* [15], 10 h with activated carbon from olive bagasse [11], 60 min with raw rice bran [28], 67 h with activated neem leaves [16], 50 min with chitosan beads [18] and 120 min with PEI immobilized acrylate magnetic beads [13]. Therefore, the time needed to reach the equilibrium depends on several factors such as the type of adsorbent, chromium concentration, pH, particle size and stirring speed. Thus the Ch-Fe present a time to reach equilibrium much smaller when compared with the adsorbents reported above, except for raw rice bran and chitosan beads.

The order of kinetics adsorbate–adsorbent interactions has been determined with two kinetics models [29]. The pseudo-first order equation is one of the most commonly used for the adsorption of solute from solution. The model is represented as follows:

$$\ln(q_{eq} - q_t) = \ln q_{eq} - K_1 t \tag{5}$$

where K_1 (1/min) is the rate constant of pseudo-first order adsorption and q_{eq} and q_t (mg/g) denote the amounts of dye adsorbed at equilibrium and at time t, respectively.

The pseudo-second order equation based on the adsorption equilibrium capacity can be expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{eq}^2} + \frac{t}{q_{eq}} \tag{6}$$

where K_2 (mg/g min) is the rate constant of pseudo-second order adsorption.

Fig. 5 shows the plots of the pseudo-second order kinetics model. The kinetics parameter for Cr(VI) adsorption is given in Table 2. Considering the correlation coefficient (R^2) the pseudo-second order equation fitted the experimental data well. R^2 values are >0.990 for all temperatures. On the other hand, the R^2 val-

ues for the pseudo-first order equation are very low. Therefore, these results indicate that the adsorption of Cr(VI) on Ch-Fe follows pseudo-second order kinetics. The suitability of the second order rate equation for the present data indicates chemisorption as the rate controlling step involving a sharing or exchange of electrons between the adsorbate and the adsorbent [30]. The suitability of the second order rate equation was reported in the literature for the removal of chromium for the adsorbents: active carbon from olive bagasse [11], magnetic beads [13] waste biomass [16] and thermally activated weed [12]. On the other hand, the results found in this work are different from those reported by Fagundes et al. [22] for adsorption of As(V) by Ch-Fe.

3.5. Effect of ionic strength

Wastewaters from electroplating industries contain various types of suspended solids and salts. The presence of ions leads to high ionic strength, which may significantly affect the performance of the adsorption process. The adsorption of Cr(VI) from the solution with a 600.0 mg/L initial concentration decreases from 285 mg/g to 53 mg/g as the ionic strength is increased from 0 M to 1.0 M, Fig. 6. It is noted that the salt concentration primarily influences Cr(VI) adsorption. The adverse effect of ionic strength on dye uptake suggests the possibility of ion exchange mechanisms being active in the adsorption process. According to the surface chemistry theory developed by Guoy Chapman, when solid adsorbent comes into contact with sorbate species in solution, the latter is surrounded by an electrically diffused double layer, the thickness of which is significantly expanded by the presence of NaCl. This expansion inhibits the adsorbent particles and Cr(VI) species from approaching each other more closely, and through decreased electrostatic attraction, leads to the decreased uptake of Cr(VI) ions.

Table 2
Kinetic parameters for Cr(VI) adsorption on ChFe at different temperatures (initial Cr(VI) concentration 600 mg/L; volume of Cr(VI) solution 20 mL; amount of ChFe 25 mg; temperature 25 °C, pH 4.8).

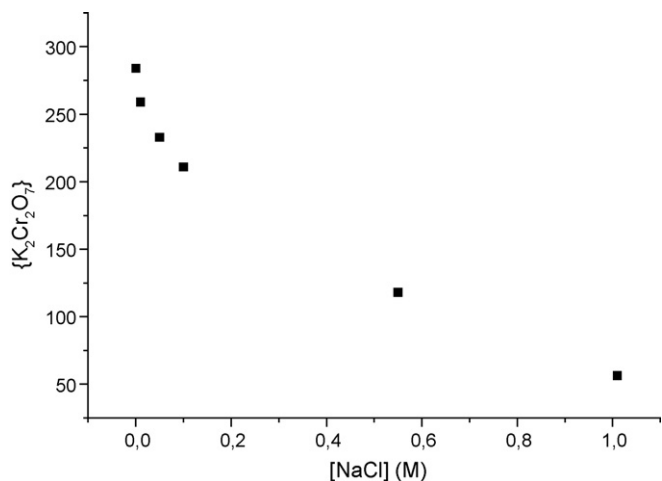| T (°C)	Pseudo-first order			Pseudo-second order		
	q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2 (g/mg min)	R^2
25°	231	0.016	0.674	22	0.007	0.996
35°	77	0.013	0.841	179	0.680	0.990
45°	106	0.003	0.729	133	0.015	0.994
55°	82	0.009	0.797	109	0.025	0.996

Fig. 6. Effect of ionic strength on adsorption of Cr(VI) (initial Cr(VI) concentration 600 mg/L; volume of Cr(VI) solution 20 mL; amount of ChFe 25 mg; temperature 25 °C; pH 4.8; contact time 60 min).

Table 3
Effect of competing ion on adsorption of Cr(VI); Cr(VI) solution concentration 600 mg/L; volume of Cr(VI) solution 20 mL; amount of ChFe 25 mg; temperature 25 °C; pH 4.8; contact time 60 min.

Salt (0.1 M)	Cr(VI) mg/g	Reduction of adsorption (%)
–	285.0	0
NaCl	168.0	32.8
$NaNO_3$	176.2	29.6
Na_2SO_4	96.0	66.3

Table 3 shows the inhibition of Cr(VI) adsorption by competing anions. The adsorption capacity is suppressed between 32% and 66%. The molar ratio [ion/Cr(VI)] was kept constant at 50 for all anions. The inhibition by competing ions is clearly dependent on the anion as well as the valence of anion. The effect of anions on chromium adsorption by ChFe followed the order $Na_2SO_4 > NaCl > NaNO_3$. The presence of competing anions decreased the chromate adsorption capacity, indicating that chromate adsorption on ChFe is an outer-sphere complex.

4. Conclusion

In this study, Ch-Fe was used for absorption of Cr(VI) from aqueous solution. The adsorption was dependent on pH and temperature. The pseudo-second order kinetic model could explain the adsorption process for adsorption of Cr(VI) by Ch-Fe. The Langmuir–Freundlich isotherm model has better correlation with the experimental data. The maximum uptake of Cr(VI) was 295 mg/g at pH 4.8. Other anions can compete with Cr(VI) by adsorption site.

Acknowledgement

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