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Adsorption of chromium from aqueous solution using chitosan beads

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Abstract A basic investigation on the removal of Cr(III) and Cr(VI) ions from aqueous solution by chitosan beads was conducted in a batch adsorption system. The chitosan beads were prepared by casting an acidic chitosan solution into an alkaline solution. The influence of different experimental parameters; pH, agitation period and different concentration of Cr(III) and Cr(VI) ions was evaluated. A pH 5.0 was found to be an optimum pH for Cr(III) adsorption, and meanwhile pH 3.0 was the optimum pH for the adsorption of Cr(VI) onto chitosan beads. The Langmuir and Freundlich adsorption isotherm models were applied to describe the isotherms and isotherm constants for the adsorption of Cr(III) and Cr(VI) onto chitosan beads. Results indicated that Cr(III) and Cr(VI) uptake could be described by the Langmuir adsorption model. The maximum adsorption capacities of Cr(III) and Cr(VI) ions onto chitosan beads were 30.03 and 76.92 mg g^{-1}, respectively. Results showed that chitosan beads are favourable adsorbents. The Cr(III) and Cr(VI) ions can be removed from the chitosan beads by treatment with an aqueous EDTA solution.

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1 Introduction

The removal of toxic and polluting heavy metal ions from industrial effluents, water supplies and mine waters has received much attention in recent years. Heavy metals such as Hg, Cr, Pb, Ni, Cu, Cd and Zn, those are usually associated with toxicity. Pollution by chromium is of considerable concern as the metal has found widespread use in electroplating; metal finishing, leather tanning, nuclear power plant and textile industries (Rengaraj et al., 2001). Chromium is found in either +3 or +6 oxidation states, as all other oxidation states are not stable in aerated aqueous media (Lee et al., 1995). The +6 is known toxic even at low concentrations, with a potential carcinogenic effect, whereas the +3 is an essential micronutrient for organisms and plants and become toxic in higher levels.

Toxic metal ions in trace quantities are difficult to remove from aqueous solution. Adsorption is a promising alternative for such situations. Activated carbon is the most popular adsorbent used for the removal of metals ions from aqueous solution and widely used in wastewater treatment applications throughout the world (El-Shafey et al., 2002). In spite of its prolific use, activated carbon remains an expensive material since the higher the quality of the activated carbon, the greater its cost. In recent years, the search for new and innovative technology to remove toxic heavy metal ions from diluted wastewater has focused on the removal of heavy metal by various low-cost materials. Low et al. (2000) defined a low-cost sorbent as abundant in nature, or as a by-product or waste material from another industry. Biosorption or sorption to material of biological origin is recognized as an emerging technique in the wastewater treatment of heavy metals.

Chitin, poly(1→4)-2-acetamido-2-deoxy-β-D-glucan is a natural polymer extracted commercially from the shells of crustaceans such as prawns, crabs, krill, insects and shrimps. Chitosan, poly(1→4)-2-amino-2-deoxy-β-D-glucan is prepared from chitin by partially deacetylating its acetamido groups with a strong alkaline solution. Chitosan has high potential in the adsorption of metal ions (Ngah and Isa, 1998; Guibal et al., 1998; Ngah et al., 2002a; Kim and Park, 2001), since it has both amine and hydroxyl groups that can serve as chelating sites for metal ions. Several methods have been used to modify raw chitosan flake either physically (Onsøyen and Skaugrud, 1990) or chemically (Guibal et al., 1999; Ngah and Liang, 1999; Yang et al., 2002; Justi et al., 2005; Yang et al., 2005). These modifications are in order to improve pore size, mechanical strength, chemical stability, hydrophilicity and biocompatibility of chitosan. Some common cross-linking agents such as glutaraldehyde (Guibal et al., 1999; Wu et al., 2001), epichlorohydrin (Ngah et al., 2002b; Chiou and Li, 2002) and ethylene glycol diglycidyl ether (Tianwei et al., 2001) have been widely used in cross-linking of chitosan beads. Although cross-linking can decrease the adsorption capacity of chitosan, the chemical stability of the biosorbents in acidic solutions can increase through cross-linking (Ngah et al., 2002b).

In this work, the equilibrium of adsorption of Cr(III) and Cr(VI) ions onto chitosan beads from aqueous solutions were investigated. Experiments were carried out as function of pH, agitation period and concentration of Cr(III) and Cr(VI) ions. The adsorption capacity for the adsorption of Cr(III) and Cr(VI) onto chitosan beads were determined using the Langmuir and Freundlich equations. These information will be useful for further applications for the system design in the treatment of practical waste effluents.

2 Materials and methods

2.1 Materials

Samples of chitosan flakes with average molecular weight $10^5 - 10^6$ and with a deacetylation percentage of approximately 61.47% (defined by an IR method), prepared from shells of prawns were kindly donated from Chitin-Chitosan Research Centre, Universiti Kebangsaan Malaysia, Bangi. They were grind by using a laboratory jar mill and sieved to a consistent particle size ($<250\ \mu$m) before use. All the reagents used were of analytical-reagent grade. Doubly distilled water used to prepare all the solutions.

2.2 Preparation of chitosan beads

Chitosan solution was prepared by dissolving 2.0 g of chitosan flakes into 60 ml of 5% (v/v) acetic acid solution (Ngah et al., 2002a). The viscous solution was left overnight before adding dropwise into a precipitation bath containing 500 mL of 0.50 M NaOH. This ensures that the acetic acid within the chitosan gel is neutralized and thereby coagulates the chitosan gel to spherical uniform chitosan gel beads. A magnetic stirrer was used to stir the aqueous NaOH solution. The chitosan beads were filtered and extensively rinsed with distilled water to remove any NaOH residue, filtered and finally dried. The beads were then grind by using a laboratory jar mill and sieved to a constant size ($<250\ \mu$m) before use.

2.3 Characterization of chitosan beads

Some physical properties of chitosan beads were measured in this work. The analyses were performed using a Micromeritics ASAP 2010 gas adsorption surface analyzer according to the BET equation. The surface morphology of the chitosan beads was observed with a Leica Cambridge S360 scanning electron microscope with energy dispersive spectroscopy.

2.4 Batch adsorption experiments

Stock solutions (1000 ppm) of Cr(III) and Cr(VI) ions were prepared by using $Cr(NO_3)_3{\cdot}9H_2O$ and $K_2Cr_2O_7$, respectively. The stock solution was then diluted to give standard solutions of appropriate concentrations.

Batch adsorption experiments were conducted in 250 ml beakers and equilibrated using a magnetic stirrer. Then 100 ml aliquot of these standard solutions were placed in 250 ml beakers and was added with 0.01 g of chitosan beads. The chitosan beads used in the batch adsorption studies are the chitosan beads prepared based on the methods elaborated in Section 2.2. These chitosan beads are not cross-linked with any cross-linking reagents. After filtration, the concentration of Cr(III) and Cr(VI) ions in supernatant were analyzed using an atomic absorption spectrophotometer (Perkin-Elmer 3100 Model). The effect of Cr(III) and Cr(VI) adsorption was studied in the pH range of 1–5. The pH of the initial solution was adjusted to the required pH value using appropriate concentration of HCl or NaOH. Chitosan beads were equilibrated at the particular pH for about 30 min at 500 rpm and at an initial Cr(III) and Cr(VI) concentration of 5 ppm. The effect of agitation period was also studied to determined the optimum condition for adsorption of Cr(III) and Cr(VI) ions onto chitosan beads.

Adsorption equilibrium studies were conducted at optimum condition using a contact time of 50 min at pH 5.0 for the adsorption of Cr(III) whereas for the Cr(VI) adsorption equilibrium studies, a contact time of 50 min at pH 3.0 was applied. Isotherm studies were conducted with a constant chitosan beads weight (0.01 g) and varying initial concentration of Cr(III) and Cr(VI) in the range of 4–14 ppm. The amount of adsorption at equilibrium was calculated using the following equation:

$$\text{Adsorption capacity } (q) = \frac{(C_\mathrm{o} - C_\mathrm{e})V}{W} \tag{1}$$

where C_o is the initial Cr(III) or Cr(VI) concentration (ppm), C_e is the final or equilibrium Cr(III) or Cr(VI) concentration (ppm), V is the volume of the Cr(III) or Cr(VI) solution (ml) and W is the weight of chitosan beads (g) used.

For the desorption studies, 0.01 g of chitosan beads were loaded with Cr(III) and Cr(VI) using 50 ml of 5 ppm of Cr(III) or Cr(VI) solution at respective optimum pH, agitation period of 50 min and the agitation rate of 500 rpm. Cr(III)- and Cr(VI)-loaded chitosan beads were collected, gently washed with distilled water to remove any unadsorbed Cr(III) or Cr(VI). The amount of Cr(III) and Cr(VI) adsorbed per gram of chitosan were determined by analyzing the supernatant solution of Cr(III) and Cr(VI) after filteration. The chitosan beads were agitated with 50 ml of EDTA and HNO_3 of various concentration (10^{-3}–10^{-5} M) and the percentage of desorption of Cr(III) and Cr(VI) was calculated from the following equation:

$$\text{Percentage of desorption} = \frac{m_\mathrm{r}}{m_\mathrm{o}} \times 100\% \tag{2}$$

where m_r is the amount of Cr(III) or Cr(VI) ions desorbed (mg) and m_o is the amount of Cr(III) or Cr(VI) ions adsorbed (mg).

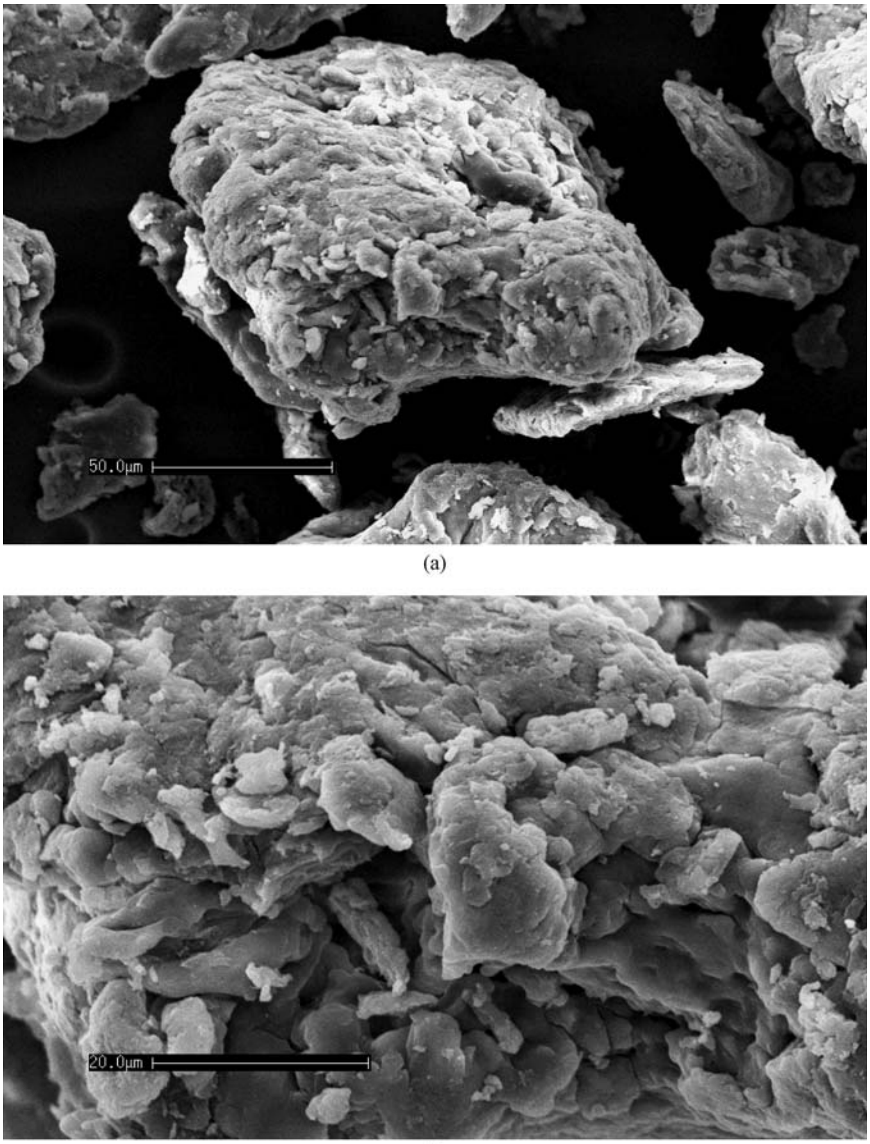
3 Results and discussion

3.1 Characterization of chitosan beads

The BET surface area and the average pore diameter of chitosan beads were found to be $1.33\,\mathrm{m^2\,g^{-1}}$ and 80.27 Å, respectively. According to the International Union of Pure and Applied Chemistry (IUPAC) classifications, the pores can be divided in broad terms according to diameter (d) into macropores ($d > 50\,\mathrm{nm}$), mesopores ($2 < d < 50\,\mathrm{nm}$) and micropores ($d < 2\,\mathrm{nm}$). It is found that chitosan beads correspond to mesopores. Scanning electron micrographs of chitosan beads reveal the surface structure and porosity of the beads. As shown in Fig. 1, chitosan beads have a rough surface area and porous internal structure.

3.2 Effect of pH

In this study, a knowledge of pH and agitation period is important because of the dependence of the adsorption of Cr(III) and Cr(VI) ions onto chitosan beads. Figure 2 shows the effect of pH on the adsorption of Cr(III) and Cr(VI) by chitosan beads. The maximum adsorption of Cr(III) onto chitosan beads was found at pH 5.0. At pH values higher than 6.0, Cr(III) precipitation occurred simultaneously. pH 5.0 was chosen for the adsorption of Cr(III) ions to avoid the formation of $Cr(OH)_3$ which will affect the adsorption by the beads. The adsorption increases with an increase in the pH of the solution. This could be explained based on the pKa value of chitosan which is 6.20, and therefore at a low pH most of the amine groups are protonated to form $\text{–}NH_3^+$ groups (Rojas et al., 2005). This will reduce the number of binding sites available for the adsorption of Cr(III). Thus, the adsorption of Cr(III) is less probable to occur.



(a)

(b)

Fig. 1 SEM micrographs of chitosan beads at: (a) 500X; (b) 1500X

Meanwhile, at higher pH adsorption of Cr(III) increases due to the inhibitory effect of H^+ decreased with an increase in pH.

Figure 2 also shows the effect of pH on the adsorption of Cr(VI) by chitosan beads. The adsorption increases with an increase in the pH of the solution until an optimum pH point was reached at about pH 3.0. A decrease in the adsorption was observed with an increase in the pH after pH 3.0. Similar observation was made on the uptake of Cr(VI) by ECH cross-linked chitosan beads (Qian et al., 2000). In contrast to Cr(III), Cr(VI) exists in anionic forms in aqueous solution as $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-} and $HCr_2O_7^-$; depending on the concentration of chromium and the pH of the solution. The adsorption of Cr(VI) ions on chitosan beads is dependent on the stability and affinity of the Cr(VI) species. In low concentration with pH in the range 2–4 the main fraction is $HCrO_4^-$, whereas the CrO_4^{2-} species increases with an increase in the pH value and becomes the main form at a pH value above 7.0 (Qin et al., 2003). These anions can interact effectively with protonated amine functional groups. Meanwhile for anions such as $Cr_2O_7^{2-}$ and $HCr_2O_7^-$, only exists at a higher concentration of Cr(VI).

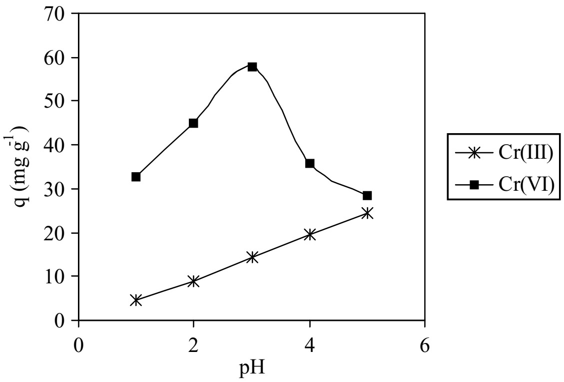


Fig. 2 Effect of pH on the adsorption of Cr(III) and Cr(VI) on chitosan beads

Chitosan beads have been known to be unstable or start to swell in solution of lower pH. Therefore, the chitosan beads did not act as an adsorbent in lower pH (pH 1–2) region (Minamisawa et al., 1999). This correlates with the results obtained at lower pH for chitosan beads. The recovery of Cr(III) and Cr(VI) was very low in the lower pH range due to the swelling of chitosan beads in the lower pH range.

3.3 Effect of agitation period

Agitation period is the amount of time required before the adsorption process becomes constant and equilibrium is reached. Figure 3 shows the effect of agitation period on the adsorption of Cr(III) and Cr(VI) by chitosan beads. The optimum period for the adsorption of Cr(III) and Cr(VI) by chitosan beads can be observed by looking at the difference in absorbance of Cr(III) and Cr(VI) solution after adding chitosan beads. The adsorption of Cr(III) and Cr(VI) increases with agitation period and attains equilibrium at about 50 min for an initial concentration of 5 ppm of Cr(III) and Cr(VI). It shows that the adsorption of Cr(III) and Cr(VI) remained constant, implying equilibrium has been reached.

3.4 Adsorption equilibrium

The equilibrium adsorption of Cr(III) and Cr(VI) on the chitosan beads as a function of the equilibrium concentration of Cr(III) and Cr(VI) are shown in Fig. 4. There was a gradual increase in the adsorption of both Cr(III) and Cr(VI) ions until an equilibrium was attained. An equilibrium concentration of Cr(III) and Cr(VI) ions was reached at about 6 ppm. This represents the saturation capacity of adsorption. The adsorption isotherm is fundamental in describing the interactive behavior between solutes and adsorbent (Chiou and Li, 2003; Ofomaja and Ho, 2006). According to Ofomaja and Ho (2006), the isotherm yields certain constant values, which express the surface properties and affinity of the adsorbent. It also plays an important role in the design of an adsorption system. The Langmuir and Freundlich models are often used to describe equilibrium adsorption isotherms. The most widely used Langmuir equation, is valid for monolayer sorption on to a surface with a finite number of identical sites. It is assumed that once a metal ion occupies a site, no further adsorption can take place at that site (Ho et al., 2002). The Langmuir equation, which is also based on the assumption that there is no reaction between molecules adsorbed

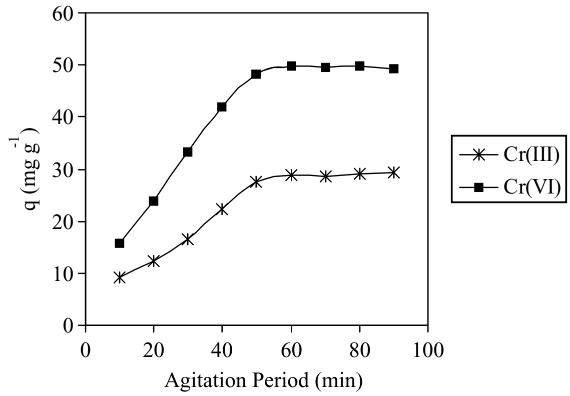


Fig. 3 Effect of agitation period on the adsorption of Cr(III) and Cr(VI) on chitosan beads

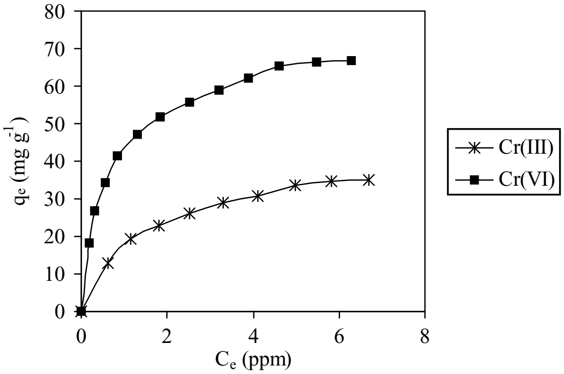


Fig. 4 Equilibrium adsorption of Cr(III) and Cr(VI) on chitosan beads

Table 1 Adsorption isotherm constants and correlation coefficients

	Langmuir			Freundlich		
Ion	Q (mg g^{-1})	b (ml mg^{-1})	R	K_F (mg g^{-1})	n	R
Cr(III)	30.03	0.1320	0.9992	5.46	5.48	0.9919
Cr(VI)	76.92	3.4210	0.9989	59.47	4.12	0.9932

on neighboring sites (Chao et al., 2004), is given by:

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{Qb} \tag{3}$$

where Q is the maximum adsorption at monolayer (mg g^{-1}), C_e is the equilibrium concentration of Cr(III) or Cr(VI) (ppm), q_e is the amount of Cr(III) or Cr(VI) adsorbed per unit weight of chitosan beads at equilibrium concentration (mg g^{-1}) and b is the Langmuir constant related to the affinity of binding sites (ml mg^{-1}) and is a measure of the energy of adsorption. A linearized plot of C_e/q_e against C_e gives Q and b.

The widely used empirical Freundlich equation based on sorption on a heterogeneous surface is given by:

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

where K_F and n are Freundlich constants indicating adsorption capacity (mg g^{-1}) and intensity, respectively. K_F and n can be determined from a linear plot of log q_e against log C_e.

The calculated results of the Langmuir and Freundlich isotherm constants are given in Table 1. It is found that the adsorption of Cr(III) and Cr(VI) onto chitosan beads correlates well ($R > 0.99$) with the Langmuir equation as compared to Freundlich equation under the concentration range studied.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L that is used to predict if an adsorption system is "favourable" or "unfavourable" (Ngah and Musa, 1998). The separation factor, R_L is defined by:

$$R_L = \frac{1}{1 + bC_f} \tag{5}$$

where C_f is the final Cr(III) or Cr(VI) concentration (ppm) and b is the Langmuir adsorption equilibrium constant (ml mg^{-1}). The parameter indicates the isotherm shape according to Table 2. The values of R_L calculated for different initial Cr(III) and Cr(VI) concentration are given in Table 3. If the R_L values are in the range of $0 < R_L < 1$, it indicates that the adsorption of Cr(III) and Cr(IV) onto chitosan beads are favourable. Thus, chitosan beads are favourable adsorbents. The mechanism of ion adsorption on porous adsorbents may involve three steps: (i) diffusion of the ions to the external surface of adsorbent; (ii) diffusion of ions into the pores of adsorbents; (iii) adsorption of the ions on the internal surface of adsorbent.

Table 2 Effect of separation factor on isotherm shape

R_L value	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

3.5 Desorption studies

The recovery of adsorbed material, as well as regeneration of adsorbents, is becoming important and useful in metal ion recycling processes. In this work, desorption studies will help to elucidate the nature of adsorption process. Moreover, it also will help to regenerate

Table 3 R_L values based on the Langmuir equation

Ion	Initial concentration, C_o (ppm)	Final concentration, C_f (ppm)	R_L value
Cr(III)	4.00	2.32	0.7656
	8.00	5.20	0.5930
	12.0	8.46	0.4724
	14.0	10.2	0.4262
Cr(VI)	4.00	0.065	0.8181
	8.00	0.389	0.4290
	12.0	0.824	0.2619
	14.0	1.22	0.1933

chitosan beads so that it can be reused to adsorb metal ions. Desorption experiments were performed by using EDTA and HNO_3 solution as the desorption agents in concentration range of 10^{-3}–10^{-5} M. This is because chitosan beads were soluble in higher concentration of EDTA and HNO_3 solution. The percentage of desorption for Cr(III) and Cr(VI) from chitosan beads are listed in Table 4. It is found that Cr(VI) can be removed easily from chitosan beads as compared to Cr(III), in higher concentration of EDTA and HNO_3. EDTA acts more efficient than HNO_3 because EDTA is a hexadentate chelating agent and capable of forming complex with Cr(III) and Cr(VI) ions much higher if compared to HNO_3. However, HNO_3 plays as a cation exchanger agent. Further studies are necessary to elucidate these desorption mechanisms.

Table 4 Percentage of desorption of Cr(III) and Cr(VI) from complex Cr(III) and Cr(VI)-chitosan beads

Desorption solution	Concentration (M)	Desorption (%)	
		Cr(III)	Cr(VI)
EDTA	1.0×10^{-3}	66.2	83.6
	1.0×10^{-4}	49.3	71.5
	1.0×10^{-5}	37.9	54.2
HNO_3	1.0×10^{-3}	32.6	64.1
	1.0×10^{-4}	25.1	48.3
	1.0×10^{-5}	14.0	25.7

3.6 Mechanism of adsorption chitosan beads for Cr(III) and Cr(VI)

It is known that in acidic media, the free amine groups ($-NH_2$) in chitosan beads are protonated to form ($-NH_3^+$) groups. Chitosan beads with positive charges can adsorb anions by charge neutralization. The stronger the attraction between positive and negative charge, the stronger the adsorption is (Qian et al., 2000). Cr(VI) exists in anionic forms ($HCrO_4{}^-$) in low pH aqueous solution, hence Cr(VI) can be strongly adsorbed by chitosan beads. From Fig. 5, it can be seen that the main adsorption peak of chitosan beads spectrum after adsorption at 1382 cm^{-1} has not changed compared to the IR spectrum before adsorption. The results indicate that the adsorption process between chitosan beads and Cr(VI) is a physical adsorption, and not a complexing reaction. The same observation has been reported on the adsorption of Mn(VII) on epoxy chloropropane cross-linked chitosan beads (Xue et al., 2001). Whereas, the IR spectrum for adsorbed Cr(III) on chitosan beads showed a sharper adsorption peak at 1382 cm^{-1}.

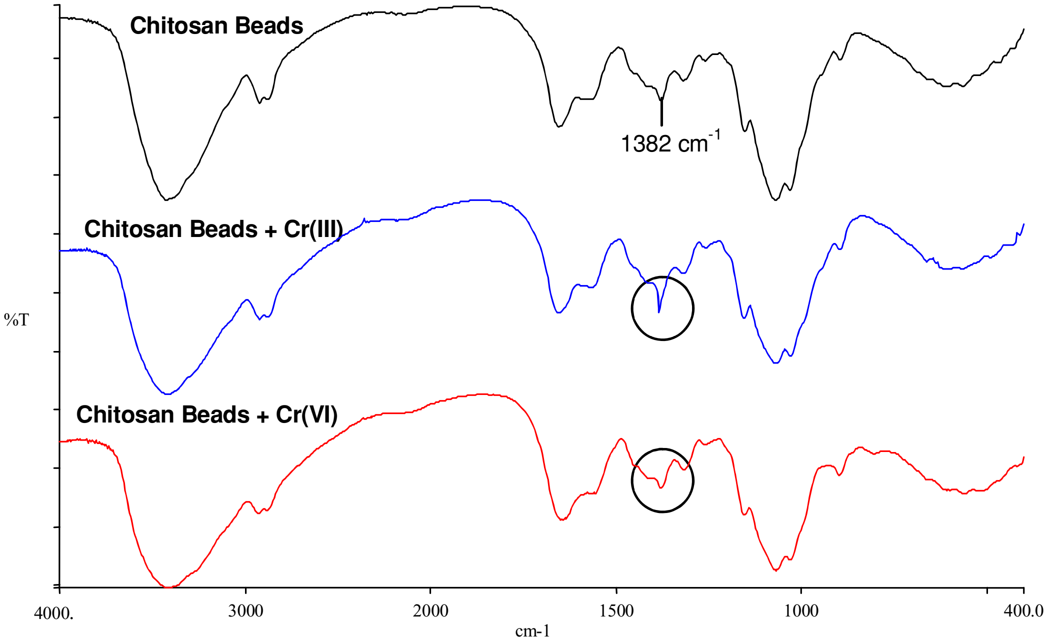


Fig. 5 The FTIR spectrum of chitosan beads before and after adsorption of Cr(III) and Cr(VI)

4 Conclusions

In this study, the capacity of chitosan beads to adsorb Cr(III) and Cr(VI) ions from aqueous solutions was examined. The adsorption isotherms could be well fitted by the Langmuir equation. The capacity of Cr(VI) adsorption using chitosan beads was about two times higher than that of Cr(III) adsorption. The adsorption of Cr(III) on chitosan beads is a physical adsorption, meanwhile the adsorption of Cr(VI) is a chemical adsorption. The Cr(III) and Cr(VI) ions can be removed from chitosan beads by treatment with aqueous EDTA and HNO_3 solution. It can be concluded that chitosan beads are an effective adsorbent for the collection of metal ions and has adsorption ability for some anions.

Nomenclature

q	Amount of Cr(III) or Cr(VI) adsorbed per unit weight of chitosan beads or adsorption capacity (mg g^{-1})
C_o	Initial Cr(III) or Cr(VI) concentration (ppm)
C_e	Equilibrium Cr(III) or Cr(VI) concentration (ppm)
C_f	Final Cr(III) or Cr(VI) concentration (ppm)
V	Volume of the Cr(III) or Cr(VI) solution (ml)
W	Weight of chitosan beads (g) used
m_r	Amount of Cr(III) or Cr(VI) ions desorbed (mg)
m_o	Amount of Cr(III) or Cr(VI) ions adsorbed (mg)
Q	Maximum adsorption at monolayer (mg g^{-1})
q_e	Amount of Cr(III) or Cr(VI) adsorbed per unit weight of chitosan beads at equilibrium concentration (mg g^{-1})
b	Langmuir constant related to the affinity of binding sites (ml mg^{-1})
K_F	Freundlich constants (mg g^{-1})
n	Intensity
R_L	Separation factor
IR	Infrared

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