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Adsorption of Fluoride from Aqueous Solution Using Low-Cost Bentonite/Chitosan Beads

Yi Zhang[1], Dongfeng Wang[1], Bingjie Liu[1], Xiang Gao[1], Wei Xu[1], Peng Liang[2], Ying Xu[1]*

[1]College of Food Science and Engineering, Ocean University of China, Qingdao, China
[2]College of Food Science and Technology, Fujian Agriculture and Forestry University, Fuzhou, China
Email: yiandzoe@163.com, *xuy@ouc.edu.cn

ABSTRACT

A new adsorbent namely bentonite/chitosan beads has been synthesized and studied for its defluoridation efficiency. Bentonite was activated and the beads were prepared using the inverse suspension polymerization method. The bentonite/chitosan beads (bentonite dosage of 3.0 g) showed an adsorption capacity of 0.895 mg/g whereas chitosan beads had only 0.359 mg/g. The optimal pH value was observed at pH 5 where the adsorbent reached the maximum defluoridation capacity of 1.164 mg/g. The effect of temperature, contact time and initial fluoride concentration on the adsorption capacity of the adsorbent has also been investigated. Scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and Fourier-transform infrared spectrometry (FTIR) were used to characterize the adsorbent. The adsorption of fluoride onto the adsorbent followed Freundlich isotherm model and pseudo-second order kinetic model. The fluoride loaded adsorbent could be regenerated using sodium hydroxide.

Keywords: Bentonite; Chitosan; Fluoride; Adsorption; Beads

1. Introduction

Adsorption technology is an efficient method for fluoride removal from water and has been widely studied [1]. Recent research work has been devoted to develop low-cost adsorbents to enhance the cost effectiveness for defluoridation. For example, chitin composite [2], modified chitosan beads [3], synthetic apatites [4] and bentonite clay [5] have been demonstrated effective adsorbents for fluoride adsorption.

Bentonite is a common group of clay minerals, which is a hydrous aluminium silicate, and it has been reported as an economical material for adsorption of fluoride from water. However, the low adsorption capacity is the major problem for its possible application. Therefore, it is important to modify the bare bentonite to overcome its drawbacks for fluoride removal. Chitosan, also named poly(β-1-4)-2-amino-2-deoxy-d-glucopyranose, is prepared from chitin by partial or total deacetylating. Chitosan is a biopolymer which has been cited as an excellent material for defluoridation from water. However, raw chitosan used in the form of flakes or powder is unstable and the adsorption capacity is minimum [6]. Thus, it is necessary to modify chitosan physically or chemically in order to im-

prove its practical use.

The present study deals with the bentonite and chitosan with crosslinker to form an inexpensive and efficient adsorbent. Adsorption equilibrium experiments were used to investigate the adsorption behavior of bentonite/chitosan beads. The effect of various parameters such as bentonite dosage, pH, temperature, initial fluoride concentration and contact time on adsorption capacity of bentonite/chitosan beads was studied. Freundlich isotherm model and Pseudo-second order kinetic model were employed to understand the adsorption process. SEM, EDAX and FTIR analysis were used to characterize the bentonite/chitosan beads before and after fluoride adsorbed. The regeneration experiments were performed to check the reusability of bentonite/chitosan beads for defluoridation.

2. Materials and Methods

2.1. Materials

All reagents were of analytical grade. Bentonite was supplied by Liuhe Group Co. Ltd. (Qingdao, China). Bentonite was used after activated with hydrochloric acid and calcined in muffle furnace at 500˚C. Chitosan (MW

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*Corresponding author.

5.1×10^5 Da and degree of deacetylation 95.4%) was purchased from Shandong Hecreat marine bio-tech Co. Ltd. (Qingdao, China). Fluoride stock solution of 100 mg/L was prepared using anhydrous sodium fluoride. Working fluoride solutions of required concentrations were prepared by appropriate dilution of the stock solution.

2.2. Preparation of Adsorbent

The bentonite/chitosan beads was prepared using inverse suspension polymerization [7]. The procedure was: 10.0 g chitosan and bentonite of required quantities namely 1.0, 2.0 and 3.0 g were dissolved respectively in 200 mL acetic acid solution (2%, v/v) for 24 h. Liquid paraffin was added to form a dispersion phase at 50°C, stirring for 10 min. Then, the system was added with formaldehyde and epichlorohydrin as crosslinker. After that, the beads was washed with petroleum ether, ethanol and deionized distilled water. The wet adsorbent was dried in a vacuum oven at 50°C. Chitosan beads was prepared without bentonite and served as control.

2.3. Adsorption Experiments

Adsorption experiments were carried out with 50.0 mL of 10 mg/L fluoride solution at a constant speed of 160 rpm at 30°C for 480 min. Adsorbent of 0.1 g was added to the fluoride solution. The adsorption of fluoride onto adsorbent was studied under different conditions including pH, temperature, contact time and initial fluoride concentration. After adsorption equilibration, fluoride concentration was measured using a fluoride ion selective electrode (PF-1, Shanghai Leici, China). The amount of fluoride adsorbed was calculated from following equation.

$$q_e = \left(\frac{c_0 - c_e}{w} \right) V \tag{1}$$

where q_e is the adsorption capacity of the adsorbent (mg/g) at equilibrium; c_0 and c_e are the initial and equilibrium fluoride concentrations (mg/L), respectively; V is the volume of solution (L) and W is the mass of adsorbent (g).

2.4. Characterization of Adsorbent

The surface microstructure of the adsorbent was observed with a scanning electron microscope (SEM) and the element composition before and after fluoride adsorption was determined by energy dispersive X-ray analysis (EDAX). In order to confirm the functional groups present in the adsorbent, FTIR spectra of chitosan, bentonite, chitosan beads and bentonite/chitosan beads were recorded on Nexus 470 FTIR spectrometer. The KBr pelleted samples were scanned over the wavenumber range 400 - 4000 cm^{-1} with resolution of 4 cm^{-1}.

2.5. Regeneration Studies

Regeneration studies were conducted using sodium hydroxide aqueous solution. The exhausted bentonite/chitosan beads was retrieved in 0.5 M NaOH for 12 h and was washed with deionized distilled water followed by drying in oven at 50°C. The regenerated adsorbent was reused in the next five adsorption experiments.

3. Results and Discussion

3.1. Effect of Bentonite Dosage on Adsorption

In order to optimize the optimal dosage for bringing down fluoride concentration from aqueous solution, bentonite/chitosan beads with 1.0 g, 2.0 g and 3.0 g bentonite and raw chitosan beads were used to adsorb fluoride under identical experimental conditions. It can be seen from the results in **Figure 1** that the dosage of bentonite in adsorbent significantly influenced the adsorption capacity of adsorbent. Bentonite/chitosan beads with bentonite dosage of 3.0 g possessed an adsorption capacity of 0.895 mg/g, whereas bentonite/chitosan beads with 2.0 g, 1.0 g and chitosan beads had 0.687 mg/g, 0.528 mg/g and 0.359 mg/g, respectively. Hence, 3.0 g of bentonite was fixed as the optimal dosage in all subsequent experiments.

3.2. Effect of pH on Adsorption

The adsorption data obtained for the effect of different pH values namely 3, 5, 7 and 9 on defluoridation were shown in **Figure 2**. The maximum adsorption capacity of 1.164 mg/g was observed at pH value of 5, however the adsorption capacity declined with the increasing of pH value. **Figure 2** also reflected that the acidic pH could offer more adsorption sites on bentonite/chitosan beads for fluoride removal but the alkaline pH was undesirable
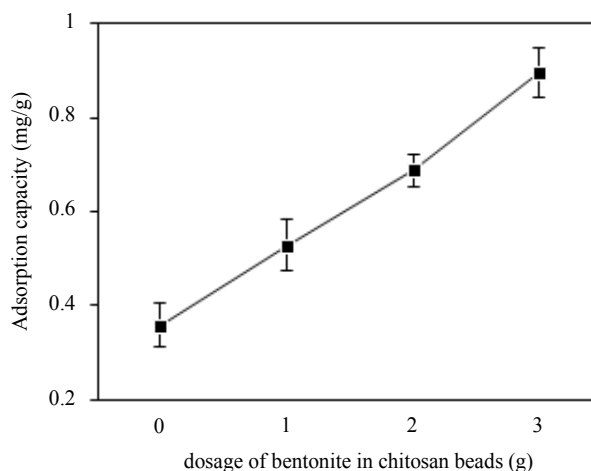

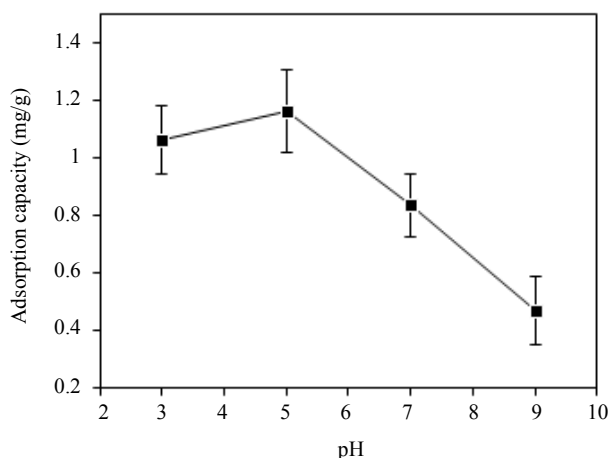**Figure 1. Effect of bentonite dosage on adsorption capacity of adsorbent for fluoride.**

Figure 2. Effect of pH on adsorption capacity of adsorbent for fluoride.

for adsorption process for fluoride.

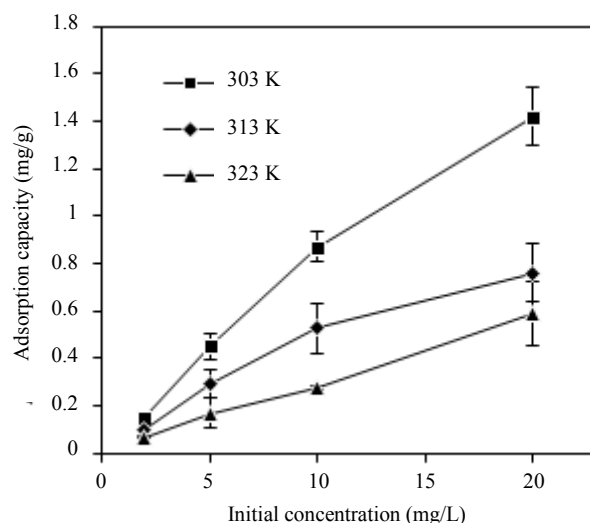### 3.3. Freundlich Isotherm Model

The effect of temperature (303 K, 313 K and 323 K) and initial fluoride concentration (2 mg/L, 5 mg/L, 10 mg/L and 20 mg/L) on adsorption capacity of adsorbent was given in **Figure 3(a)**. The adsorption capacity of bentonite/chitosan beads went up to 1.575 mg/g at 303 K with initial fluoride concentration of 20 mg/L. Apparently, the adsorption capacity of adsorbent declined with the rise in temperature, which is perhaps because the high temperature resulted in the unstability of bentonite/ chitosan beads. **Figure 3(a)** also indicated the initial fluoride concentration could enhance the adsorption of fluoride onto adsorbent.

Freundlich isotherm is a commonly used isotherm model to analyze adsorption data. Freundlich isotherm model can be written as:

$$\ln q_e = \ln K_f + \frac{\ln C_e}{n} \tag{2}$$

where q_e is the adsorption capacity of adsorbent (mg/g) at equilibrium and c_e is the fluoride concentration in the equilibrium solution (mg/L). The Freundlich constant K_f (mg/g) (L/mg)$^{1/n}$ characterizes the adsorption capacity of adsorbent, and the Freundlich constant $1/n$ reflects the adsorption intensity of adsorbent.

The fitting curve of Freundlich adsorption isotherm for fluoride adsorption using bentonite/chitosan beads was shown in **Figure 3(b)** and the Freundlich parameters calculated from fitting curve of Freundlich model were listed in **Table 1**. The correlation coefficients (R^2) values showed that the adsorption data could be well described by Freundlich isotherm model, which suggested the bentonite/chitosan beads was a heterogeneous adsorbent. The magnitudes of $1/n$ lying between 0 and 1 suggested

(a)
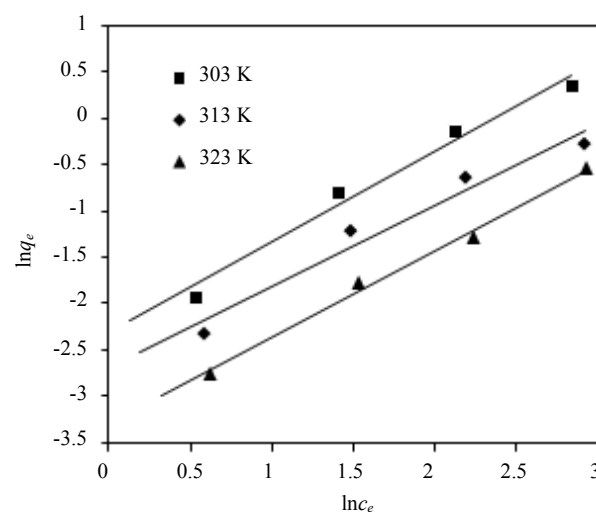
(b)

Figure 3. (a) Effect of temperature and initial fluoride concentration on adsorption capacity of adsorbent; and (b) Fitting curve of Freundlich adsorption isotherm of adsorbent.

Table 1. Freundlich isotherm parameters of adsorbent.

Temperature (K)	Freundlich isotherm parameters		
	$1/n$	K_f	R^2
Bentonite/chitosan beads			
303	0.9847	0.0979	0.9790
313	0.8832	0.0672	0.9636
323	0.9365	0.0366	0.9929

the adsorption of fluoride onto bentonite/chitosan beads was favourable.

3.4. Pseudo-Second Order Kinetic Model

The effect of contact time (30 min, 60 min, 120 min, 240

min and 480 min) on adsorption of fluoride using bentonite/chitosan beads was shown in **Figure 4(a)**. The adsorption capacity of adsorbent increased with increasing time and finally reached saturation at around 480 min.

Pseudo-second order kinetic assumes that chemisorption control the adsorption rate [8]. In order to gain the adsorption behavior through the whole range of process, pseudo-second order kinetic model was employed to analyze the adsorption data. The linear form of pseudo-second order kinetic can be expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

where t is the contact time (min). q_t and q_e are the amounts of fluoride adsorbed (mg/g) at arbitary time t and at equilibrium, respectively. K_2 is the adsorption rate constant (g/mg min).

The plots for pseudo-second order kinetic model of adsorbent was shown in **Figure 4(b)**. The correlation coefficients (R^2) value was larger than 0.9 (**Table 2**) which suggested the adsorption followed pseudo-second order kinetic model. Thus, the adsorption process of bentonite/chitosan beads for fluoride was governed by both physisorption and chemisorption.

3.5. Characterization

The SEM analysis graph (**Figure 5**) showed that the sizes of bentonite/chitosan beads were between 50 um and 150 um. The holes on the surface of beads could increase the adsorption sites. The EDAX spectra of the adsorbent (**Figure 6(a)**) showed the presence of elements in bentonite/chitosan beads. The emergence of fluoride peak in fluoride treated beads (**Figure 6(b)**) demonstrated the adsorption of fluoride onto adsorbent.

The FTIR spectra of chitosan, bentonite, chitosan beads and bentonite/chitosan beads were compared in **Figure 7**. The broad band at the region of 3500 - 3200 cm^{-1} is the overlapping peak of $-NH_2$ and $-OH$ stretching vibrations [9]. As for chitosan beads (**Figure 7(c)**), the band at 2925 cm^{-1} and 2884 cm^{-1} was the characteristic of $-CH_3$ and $-CH_2$ stretching vibrations, respectively. The adsorption peak at 1649 cm^{-1} assigned to $-NH_2$ bending vibration. The absorbance peak of symmetric stretching of $-CO$ on C_3 appeared at 1030 cm^{-1} suggested that $-OH$ on C_3 reacted with crosslinker to form chitosan beads [10]. The FTIR spectrum of bentonite/chitosan beads was given in **Figure 7(d)**, which presented the characteristic of chitosan (**Figure 7(a)**) and bentonite (**Figure 7(b)**). Bands at 1399 cm^{-1} and 519 cm^{-1} were the $-Si-O-$ stretching and bending vibration, respectively [11]. The FTIR spectra confirmed the successful synthesis of bentonite/chitosan beads.

3.6. Regeneration of Adsorbent

The results of regeneration studies shown in **Figure 8** indicated the adsorption capacity of adsorbent decreased from 0.92 mg/g to 0.69 mg/g with 25% loss in five
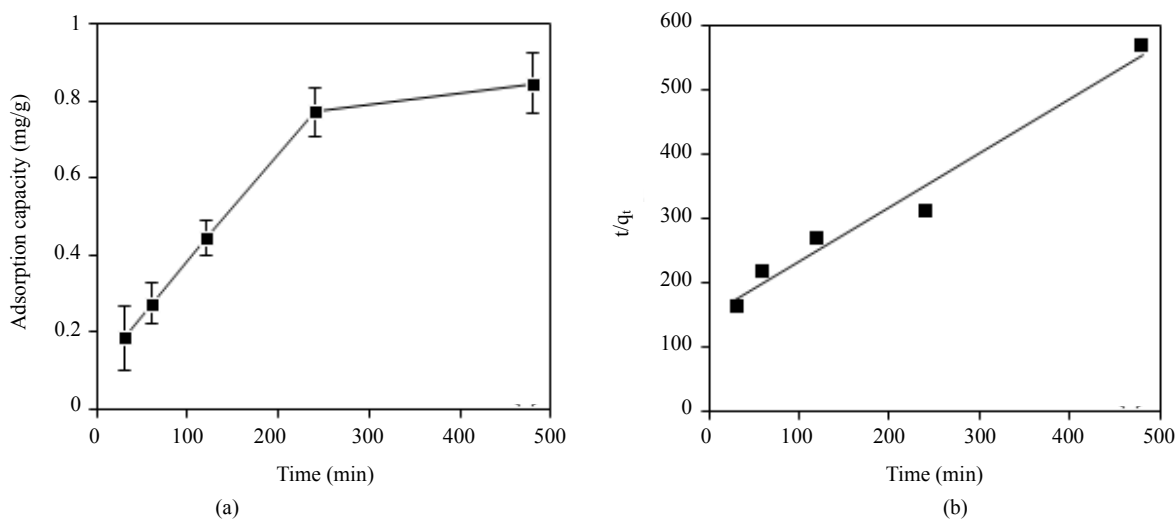
Figure 4. (a) Effect of contact time on adsorption capacity of adsorbent for fluoride; and (b) Plots for pseudo-second order kinetic model of adsorbent.

Table 2. Pseudo-second order kinetic parameters of adsorbent.

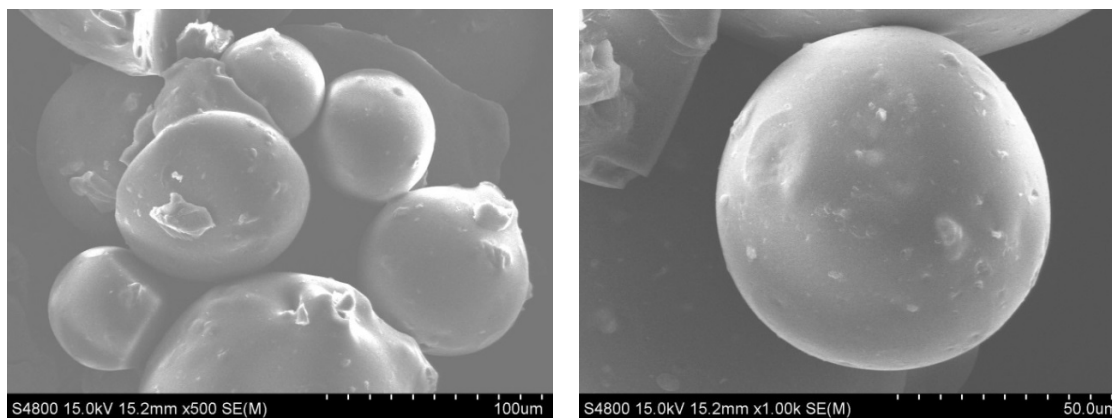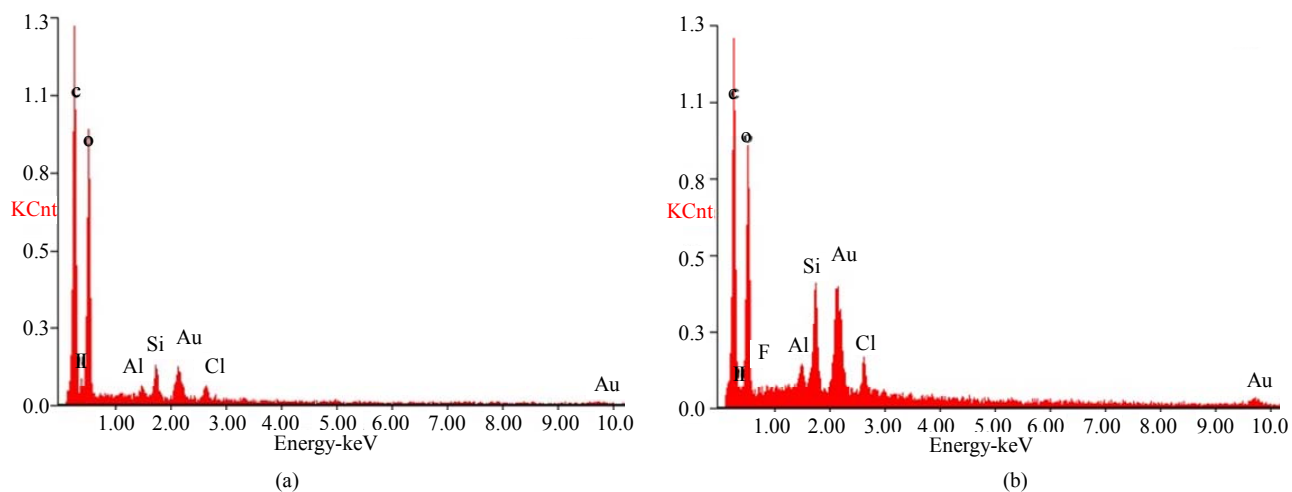|	Pseudo-second kinetic equation	K_2	q_e	R^2
Bentonite/chitosan beads	$t/q_t = 0.8417t + 149.67$	149.67	1.188	0.9719

Figure 5. SEM image of adsorbent.

Figure 6. EDAX spectra of (a) adsorbent and (b) fluoride treated adsorbent.
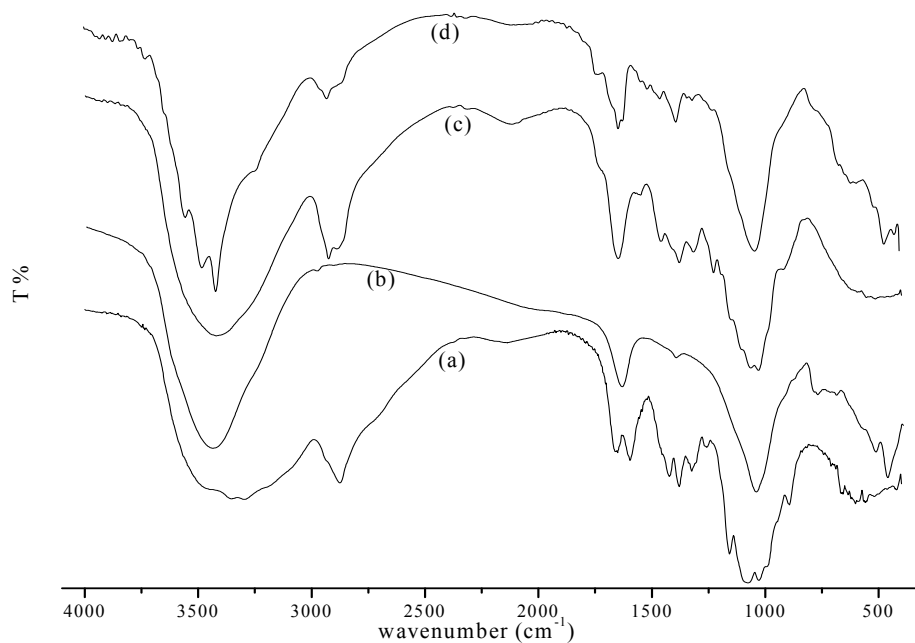

Figure 7. FTIR spectra of (a) Chitosan; (b) Bentonite; (c) Chitosan beads; (d) Bentonite/chitosan beads.
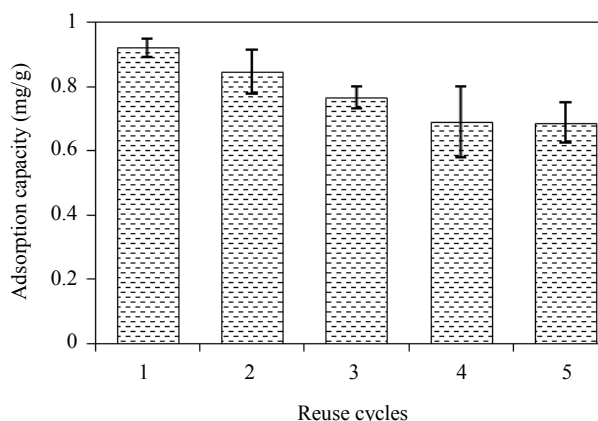

Figure 8. Relationship between reuse cycles and adsorption capacity of adsorbent.

successive adsorption experiments. Therefore, bentonite/chitosan beads had excellent regeneration ability.

4. Conclusions

1) The low-cost bentonite/chitosan beads were successfully prepared for adsorption of fluoride from aqueous solution using inverse suspension polymerization.

2) The optimal dosage of bentonite was 3.0 g with adsorption capacity of 0.895 mg/g. The optimal pH value for fluoride adsorption was pH 5 where the adsorption capacity of adsorbent was 1.164 mg/g.

3) The adsorption followed Freundlich isotherm model and pseudo-second order kinetic model.

4) Bentonite/chitosan beads were a low-cost, effective and reusable adsorbent for adsorption of fluoride.

5. Acknowledgements

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