

## Adsorption of fluoride from aqueous solution by enhanced chitosan/bentonite composite

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### ABSTRACT

In this work, enhanced chitosan/bentonite composite was prepared by treating chitosan/bentonite composite with concentrated hydrochloric acid (HCl). The adsorption of fluoride ions from aqueous solution onto the enhanced chitosan/bentonite composite was investigated. Adsorption studies were performed in a batch system, and the effects of various parameters, such as the pH value of the solution, adsorbent dosage and initial fluoride concentration, were evaluated. The optimum operating conditions for fluoride removal by the enhanced chitosan/bentonite composite were pH = 7 or so, and adsorbent dosage = 1.2 g. Increasing initial fluoride concentration reduced the adsorption of fluoride onto the enhanced chitosan/bentonite composite. Furthermore, the presence of other co-anions weakened the adsorption of fluoride onto this adsorbent. The equilibrium adsorption isotherms were well described by both the Freundlich and Langmuir models. The maximum monolayer adsorption capacity was 2.95 mg/g at 293 K.

**Key words** | adsorption, enhanced chitosan/bentonite composite, fluoride, isotherms

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### INTRODUCTION

Fluoride is an essential element, indispensable for the maintenance of dental health. Nevertheless, fluoride concentrations in drinking water above 1.5 mg/L may be detrimental to human health, leading to dental or skeletal fluorosis. According to the World Health Organization (WHO) the maximum allowable concentration of fluoride is 1.5 mg/L (Ayoob & Gupta 2006). At present, an increasing amount of wastewater containing fluoride is being released from various engineering processes, such as semiconductor manufacturing, coal power plants, electroplating, rubber and fertilizer production, etc. (Lee *et al.* 2010). Fluoride in high concentrations seriously threatens human health. Currently, the most widely employed technologies for fluoride removal are based on physico-chemical processes, including nanofiltration, ion-exchange, chemical precipitation, adsorption and membrane systems (Amine *et al.* 2010; Hisao *et al.* 2010; Bhaumik *et al.* 2011; Hou *et al.* 2010; Nie *et al.* 2012; Chen *et al.* 2012). Among these methods, adsorption is widely used and offers satisfactory results and seems to be a more attractive method for the removal of fluoride in terms of cost, simplicity of design and operation. Activated carbon is currently the most widely used adsorbent. However, it is very expensive and has a

high operating cost (Gong *et al.* 2005). Therefore, considerable attention has been devoted to the study of different types of low-cost materials such as kaolinite, bentonite, red mud, etc. for the removal of fluoride from aqueous solution (Ma *et al.* 2011; Jha & Mishra 2012; Wei *et al.* 2012).

Bentonite is primarily expandable montmorillonite clay. However, bentonite weakly adsorbs anionic pollutants because of repulsion between the anion and the negative charge on the edge of the bentonite sheet. Some attempts have been made to remove these anionic pollutants using modified bentonite. For example, the adsorption capacity of fluoride on acid-activated bentonite is as high as 1.15 mg/g (Srimurali *et al.* 1998).

Chitosan is a deacetylated derivative of chitin, the second most abundant organic compound in nature next to cellulose. It has several desirable characteristics, such as biocompatibility, biodegradability, renewability, bioactivity and non-toxicity. It has a broad application in the treatment of wastewater containing dye, heavy metal ions and organic pollutants due to the large number of  $-NH_2$  and  $-OH$  groups. However, chitosan naturally occurs in the form of flakes or powders, which has limited its utility, in particular, due to its dissolution in acid and the difficulty of separation,

etc. Cross-linking has often been used to overcome such drawbacks. Also, it has been found that further protonation improved the removal of fluoride after chitosan was cross-linked, although it was quite expensive (Huang *et al.* 2012).

In this study, chitosan was immobilized in bentonite to synthesize a composite material. A lower quantity of chitosan would then be needed in the adsorption process and this adsorption would then become a more cost-effective and environmentally friendly process. This chitosan/bentonite composite was further treated with concentrated hydrochloric acid (HCl) to increase the adsorption capacity for anionic pollutants. Here, the concentrated HCl was applied in the protonation of  $-\text{NH}_2$  in chitosan as well as in the activation of bentonite. The enhanced composite would act as an adsorbent for the adsorption of fluoride. The effects of adsorbent dosage, the pH value of the solution and the initial fluoride concentration on the adsorption of fluoride were studied in a batch system. In addition, the adsorption isotherms of fluoride onto enhanced chitosan/bentonite composite were evaluated.

## EXPERIMENTAL

### Materials and apparatus

Chitosan powder (90% deacetylated) was acquired from Sino-pharm Group Chemical Reagent Limited Company (China). Bentonite powder with a particle size of 200-mesh was acquired from the chemical factory of Shentai, Xinyang, Henan, China. All reagents used in this study, including NaF,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ , HCl, NaOH,  $\text{NaHCO}_3$ ,  $\text{Na}_3\text{PO}_4$ , acetic acid and glutaraldehyde, were of analytical grade. The fluoride concentration was measured using the Shanghai Leici acidity meter with the fluoride ion selective electrode PF-1 (Leici, Shanghai). The pH measurements were carried out with the same instrument with a pH electrode.

### Preparation of chitosan/bentonite composite

The chitosan/bentonite composite (CH/BT) was prepared using the following method: 2 g of chitosan was dissolved in 100 mL of 2% (v/v) HAc solution. Bentonite (5 g) was slowly added into the solution and stirred for 2 hours. 10 mL of 25 wt% glutaraldehyde was added into this solution. The cross-linking reaction occurred for 23 h at 60 °C and then the cross-linked chitosan/bentonite composite was washed with distilled water to remove any free glutaraldehyde and dried in an oven. The cross-linked

chitosan/bentonite composite was treated with concentrated HCl for 90 min for the protonation of chitosan (Viswanathan *et al.* 2009a; Xie *et al.* 2010) as well as the activation of bentonite (Srimurali *et al.* 1998). The resulting enhanced composite was washed with distilled water to neutral pH, dried at room temperature and ground to obtain 100 mesh-size particles, which were then used for adsorption studies.

### Adsorption experiments

Adsorption experiments were carried out at 20 °C using the batch method in duplicate. A certain amount of adsorbent was added into 50 mL of sodium fluoride solution with a desired pH value. The pH of the medium was adjusted with 0.1 M HCl or 0.1 M NaOH. The mixture was shaken in a shaker at a speed of 200 rpm at 20 °C. Samples were taken at predetermined time intervals for the analysis of fluoride concentrations in the solutions until adsorption equilibrium was reached. The removal of fluoride was studied for different conditions, including adsorbent dosage, contact time, pH value of the solution, and initial fluoride concentrations. The effect of competitor anions on the removal of fluoride was also investigated.

### Desorption study

After performing the equilibrium study with different initial fluoride concentrations ranging from 10 to 50 mg/L, fluoride-adsorbed powders were collected by filtration, and regenerated using 50 mL of 0.1 M NaOH, 0.1 M HCl and 0.1 M  $\text{H}_2\text{SO}_4$  solutions, respectively. These solutions were stirred for 1 hour at a stirring speed of 200 rpm. The adsorbents were removed, rinsed with distilled water and then reused for new adsorption with regard to fluoride.

### Adsorption isotherms

At present, various adsorption isotherm models have been used to study the adsorption capacity and equilibrium coefficients for the adsorption of fluoride. Two commonly used isotherms (*viz.* Langmuir and Freundlich isotherm models) were studied.

The Langmuir isotherm is based on the assumption of monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of the surface (Mall *et al.* 2006). Langmuir's equation involves

two parameters, expressed as follows:

$$q_e = \frac{q_m b c_e}{1 + b c_e} \quad (1)$$

where  $q_e$  is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g),  $c_e$  is the equilibrium concentration of the solute in the bulk solution (mg/L),  $q_m$  is the maximum adsorption capacity (mg/g) and  $b$  is the constant related to the free energy of adsorption (L/mg) (Tan *et al.* 2008).

The Freundlich isotherm describes a heterogeneous system and reversible adsorption and is not restricted to monolayer formation (Do *et al.* 2008); it is expressed as follows (Barka *et al.* 2009):

$$q_e = K_F c_e^{1/n} \quad (2)$$

where  $K_F$  is a constant, which indicates the relative adsorption capacity of the adsorbent ( $\text{mg}^{1-(1/n)} \cdot \text{L}^{1/n} / \text{g}$ ) and  $1/n$  is the adsorption intensity. The linearized equations of Langmuir and Freundlich are shown in Table 1. The Langmuir isotherm equation can be linearized into four forms.

The correlation coefficient,  $r^2$  values were used to predict the best fit equation. However, it does not describe the equilibrium data adequately based only on  $r^2$  values, according to these studies (Vasanth & Sivanesan 2005; Carl & George 2006; Subramanyam & Das 2009). Chi-square and average percentage errors (APE) are often adopted to determine the proper isotherm model further. Chi-square and APE are calculated by using Equations (3) and (4), respectively, indicating the fit between the experimental and calculated values of adsorption capacity.

$$\chi^2 = \sum \frac{(q_{e,\text{exp}} - q_{e,\text{cal}})^2}{q_{e,\text{cal}}} \quad (3)$$

**Table 1** | Non-linearized and linearized isotherm equations

isotherm	Non-linearized equation	Linearized equation
Langmuir-I	$q_e = \frac{q_m b c_e}{1 + b c_e}$	$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{b q_m}$
Langmuir-II		$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{b q_m}\right) \frac{1}{c_e}$
Langmuir-III		$q_e = q_m - \left(\frac{1}{b}\right) \frac{q_e}{c_e}$
Langmuir-IV		$\frac{q_e}{c_e} = b q_m - b q_e$
Freundlich	$q_e = K_F c_e^{1/n_F}$	$\log(q_e) = \log(K_F) + \frac{1}{n_F} \log c_e$

$$\text{APE} = \frac{\sum_{i=1}^N |q_{e,\text{exp}} - q_{e,\text{cal}}| / q_{e,\text{exp}}}{N} \times 100 \quad (4)$$

where  $q_{e,\text{cal}}$  is equilibrium capacity obtained by calculating from the model (mg/g) and  $q_{e,\text{exp}}$  is experimental data on the equilibrium capacity (mg/g). If data from the model are similar to the experimental data, chi-square and APE will be a small number.

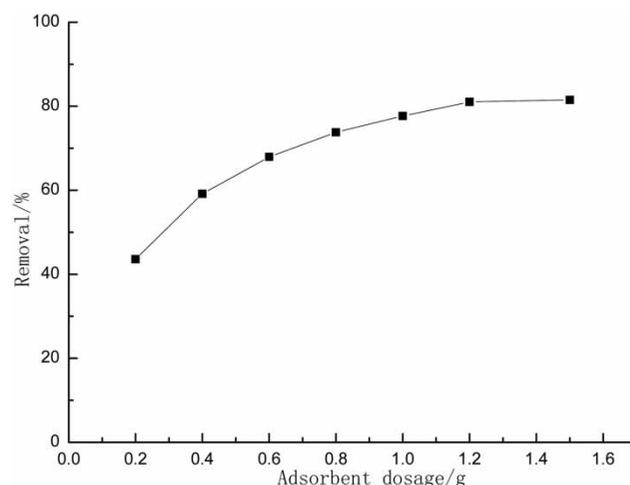
## RESULTS AND DISCUSSION

### Effect of adsorbent dosage

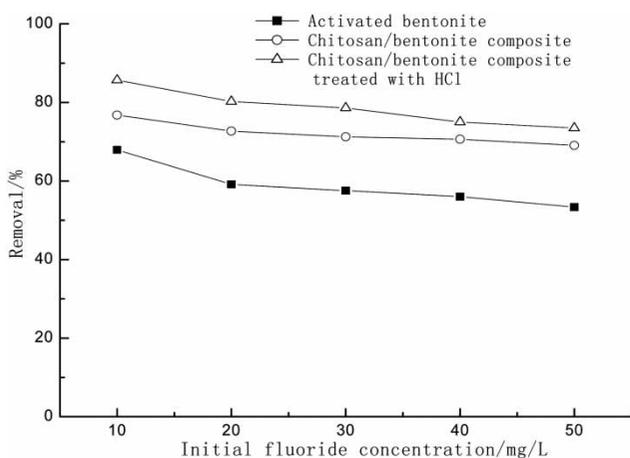
The effect of adsorbent dosage on the removal of fluoride (20 mg/L) with a neutral pH at 293 K was evaluated in the range of 0.1–1.8 g (Figure 1). The removal of fluoride significantly increases with increasing adsorbent dosage, which results from an increase in adsorption sites as the dosage increases. However, for adsorbent dosage more than 1.2 g, no significant increase in fluoride removal (81.0%) is observed. Similar results were reported for the removal of fluoride ions using cuttlefish bones (Nasr *et al.* 2011) and protonated cross-linked chitosan beads (Viswanathan *et al.* 2009a). This study utilized an adsorbent dosage of 1.2 g.

### Effect of initial fluoride concentration

Figure 2 shows the effect of initial fluoride concentrations ranging from 5 to 50 mg/L with a neutral pH at 293 K.

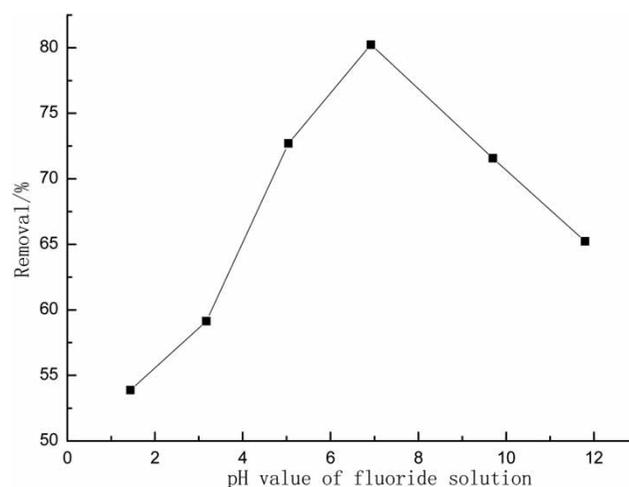


**Figure 1** | Effect of adsorbent dosage on adsorption.



**Figure 2** | Effect of initial fluoride concentration on adsorption.

Here, activated bentonite was obtained after raw bentonite was treated with concentrated HCl. Cross-linked chitosan/bentonite composite was prepared according to the procedure mentioned earlier in the section, Preparation of chitosan/bentonite composite, but this composite was not treated further with concentrated HCl. In this study, the adsorbent tested was the cross-linked chitosan/bentonite composite treated further with concentrated HCl. It was found that the removal of fluoride decreases with the increase in initial concentrations of fluoride. Similar types of results were reported for fluoride removal (Jagtap *et al.* 2009; Huang *et al.* 2012). The removal of fluoride decreases from 89.2 to 73.5% when the initial fluoride concentration increases from 5 to 50 mg/L. This trend may be due to the fact that with increasing fluoride concentration, the binding capacity of the adsorbent approaches saturation, resulting in a decrease of overall removal. Furthermore, it is observed that the composite with concentrated HCl allows higher removals with regard to fluoride than both the cross-linked composite and activated bentonite. Increasing removals for the cross-linked chitosan/bentonite composite treated further with concentrated HCl may be attributed to the protonation of  $-NH_2$  and the activation of bentonite. In our previous study, we investigated the adsorption of fluoride onto protonated cross-linked chitosan, and it was found that protonation was an effective method to improve the adsorption of anions onto chitosan (Huang *et al.* 2012). In this study, chitosan was immobilized in bentonite to prepare a composite material. After this composite was treated with concentrated HCl, both the protonation of  $-NH_2$  and the activation of bentonite were achieved, thus the removal of fluoride onto the enhanced composite increased. As a result, a lower amount of chitosan was applied during the

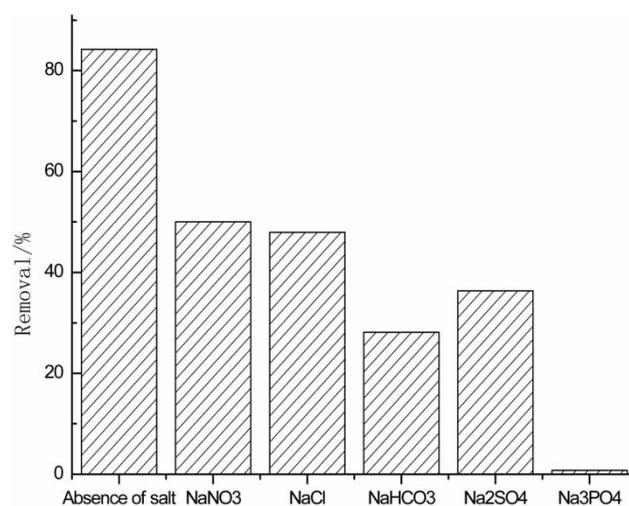


**Figure 3** | Effect of pH value of solution on adsorption.

adsorption process. When initial fluoride concentration was lower than 30 mg/L, fluoride removal was higher than 80%.

#### Effect of the pH value of the solution

The removal of fluoride ions from aqueous solution was highly dependent on the pH value of the solution. The adsorption of fluoride onto this adsorbent was studied with a 20 mg/L initial fluoride concentration at different pH values. Figure 3 shows the removal of fluoride ions as a function of pH. The maximum removal (82.3%) was observed at pH 6.7, while fluoride removal was observed to decrease both in acidic the pH range (from 82.3 to 53.9%) and in the alkaline pH range (from 82.3 to 65.2%). After the composite was treated with concentrated



**Figure 4** | Effect of the presence of other co-ions on adsorption.

HCl, the positively charged characteristic of this composite increased. The strong electrostatic interactions between the negatively charged fluoride ions and positively charged surface enhanced the adsorption of fluoride onto this adsorbent. However, the progressive decrease of fluoride at an alkaline pH may be mainly due to the competition between the anions' fluoride and  $-OH$  for adsorption sites on the surface of the adsorbent. Decreased removals at acid pH may be attributed to the formation of hydrofluoric acid, which weakened the adsorption of fluoride ions onto the adsorbent. Jagtap

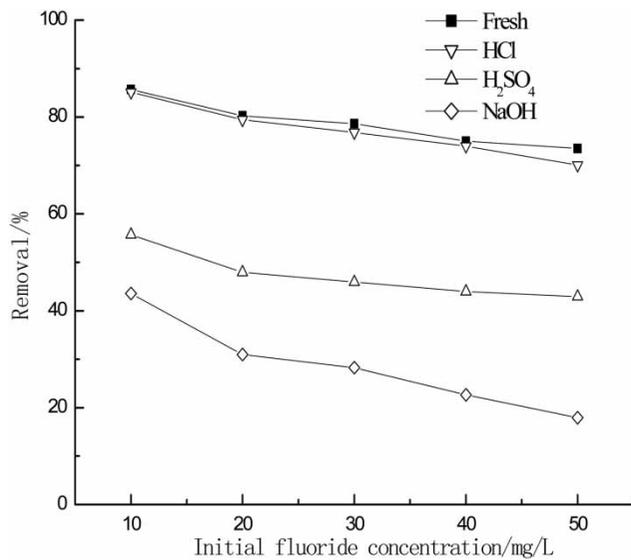


Figure 5 | Regeneration of adsorbent.

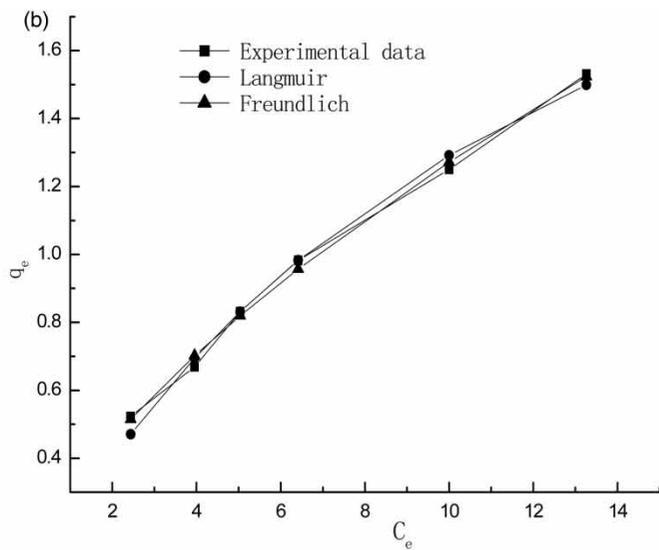
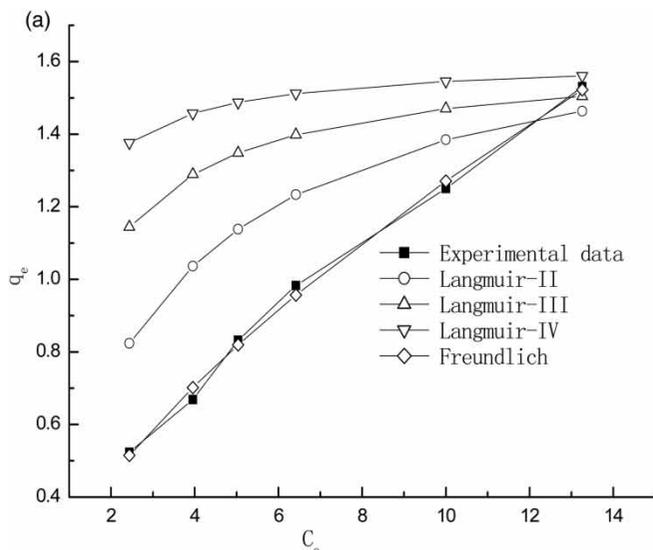


Figure 6 | Isotherm models for fluoride adsorption: (a) linearized models; (b) non-linearized models.

*et al.* (2009) also found similar results when they investigated the removal of fluoride onto chitosan-based Ti macrospheres. The original pH value of fluoride solution is 7 or so, therefore, pH values of the solutions tested were unadjusted in the following experiments.

### Effect of the presence of other co-anions

Fluoride-contaminated drinking water always contains several other anions, which can compete in the adsorption process. In order to study the effect of interfering ions, the adsorption studies were carried out in the presence of 0.1 M salt solutions of chloride, sulphate, nitrate, bicarbonate and phosphate, respectively. The effect of other anions on the removal of fluoride is shown in Figure 4. These results show that the presence of  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $HCO_3^-$  and  $PO_4^{3-}$  ions reduces the removal of fluoride. In addition, both the anions  $HCO_3^-$  and  $PO_4^{3-}$  showed low removal for fluoride. For  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ , decreased removals with regard to fluoride may be due to the competing effect of these co-anions. However, for  $HCO_3^-$  and  $PO_4^{3-}$ , their addition resulted in an increased pH of fluoride solution. As mentioned in the previous section, the removal level reduced at an alkaline pH range. Therefore, an obvious decrease in the removal of fluoride may be attributed to the competing effect of these co-anions as well as the increased pH value of fluoride solution, especially in the presence of  $PO_4^{3-}$ . As shown in Figure 4, removal with regard to fluoride was close to zero in the presence of  $PO_4^{3-}$ .

## Desorption and regeneration

Desorption studies will help to regenerate the adsorbent so that it can be reused to adsorb fluoride. All of the regeneration experiments were carried out at 20 °C. The desorption experiments of the adsorbent were carried out using 0.1 M HCl, 0.1 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M NaOH as eluents. After the exhausted adsorbent was regenerated with 0.1 M HCl solution, this adsorbent still allows high levels of removal with regard to fluoride, as shown in Figure 5. Of the three eluents, HCl has been identified as the best eluent.

## Adsorption isotherms

Plots between  $c_e$  versus  $q_e$  using the experimental and predicted values by non-linearized and linearized models are shown in Figure 6. The parameters ( $q_m$ ,  $b$ ,  $K_F$  and  $n$ ) obtained from linearized and non-linearized isotherms together with  $r^2$ , chi-square and APE are listed in Table 2 and Table 3, respectively. For Langmuir isotherms, the type-II linearized Langmuir equation shows a higher value of correlation coefficient ( $r^2 = 0.9911$ ) than those from the other three linearized equations. Although the linearized equations derive from the original non-linearized equation, the variation in adsorption capacity ' $q_m$ ' and adsorption constant ' $b$ ' may be attributed to the errors in the computation of parameters during linearization (Vasanth & Sivanesan 2005; Carl & George 2006; Subramanyam & Das 2009). The lower correlation coefficient values suggest that it was not appropriate to use this type of linearization. However, it is not enough to obtain the appropriate isotherms only according to the correlation coefficient values. In order to verify the validity of the Langmuir isotherm model, it is essential to calculate the average percentage errors and chi-square values. From Table 2, it is clear that the values of APE and chi-square from the linearized Langmuir models (type-I, type-II, type-III and type-IV) are very high. The high APE and chi-square values indicate that these linearized Langmuir models were not able to describe equilibrium data. The plot of type-I is not shown in Figure 6(a) due to obviously high values of APE and chi-square. However, Table 3 shows that the correlation coefficient value of the non-linearized Langmuir model is high ( $r^2 = 0.9968$ ), and the values of APE and chi-square are considerably lower values (3.25 and 0.0089, respectively). Therefore, the non-linearized Langmuir model can describe equilibrium data better compared with the linearized Langmuir model, as shown in Figure 6(b). The obvious difference resulted from the errors in the computation of parameters during

Table 2 | Linearized isotherm parameters for fluoride adsorption

Isotherm models	Values
<i>Langmuir-I</i>	
$q_m$	2.818
$B$	0.0844
$r^2$	0.9815
Chi-square	46.95
APE	899.1
<i>Langmuir-II</i>	
$q_m$	2.326
$B$	0.1140
$r^2$	0.9911
Chi-square	0.3893
APE	31.63
<i>Langmuir-III</i>	
$q_m$	2.527
$B$	1.005
$r^2$	0.9441
Chi-square	0.9905
APE	55.86
<i>Langmuir-IV</i>	
$q_m$	2.718
$B$	0.8962
$r^2$	0.9441
Chi-square	1.486
APE	73.16
<i>Freundlich</i>	
$K_F$	0.2911
$1/n_F$	0.6400
$r^2$	0.9975
Chi-square	0.0030
APE	2.17

linearization. Similar results have been described by Subramanyam & Das (2009) when they studied the adsorption of aqueous phenol solution in soil using linearized and non-linearized isotherm models.

For the Freundlich isotherm, the values of the correlation coefficient ( $r^2 > 0.99$ ) for both linearized and non-linearized isotherms were found to be close to each other (Table 2 and Table 3), unlike the variation in Langmuir's linearized and non-linearized models. Furthermore, the values of the APE and chi-square were low. Therefore, it was seen that the Freundlich model also described equilibrium data perfectly. The coefficients (viz.  $K_F$  and  $1/n_F$ ) for both

**Table 3** | Non-linearized isotherm parameters for fluoride adsorption

Isotherm models	Values
<i>Langmuir</i>	
$q_m$	2.952
$B$	0.0778
$r^2$	0.9968
Chi-square	0.0089
APE	3.25
<i>Freundlich</i>	
$K_F$	0.2908
$1/n_F$	0.6408
$r^2$	0.9974
Chi-square	0.0030
APE	2.157

**Table 4** | Comparison of maximum monolayer adsorption capacity of fluoride on various adsorbents based on chitosan

Adsorbents	Adsorption capacity/mg/g	Reference
Protonated chitosan beads	7.32	Viswanathan <i>et al.</i> (2009a)
Carboxylated cross-linked chitosan beads	11.11	Viswanathan <i>et al.</i> (2009b)
Chitosan-based Ti microspheres	7.21	Jagtap <i>et al.</i> (2009)
Chitosan supported Zr (IV) tungstophosphate composite	7.63	Viswanathan & Meenakshi (2010)
La-chitosan beads	4.7	Bansiwal <i>et al.</i> (2009)
Zr(IV) impregnated dithiocarbamate modified chitosan beads	9.84	Liu <i>et al.</i> (2013)
Protonated cross-linked chitosan particles	8.10	Huang <i>et al.</i> (2012)
Raw chitosan beads	0.052	Viswanathan <i>et al.</i> (2009a)
Chitosan/bentonite composite	2.95	This study

linearized and non-linearized isotherms are found to be high, as shown in Table 2 and Table 3. The magnitude of the Freundlich adsorption capacity ' $n$ ' gives an indication of favourability of adsorption. Thus, a conclusion was obtained that the adsorption of fluoride ions onto this adsorbent followed both Langmuir and Freundlich models, but linearized Langmuir isotherms were not suitable to describe

the adsorption of fluoride ions onto this adsorbent. Table 4 lists the comparison of the maximum monolayer adsorption capacity of fluoride on various adsorbents based on chitosan. From Table 4, it was found that the adsorbents studied had a relatively low adsorption capacity towards fluoride. However, the dosage of chitosan in this composite is lower.

## CONCLUSIONS

In this study, the enhanced chitosan/bentonite composite was used for fluoride removal from an aqueous solution. Batch experiments were conducted to investigate the adsorption capability and the regeneration feasibility of this adsorbent. The protonated amino groups in chitosan were favourable for fluoride adsorption; pH 7.0 was chosen as the optimal value. The equilibrium data fitted well with the Langmuir and Freundlich isotherm models, and the maximum monolayer adsorption capacity was 2.95 mg/g. The presence of co-existing anions resulted in less fluoride adsorption, especially to high valence anions such as phosphate. The exhausted adsorbent may be regenerated by 0.1 M HCl solution. Electrostatic attraction was the main driving force for fluoride adsorption. The results indicate that the enhanced chitosan/bentonite composite has the potential for application to fluoride removal from contaminated water.

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