



COMPARATIVE STUDY OF ADSORPTION OF FLUORIDE
IONS ON CHITOSAN GEL BEADS AND CROSS-LINKED CHITOSAN
GEL BEADS



Otman Goudali, Rachid El Kaimbillah, Mahfoud Agunaou, Mohammed El Azhar, Abdessadik Soufiane

Laboratory of Chemistry of Coordination and Analytics, Faculty of Sciences, B.P. 24000, El Jadida, Morocco

Abstract

The presence of fluoride in water has become a major concern worldwide because of its chronic carcinogenic behavior in humans. In order to remove fluoride from aqueous solution we synthesized chitosan gel beads (CB) and cross-linked chitosan gel beads (CCB) in a batch reactor. Thus, a series of experiments was carried out to study the influence on the adsorption capacity of certain parameters such as initial fluoride concentration, adsorbent mass, pH solution and contact time. The results obtained show that the percent removal of fluoride reached a maximum of 62% after 25 min for chitosan gel beads and 72% after 30 min for cross-linked chitosan gel beads. Adsorption kinetics of the fluoride ions on the two adsorbents is well described by the pseudo-first order model and that the adsorption isotherms are followed by the Langmuir model.

Keywords: Fluoride; Adsorption; Chitosan beads; Cross-linking.

1. Introduction

Fluoride is a chemical element of great interest in the prevention of tooth decay. However, at high doses, fluoride can cause acute poisoning, rarely encountered, or chronic manifestations of bone, kidney, nerve and especially dental.

Several processes are used to remove excess fluorine in water such as nanofiltration [1,2], electrodialysis [3], ion exchange resins [4,5], precipitation [6] and adsorption [7,8] which is the most studied technique with the exploration of new adsorbents and in particular those resulting from abundant natural resources [9-11]. Thus, in our laboratory, we investigated the properties of chitin and chitosan as adsorbents for defluoridation [12-14] and denitrification [15] of contaminated water.

This work focused on the preparation, characterization and study of the adsorption capacity of fluoride ions on cross-linked and non-cross-linked chitosan gel beads, thus the adsorbents obtained were

characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The influence of various physicochemical parameters on adsorption (such as adsorbent mass, contact time, pH, initial fluoride concentration, and temperature), adsorption isotherms and adsorption kinetics were studied.

2. MATERIALS AND METHODS

2.1. Materials

Chitosan has been prepared from local shrimp waste [15,16]. Sodium fluoride (NaF), glutaraldehyde, glacial acetic acid, hydrochloric acid (HCl) and sodium hydroxide (NaOH) are all purchased from Sigma-Aldrich. The fluoride concentration was determined using a specific electrode of ISE 67B type according to standard NF T 90-004.

*Corresponding author e-mail: goudali.doct@gmail.com;

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2.2. Chitosan gel beads preparation

Chitosan gel beads were prepared by dissolving in 60 mL of (5% (v/v)) acetic acid, 2 g of chitosan, mixture is then poured dropwise into a 500 mL of NaOH (0.5M) solution, the beads thus obtained are filtered and then stored in deionized water for use [17].

2.3. Preparation of cross-linked chitosan gel beads

The prepared chitosan gel beads were suspended in a 0.025 M glutaraldehyde solution. The chitosan gel beads were held for 24 hours in the glutaraldehyde solution at room temperature. After 24 hours, the cross-linked chitosan beads were intensively washed with distilled water, filtered and then stored in deionized water for use.

2.4. Characterization

The X-ray diffraction (XRD) patterns were recorded with a D8 Advance Eco mark diffractometer (Bruker D8) with Cu K α (1.5406 Å) and generated radiation at 50 kV and 20 mA. The 2θ range from 5° to 40°. Infrared absorption spectra were conducted on a Thermo-Scientific Fourier transform infrared (FT-IR) spectrometer (Chouaib Doukkali University, Morocco), in the range of 600 cm⁻¹ and 4000 cm⁻¹.

2.5. Adsorption tests

Adsorption tests were carried out in a closed reactor by stirring the synthetic solutions in the presence of each of the adsorbents, cross-linked and chitosan gel beads. The influence of certain main physic-chemical parameters on adsorption capacity was studied, and each experiment was replicated three times and error bars were presented in all graphs. Adsorption isotherms and adsorption kinetics have been studied for more information on the adsorption process.

3. Results and discussion

Chitosan gel beads and cross-linked chitosan gel beads characterization.

3.1. Analysis by FTIR

Fig.1 show that chitosan gel beads (CB) had characteristic bands at 3292 (cm⁻¹) and 3359 (cm⁻¹) which attributed to -NH₂ elongation vibration and -OH vibration, band at 2875 (cm⁻¹) is attributed to CH stretching vibration, band at 1644 (cm⁻¹) is assigned to C=O stretching vibration (amide I), the band at 1587 (cm⁻¹) is characteristic to amide II according to other studies [18]. The bands at 1420 (cm⁻¹) and at 1373 (cm⁻¹) attributed to CH deformation vibration and the band at 1324 (cm⁻¹) is attributed to amide III vibration (C-N).

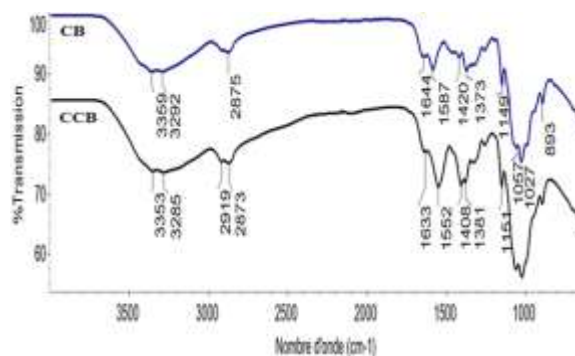


Fig.1 FTIR spectra of chitosan gel beads (CB) and cross-linked chitosan gel beads (CCB).

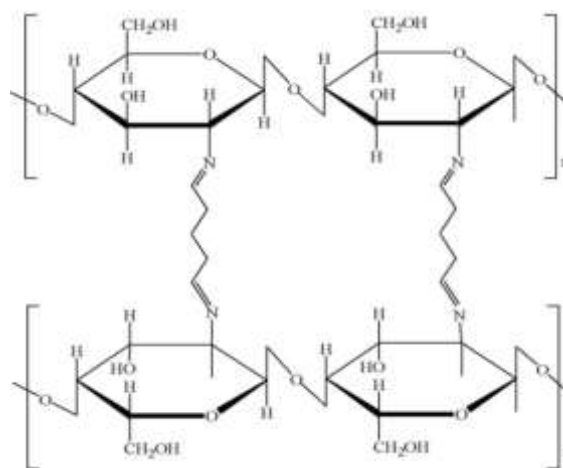


Fig.2 Cross-linked chitosan gel beads structure.

Fig. 2 shows an absorption peak at 1633 (cm⁻¹) attributed to the imine (C=N) band and peak at 1552 (cm⁻¹) attributed to ethylenic (C=C) band [19] and also shows the disappearance of the CH band at 1408 (cm⁻¹). These changes, that accompany the cross-linking, suggest that chitosan has been well cross-

linked and that glutaraldehyde has completely reacted with chitosan which is in good agreement with the absence of the $1720\text{ (cm}^{-1}\text{)}$ peak characteristic of the aldehyde function of glutaraldehyde [20].

3.2. Analysis by DRX

Fig.3 (CB) exhibits characteristic peaks at 2θ at 10.16° , 19.64° and 21.88° which correspond to a polymorph of chitosan, which is mentioned in the literature as the polymorphic hydrate (tendon) [21-23]. The reflection at $2\theta = 10^\circ$ was attributed to crystal forms I and the reflection at $2\theta = 20^\circ$ corresponds to crystal forms II characteristic at the high degree of crystallinity of chitosan [24,25].

Fig.3 (CCB) shows, that the two characteristics diffraction peaks of chitosan at $2\theta = 10.14$ and $2\theta = 21.88$ have sharply diminished and broadened. This broadening implies that the chain alignment of chitosan gel beads turns to be more disordered after the cross-linking reaction with glutaraldehyde [26]. This implies an increase in the amorphous phase, thus increasing the adsorption capacity. These modifications show that chitosan gel beads cross-linking has been successful imply.

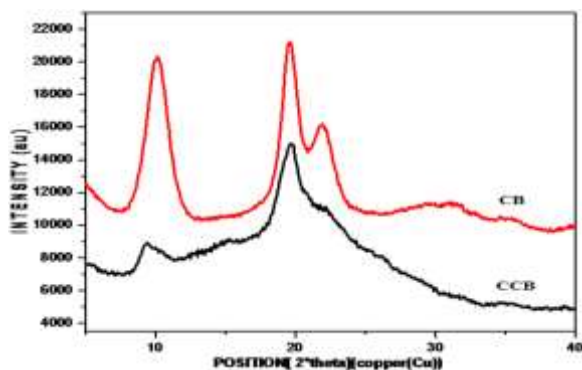


Fig.3 DRX of chitosan gel beads (CB) and cross-linked chitosan gel beads (CCB)

3.3. Effect of contact time

The tests were carried out by stirring 100 mg of the adsorbent for 120 min in solutions whose concentration 10 mg/L. The tests were carried out at $\text{pH} = 6.70$ with stirring at 100 rpm at room temperature. The residual concentrations were determined and then exploited (Fig.4).

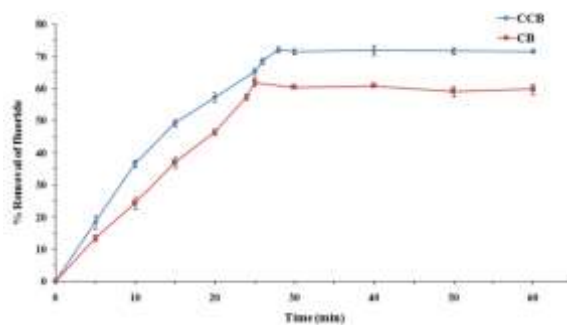


Fig.4: Contact time effect on the fluoride adsorption on chitosan gel beads (CB) and cross-linked chitosan gel beads (CCB), ($C_0 = 10\text{ mg/L}$; $m = 100\text{ mg}$; $\text{pH} = 6, 70$; Stirring speed = 100 rpm; $V = 100\text{ mL}$ and $T = 24 \pm 2^\circ\text{C}$).

3.4. Effect of concentration

Tests were carried out by stirring 100 mg of the adsorbent for 30 min in solutions whose fluoride concentration varies from 2 to 14 mg/L. The tests were carried out at $\text{pH} = 6.70$ with stirring at 100 rpm at room temperature. The residual concentrations were determined and then exploited in figure 5. The results show that adsorption capacity increases when fluoride initial concentration increases, the saturation of the active sites of the two adsorbents is reached at initial fluoride concentration of 10 mg/L.

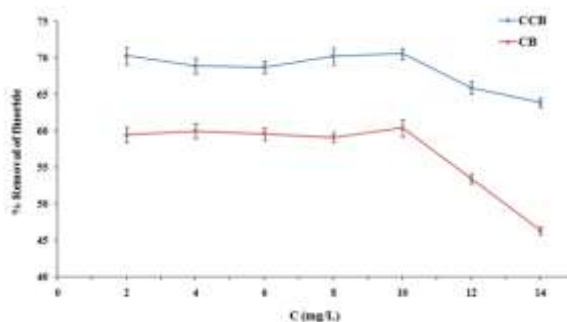


Fig.5 Effect of initial fluoride concentration on chitosan gel beads and cross-linked chitosan gel beads ($\text{pH} = 6, 70$; $m = 100\text{ mg}$; $V = 100\text{ mL}$; Stirring speed = 100 rpm and $T = 24 \pm 2^\circ\text{C}$).

3.5. Effect of pH

The effect of pH was carried out by varying the pH from 3 to 10 using a solution of HCl (0,1M) or NaOH (0,1M) according to the desired pH. The results obtained during these tests are shown in figure 6.

Figure 6 shows that below and above pH = 6.7 there is a decrease in adsorption for both adsorbents. This decrease can be explained in the alkaline pH range by the competition between fluoride and an excess of hydroxyl OH⁻. While in the acidic pH range, it can be attributed to the formation of hydrofluoric acid [27].

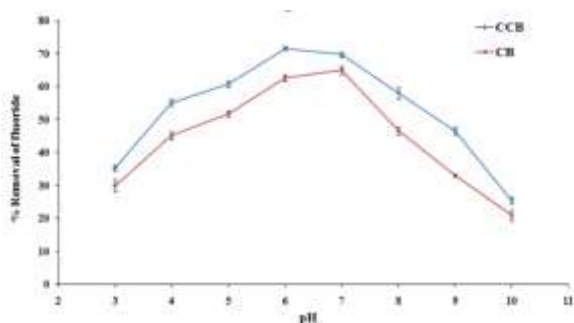


Fig.6 Removal of fluoride on chitosan gel beads (CB) and cross-linked chitosan gel beads (CCB) as a function of pH ($m = 100$ mg; $V = 100$ mL; $C_0 = 10$ mg/L; Stirring speed = 100 rpm and $T = 24 \pm 2^\circ\text{C}$).

3.6. Effect of adsorbent mass

Tests were carried out by placing 40, 60, 80, 100, 120 and 140 mg of adsorbent in a volume of 100 mL of fluoride, of concentration $C_0 = 10$ mg/L. The stirring of the solutions was carried out at a speed of 100 rpm at $24 \pm 2^\circ\text{C}$.

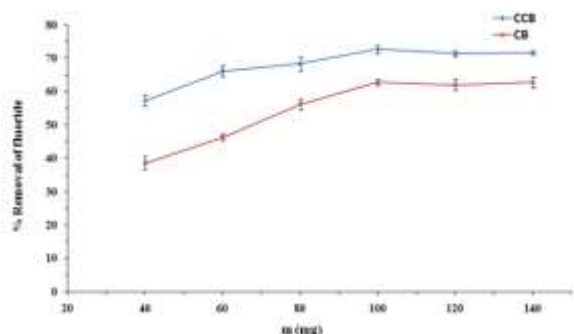


Fig.7 Removal of fluoride ions on chitosan gel beads and cross-linked chitosan gel beads (pH = 6,70; $V = 100$ mL; $C_0 = 10$ mg/L; Stirring speed = 100 rpm and $T = 24 \pm 2^\circ\text{C}$).

Figure 7 shows that fluoride removal increases as the adsorbent dose increases. This may be due to increase in adsorption sites, but starting at 100 mg,

fluoride removal becomes constant, (72%) for cross-linked chitosan gel beads and (62%) for chitosan gel beads. The optimum adsorbent dose was 100 mg for both adsorbents.

3.7. Kinetic study and adsorption isotherms

3.7.1 Adsorption isotherms

Langmuir and Freundlich models allowed us to calculate the maximum adsorption capacity and the adsorption parameters [28].

Langmuir model :

$$\frac{1}{q_e} = \frac{1}{q_m \cdot K_L} \cdot \frac{1}{C_e} + \frac{1}{q_m}$$

Freundlich model :

$$\text{Log}(q_e) = \text{Log}(K_F) + \frac{1}{n} \text{Log}(C_e)$$

$$q_e = (C_0 - C_e) \times \frac{V}{m}$$

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); m is the mass of adsorbent (g); K_L is the Langmuir constant (L/mg); K_F and n are the constants characteristic of the efficiency of an adsorbent with respect to a given solute.

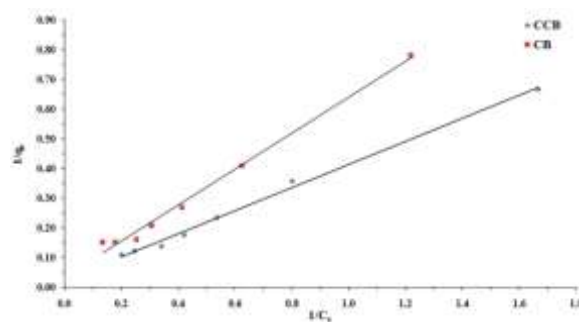


Fig.8 Linearization of the Langmuir equation for the adsorbent/adsorbate systems studied (pH = 6,70; $V = 100$ mL; $m = 100$ mg; Stirring speed = 100 rpm; $T = 24 \pm 2^\circ\text{C}$).

The adsorption isotherms were studied by stirring a mass of the adsorbent (100 mg) in solutions of different fluoride concentrations ions 2 to 14 mg/L. Adsorbent and adsorbate were contacted for 30 minutes with 100 rpm stirring. After the determination of the residual concentrations, we have

followed the evolution of $1/q_e$ according to the Langmuir model and, the evolution of $\log(q_e)$ according to Freundlich model. The results obtained are illustrated in figures 8 and 9.

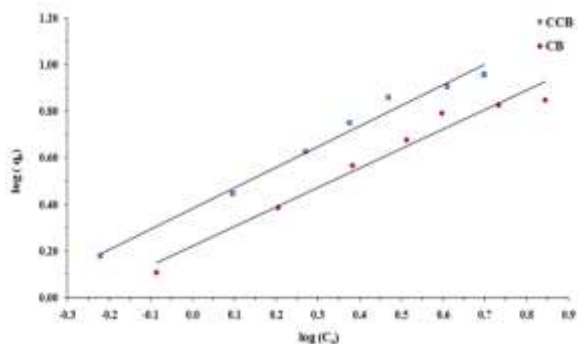


Fig.9 Linearization of the Freundlich equation for the adsorbent/adsorbate systems studied (pH = 6,70; V = 100 mL; m = 100 mg; Stirring speed = 100 rpm; T = 24 ± 2 °C).

The linear representations of the experimental values of this adsorption process allowed us to determine the parameters at equilibrium and Langmuir and Freundlich constants values, calculated by linear regression (Table 1).

Table 1. Parameters of Freundlich and Langmuir isotherm

Parameter	Freundlich isotherm			Langmuir isotherm		
	N	K_f (L/g)	R^2	q_m (mg/g)	K (L/mg)	R^2
CB	1,195	1,656	0,992	27,778	0,06	0,996
CCB	1,133	2,415	0,984	40	0,064	0,998

The values of the regression coefficients indicate that the adsorption process of fluoride ions by chitosan gel beads and cross-linked chitosan gel beads is favorably described by the Langmuir isotherm (with excellent linear regression coefficients R^2 which are almost equal to 1).

3.7. 2 Study of adsorption kinetics

Experiments were carried out under the same operating conditions. A solution of fluoride (100 mL) containing 100 mg of the supports is stirred at 100 rpm. The results obtained are shown in figures 12 and 13. The first-order adsorption rate constant is

deduced from the Lagergreen model [29]. The law of speed is written according to the following equation:

$$\text{Log}(q_e - q_t) = \text{Log}(q_e) - \frac{K_1 \cdot t}{2.303}$$

Adsorption kinetics is determined by the pseudo-second order model. It takes into account the rapid fixation of solutes on the most reactive sites according to the following equation [30].

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

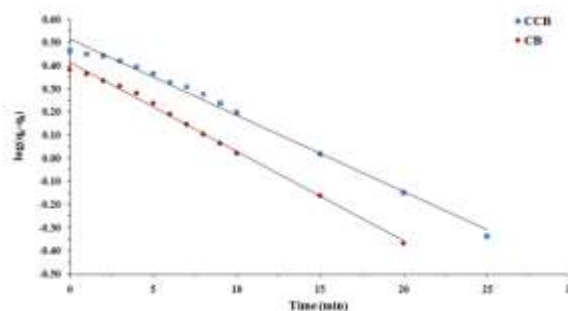


Fig.10 Pseudo-first order plot for fluoride adsorption onto chitosan gel beads (CB) and cross-linked chitosan gel beads (CCB).

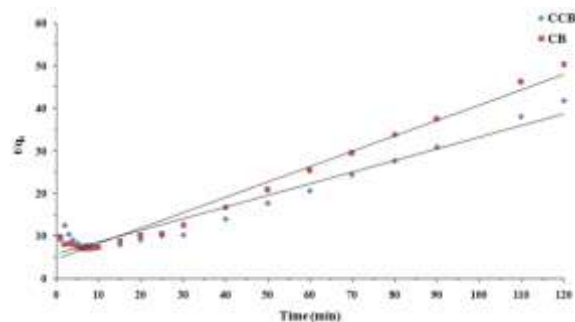


Fig.11 Pseudo-second order plot for fluoride adsorption onto chitosan gel beads (CB) and cross-linked chitosan gel beads (CCB).

The results obtained of the pseudo-first order and pseudo-second order are shown in Table.2. The equilibrium adsorbed at the experimental level is closer to that calculated by pseudo-first order model but is different to that calculated by the pseudo-second order. The fluoride adsorption kinetics on the two materials is described by the pseudo-first order model.

Table 2. Kinetic parameters for the adsorption of fluoride ions on chitosan gel beads (CB) and cross-linked chitosan gel beads (CCB) using the pseudo-first order and pseudo-second order equations.

Parameters	Pseudo-first order			Pseudo-second order			
	K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g/mg.mn)	q_e (mg/g)	R^2	q_e (exp)(mg/g)
CB	0,069	6,7	0,986	0,01	10,53	0,909	6,18
CCB	0,078	7,6	0,997	0,012	10,1	0,962	7,21

4. CONCLUSION

In this work the chitosan gel beads and cross-linked chitosan gel beads by glutaraldehyde were prepared and characterized by Fourier-transform infrared spectrometry (FTIR) and X-ray diffraction (DRX). Were used to obtain better natural adsorbents to remove fluoride ions from aqueous solutions.

The study of this work revealed that the adsorption efficiency of fluoride ions by chitosan gel beads and cross-linked chitosan gel beads are influenced by the contact time, the pH solution, the adsorbent mass and initial fluoride concentration.

The best adsorption of the fluoride ions was obtained by the cross-linked chitosan gel beads the percent removal of fluorine reached a maximum of 71% after 30 (min) and 59% after 25 (min) for chitosan gel beads as fluoride removal percentage whereas it was 59% for the chitosan beads at a pH of 6,7. Kinetic studies have shown that adsorption follows a pseudo-first order model. The study of the adsorbent systems adsorption showed that they are described by the mathematical model of Langmuir. This study showed that chitosan gel beads is an adsorbent effective for the fluoride adsorption with superiority for cross-linked chitosan gel beads.

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