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SYNTHESIS AND CHARACTERIZATION OF CROSS-LINKED CHITOSAN FOR THE ADSORPTION OF FLUORIDE IONS IN AQUEOUS SOLUTION

O. Goudali*, M. El Azhar, M. Agunaou, A. Soufiane
* Laboratory of Chemistry of Coordination and Analytics, Faculty of Sciences, B.P. 24000, El Jadida, Morocco

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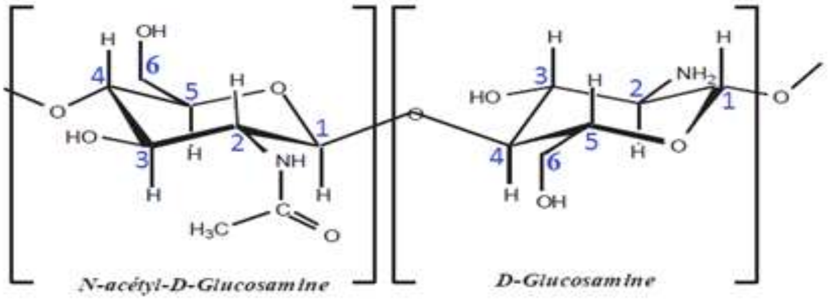
ABSTRACT

The aim of this study is to prepare and characterize chitosan (CS) and cross-linked chitosan (CCS) by glutaraldehyde in order to obtain better natural adsorbents to remove fluoride ions from aqueous solutions. The characterization was carried out by Fourier-transform infrared spectrometry (FTIR) and X-ray diffraction (XRD).These adsorbents were used to remove the fluoride ions in aqueous solution in a batch reactor. Experiments have been carried out to study the influence of certain parameters such as initial fluoride concentration, adsorbent dose, pH solution and contact time on adsorption capacity in order to determine the optimum values leading to better adsorption. The results obtained showed that the adsorption kinetics of the fluoride ions on the two adsorbents is described by the pseudo-second order model and that the adsorption isotherms are described by the Langmuir mathematical model.

INTRODUCTION

Fluoride is a fairly common element that is not naturally found in elemental form because of its high reactivity. Fluoride is the 13th element abundant in the earth's crust [1], and exists in the form of fluorides in various minerals such as fluorine (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($Ca_5(PO_4)_3F$). Thus, fluorides are in soil, plants and groundwater [2]. Fluorine in low doses has beneficial effects on human health such as bone strengthening and the prevention of dental caries [3], but at excessive doses fluoride is very harmful to human health. Several techniques are developed for the removal of these heavy metals such as electroplating, reverse osmosis, lime treatment, ion exchange and especially adsorption which has shown great abatement capacities. This adsorption technique has been used in several fields of application with encouraging results, especially in the case where the adsorbent is of natural origin. Chitin is a natural polymer extracted from the exoskeleton of the arthropods such as shrimps, crabs or the endoskeleton of cephalopods such as squid. Chitin is the second most abundant natural polysaccharide on earth after cellulose [4]. Chitosan is a polysaccharide composed of the random distribution of D-glucosamine linked to β-(1-4) (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit) (Fig.1), it is prepared from chitin by deacetylating its acetoamide groups with a strong alkali solution. Chitosan has many beneficial properties, such as biodegradability [5], biocompatibility [6] and its healing quality [7] chitosan has high adsorption capacity due to the presence of the amino (-NH) and hydroxyl (-OH) at the positions C-2 and C-6 (Fig.1) which serve as coordination sites and exhibit a strong chelation of the metal ions [4,8,9].



(a) (b)

Figure 1: Structure of chitin (a) and chitosan (b)

The main objective of this work is to investigate the influence of experimental variables on the adsorption capacity of fluoride from aqueous synthetic solutions by uncross-linked and cross-linked chitosan and to study kinetics and adsorption isotherms in order to know the reaction mechanism related to the adsorption process.

MATERIALS AND METHODS

Materials

Chitosan was prepared in our laboratory from chitin, itself obtained from shrimp shells from the city of El Jadida. Sodium fluoride (NaF), glutaraldehyde, glacial acetic acid, hydrochloric acid (HCl) and sodium hydroxide (NaOH), were purchased from Sigma-Aldrich. 1000 mg/L fluoride stock solution was prepared by dissolving 2,221 g of anhydrous fluoride in distilled water and up to 1000 mL in a polyethylene volumetric flask. The working solutions were prepared by appropriate dilution of the stock solution.

Preparation of chitosan from chitin

Chitin was prepared from the shrimp shell in two steps: demineralization (DM) and deproteinization (DP). The demineralization was carried out using a hydrochloric acid solution at 25 °C. Deproteinization (DP) was performed using aqueous sodium hydroxide to remove proteins, dyes, lipids and pigments. Chitosan was prepared by deacetylation of chitin (DA): The chitin was put in a NaOH solution (50%) in a ratio of 1g/20 mL at 100 °C for 6 hours to remove the maximum of the acetyl groups from the chitin. The product obtained is chitosan, it was filtered and washed several times with distilled water at a pH of 7 and dried in an oven at 50 °C.

Preparation of cross-linked chitosan by glutaraldehyde

The cross-linked chitosan was prepared by dissolving 1 g of chitosan in 100 mL of a 1% (v/v) acetic acid solution and then adding the 0.025 M glutaraldehyde to the chitosan solution. The mixture is then stirred for 24 hours. Finally the cross-linked chitosan obtained is washed with distilled water and dried in an oven at 50 °C.

Adsorption tests

The adsorption tests were carried out in a closed reactor by stirring the synthetic solutions in the presence of the adsorbent (chitosan or cross-linked chitosane). The effects of the main parameters influencing on the adsorption capacity were studied such as the adsorbent dose, the pH solution, the contact time, the initial concentration of the fluoride ions and the temperature. The adsorption isotherms have been studied for accurate information on the adsorption efficiency. The concentration of the fluoride ions was determined using a specific electrode of ISE 67B type according to standard NF T 90-004.

RESULTS AND DISCUSSION

Characterization of chitosan and cross-linked chitosan

Analysis by FTIR

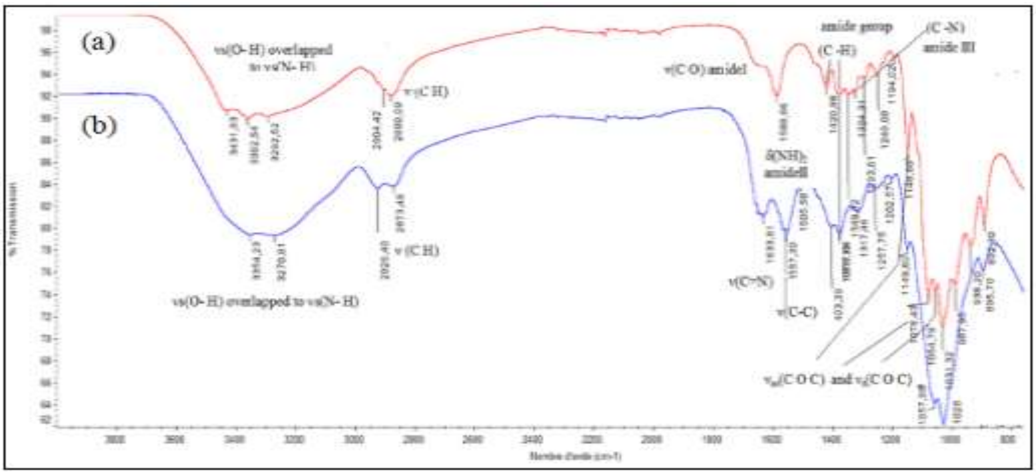


Figure 2: FT-IR spectra of chitosan (a) cross-linked chitosan with glutaraldehyde (b)

Spectrum (a) shows that the chitosan had characteristic bands at 3362 cm^{-1} and 3292 cm^{-1} which are attributed to the elongation vibration of the –NH$_2$ function and –OH stretching vibration, related to extra-molecular hydrogen bonding of molecules. The distinctive absorption bands of chitosan at 2904 cm^{-1} and 2880 cm^{-1} are attributed to the deformation and stretching of (CH), band at 1659 cm^{-1} is assigned to the stretch of (C=O) (amide I) (group (-NHCOCH$_3$)), band at 1588 cm^{-1} is characteristic to (group (NH-C=O)) (amide II) and (group (-NHCOCH$_3$)) according to other studies [10]. These peaks indicated the partially deacetylated form of chitin. The bands at 1420 cm^{-1} and 1380 cm^{-1} are assigned to deformation (CH), at 1324 cm^{-1} to amide III. The bands at 1150 cm^{-1}, 1084cm^{-1} and 1031 cm^{-1} are attributed to the stretch (νas(C O C) and νs(C O C) (asymmetric stretching of the C–O–C bridge), (skeletal vibration involving the C–O stretching), they are characteristics of the glucosamine residues in chitosan [11,12].

Spectrum (b) results of a glutaraldehyde cross-linked chitosan shows two typical absorption peaks; the peak centered at 1633 cm^{-1} is attributed to the imine bond (C=N) and the peak at 1557 cm^{-1} is associated with an ethylenic bond (C-C) [13]. Fig.2 (b) shows that the cross-linking caused an increase in the intensity of the stretching vibration frequency CH at 2926 cm^{-1}. These changes confirm that cross-linking of the chitosan has occurred. The absence of peak at around 1720 cm^{-1} confirm that there is no unreacted aldehyde group and that glutaraldehyde has completely reacted with chitosan [14]. The comparison of the FT-IR absorption bands of chitosan and cross-linked chitosan is given in table 1.

Table 1. Comparison of the FT-IR absorption bands of chitosan and cross-linked chitosan

Bands	Chitosan	Bands	Cross-linked chitosan
νs(O- H) overlapped to νs(N- H)	3362 - 3292 cm^{-1}	νs(O- H) - νs(N- H)	3354 - 3270 cm^{-1}
ν(C H)	2904 cm^{-1}	ν(C H)	2929 cm^{-1}
ν(C H)	2880 cm^{-1}	ν(C H)	2873 cm^{-1}
ν(C O) amide I	1659 cm^{-1}	ν(C=N) imine	1633 cm^{-1}
δ(NH)$_2$ amide II	1588 cm^{-1}	ν(C-C)	1557 cm^{-1}
(C -H) amide group	1420 - 1380 cm^{-1}	(C -H) amide group	1406 - 1380 cm^{-1}
(C-N) amide III	1324 cm^{-1}	(C-N) amide III	1317 cm^{-1}
νas(C O C) and νs(C O C)	1149 - 1079 -1031	νas(C O C) and νs(C O C)	1156 - 1071 - 1028

Analysis by XRD

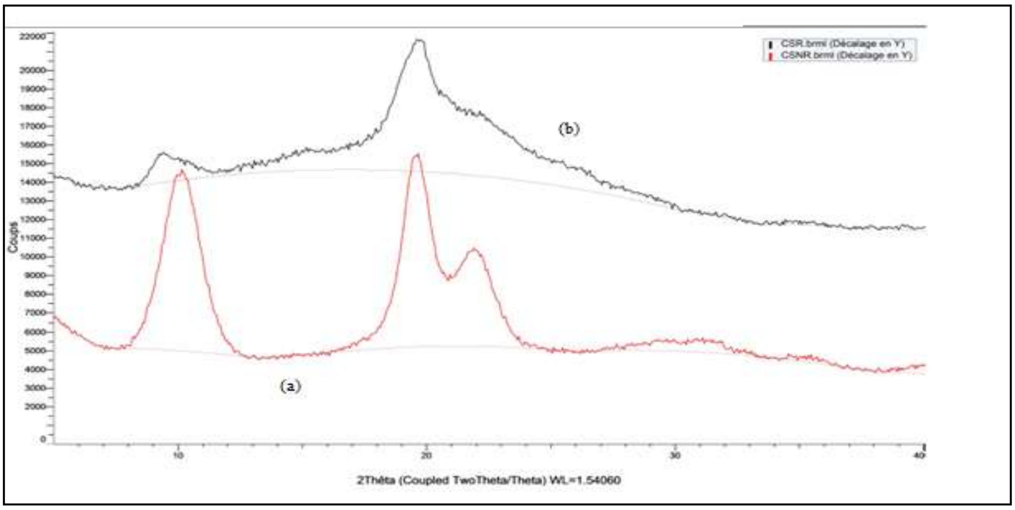


Figure 3: XRD pattern of chitosane (a), cross-linked chitosan with glutaraldehyde (b)

The X-ray diffraction pattern of chitosan (Fig.3 (a)) exhibits characteristic peaks at 2θ at 10.14, 19.60 and 21.88 which correspond to a polymorph of chitosan, which is mentioned in the literature as the polymorphic hydrate (tendon) [15-17]. Zhang and al [18] Samuels et al [19] reported that the reflection falls at 10 was assigned to crystal forms I and the strongest reflection appears to 20 which corresponds to crystal forms II indicating the high degree of crystallinity of chitosan.

The X-ray diffraction pattern of chitosan cross-linked by glutaraldehyde (Fig.3 (b)) 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 turns to be more disordered after the cross-linking reaction with glutaraldehyde [20]. This implies an increase in the amorphous phase, thus increasing the adsorption capacity. These modifications show that the cross-linking of the chitosan has been successful imply.

Effect of contact time

The tests were carried out by stirring 400 mg of the adsorbent for 30 minutes in solutions whose concentration 10 mg/L. The tests were carried out at pH = 6.70 with stirring at 600 rpm at room temperature. The residual concentrations were determined and then exploited to monitor the evolution of the adsorbed quantity per unit mass as a function of time (Fig. 4).

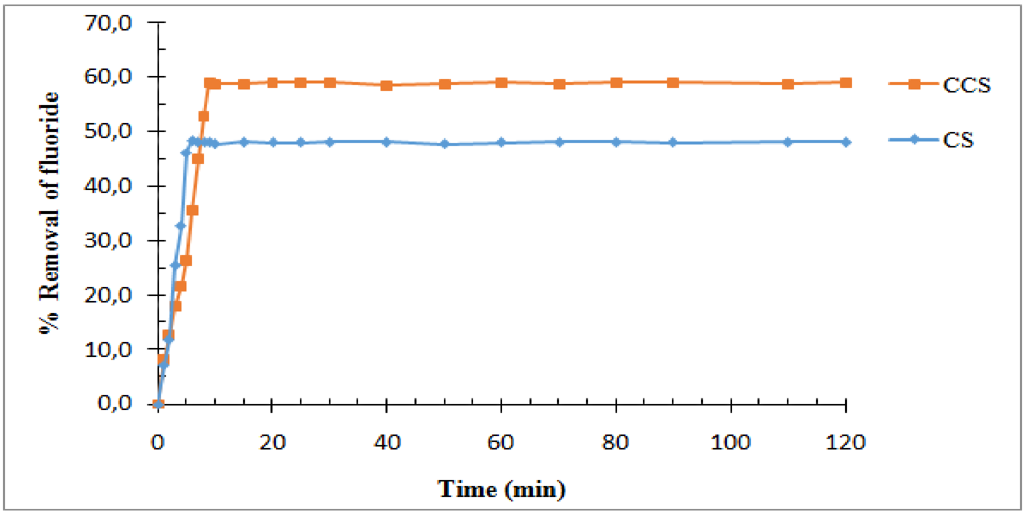


Figure 4: Effect of contact time on the adsorption of fluoride ions by chitosane(CS) and cross-linked chitosane(CCS) (C_0 = 10 mg/L, m = 400 mg, pH = 6.70, Stirring = 600 rpm, V= 100 mL and T = 26 ± 1 °C).

The percentage of adsorption of fluoride ions increases when the contact time increases the equilibrium has been reached after 25 minutes for the chitosan and 30 min for the cross-linked chitosan with percentage removal of fluoride ions from 50% for the chitosan and 60% for the cross-linked chitosan. The effect of the contact time on the removal of fluoride ions is illustrated in figure 4.

Effect of concentration

The tests were carried out by stirring 400 mg of the adsorbent for 30 minutes in solutions whose concentration varies from 2 to 14 mg/L. The tests were carried out at pH = 6.70 with stirring at 600 rpm at room temperature. The residual concentrations were determined and then exploited to monitor the evolution of the adsorbed quantity per unit mass as a function of the initial concentration (Fig.5).

The results show that the adsorption capacity increases with the increase in the initial concentration of the fluoride ions. Beyond a concentration of 10 mg/L, a plateau is observed due to the saturation of the active sites of the two adsorbents.

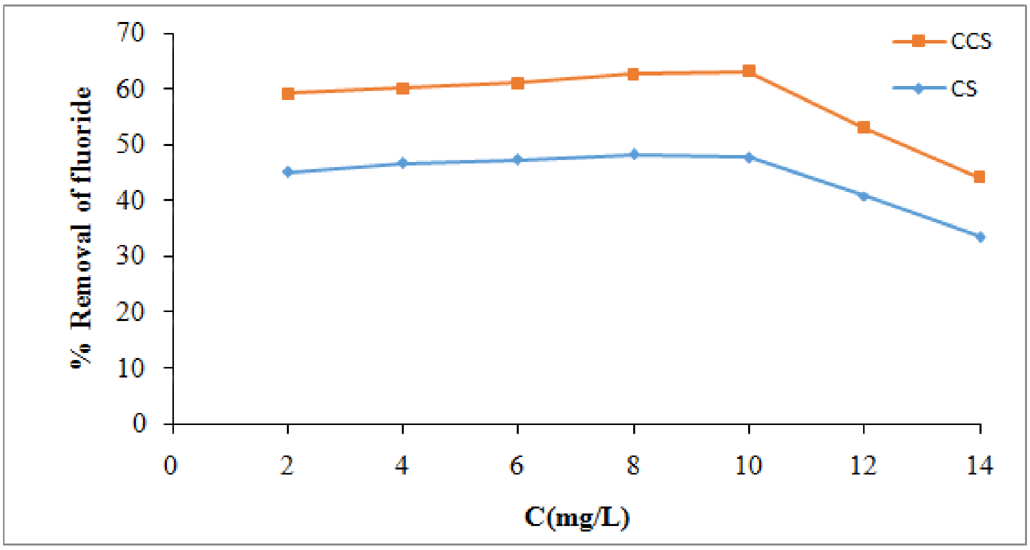


Figure 5: Effect of fluoride ion concentration on chitosan and cross-linked chitosan (pH = 6.70, m = 400 mg, V = 100 mL, stirring = 600 rpm, T = 26 ± 1 ° C).

Effect of pH

pH is an important factor in any adsorption study because it can influence both the adsorbent and adsorbent structure as well as the adsorption mechanism. In this article, we studied the adsorption efficiency of fluoride ions 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.

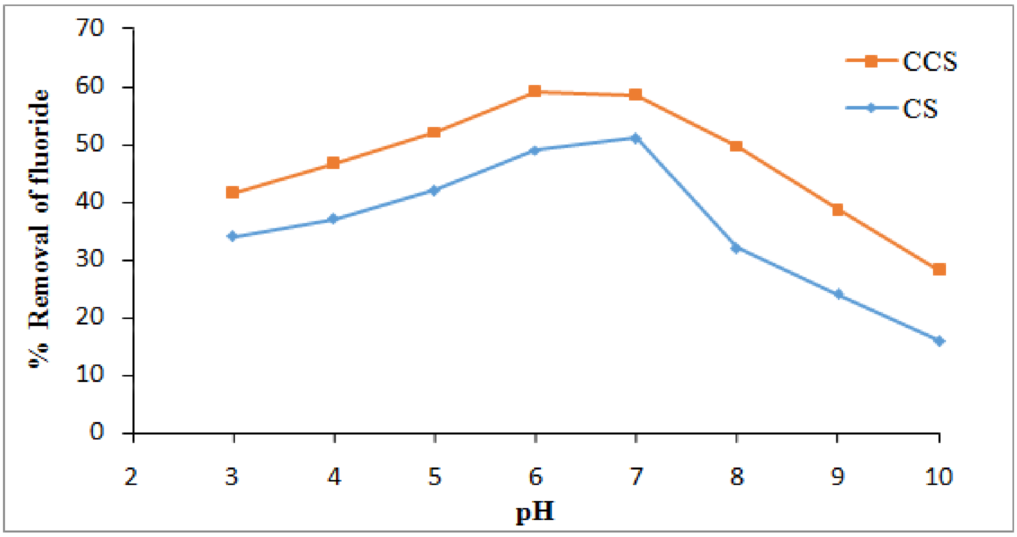


Figure 6: Elimination of fluoride ions on chitosan and cross-linked chitosan as a function of pH (m = 400 mg, V = 100 mL, C0 = 10 mg / L, stirring = 600 rpm, T = 26 ± 1 ° C)

Figure 6 shows that below and above pH = 6,7 there is a decrease in the adsorption for the two adsorbents. This decrease can be explained in an alkaline pH range by competition between fluoride and an excess of hydroxyl OH^-. While in the acid pH range, can be attributed to the formation of HF hydrofluoric acid [21].

Effect of mass of adsorbent

The effect of the adsorbent dose was carried out by placing 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g 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 600 rpm at 26 °C.

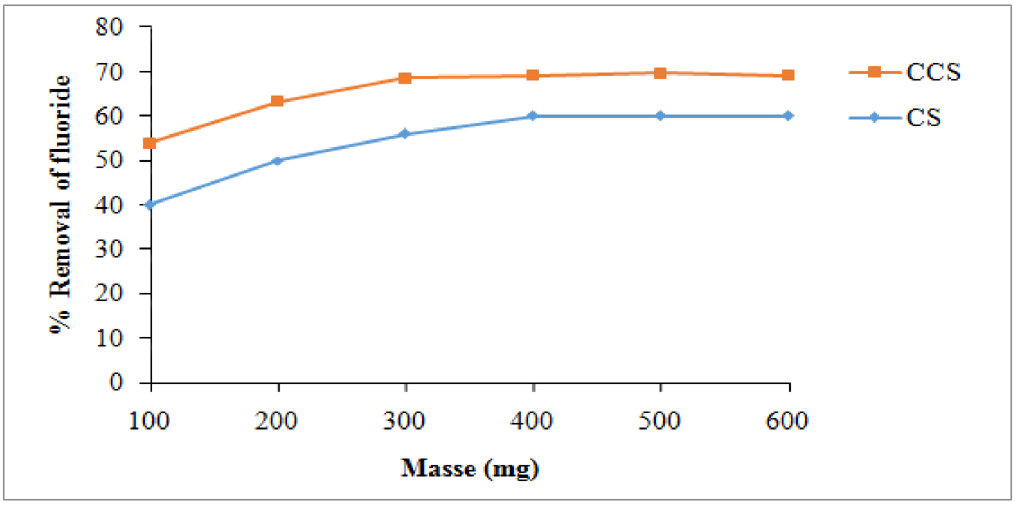


Figure 7: Elimination of fluoride ions by chitosan and cross-linked chitosan as a function of adsorbent mass (pH = 6,70, V = 100 mL, C_0 = 10 mg/L, stirring = 600 rpm, T = 26 ± 1 °C)

Fig.7 shows that the removal efficiency of fluoride increases with increasing adsorbent dosage, This is due to an increase in adsorption sites as the dosage increases. However, for adsorbent dosage more than 0.4 g, no significant increase in fluoride removal (68 %) for cross-linked chitosan and (59 %) for chitosan were observed. The optimum adsorbent dosage was 0.4 g for both adsorbent.

Kinetic study and adsorption isotherms

Adsorption isotherms

The Langmuir models (equation (1)) and Freundlich (equation (2)) were studied. The Langmuir model assumes that the adsorption takes place on a monolayer without interaction between the adsorbed molecules.

Langmuir model : $$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{KQ_mC_e} \qquad \text{(Eq. 1)}$$

Freundlich model : $$\log Q_e = \log k_f + \frac{1}{n}\log C_e \qquad \text{(Eq. 2)}$$

With: $$Q_e = \frac{(C_0 - C_e)\,V}{m} \qquad \text{(Eq. 3)}$$

Q_e: Equilibrium adsorption capacity (mg/g).
V: Solution volume (mL).
M: Mass of the adsorbent (g).
C_0: Initial concentration of adsorbate (mg/L).
C_e: Residual concentration of the equilibrium solution (mg/L).
Q_m: Maximum adsorption capacity (mg/g).
K: Adsorption equilibrium constant for the solute/adsorbent couple (L/mg).
K_f et n: Constants characteristic of the efficiency of an adsorbent with respect to a given solute.

The adsorption isotherms were studied by stirring a mass of the adsorbent (400 mg) in solutions of different concentrations of fluoride ions ranging from 2 to 14 mg/L. The adsorbent and the adsorbate were contacted under stirring at 600 rpm for 10 minutes. After the determination of the residual concentrations, we have followed the evolution of $1/Q_e$ as a function of $1/C_e$ according to the Langmuir model and, the evolution of log Q_e as a function of log C_e according to the Freundlich model. The results obtained are illustrated in figures 8 and 9.

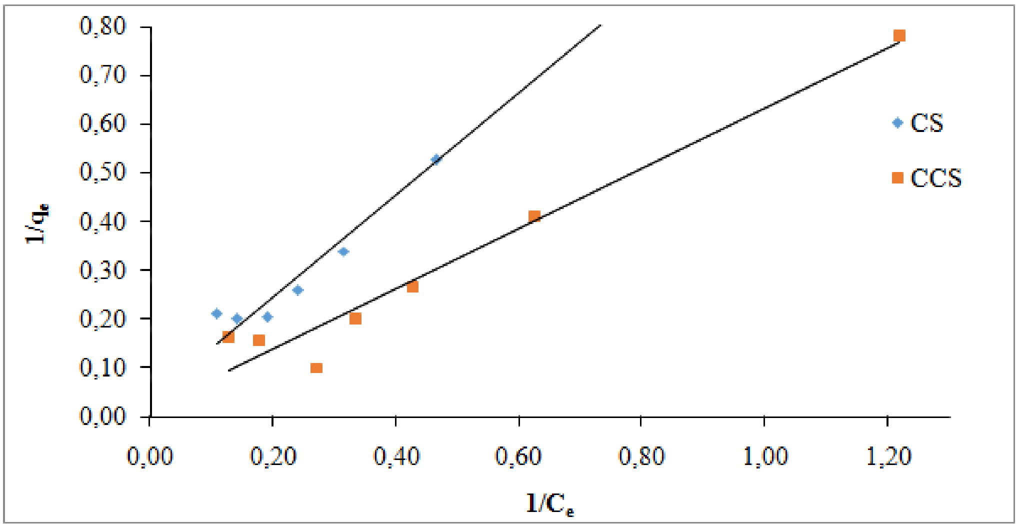


Figure 8: Linearization of the Langmuir equation for the adsorbent/adsorbate systems studied (pH = 6,70; V = 100 mL; m = 400 mg; stirring speed = 600 rpm; T = 26 ± 1 °C).

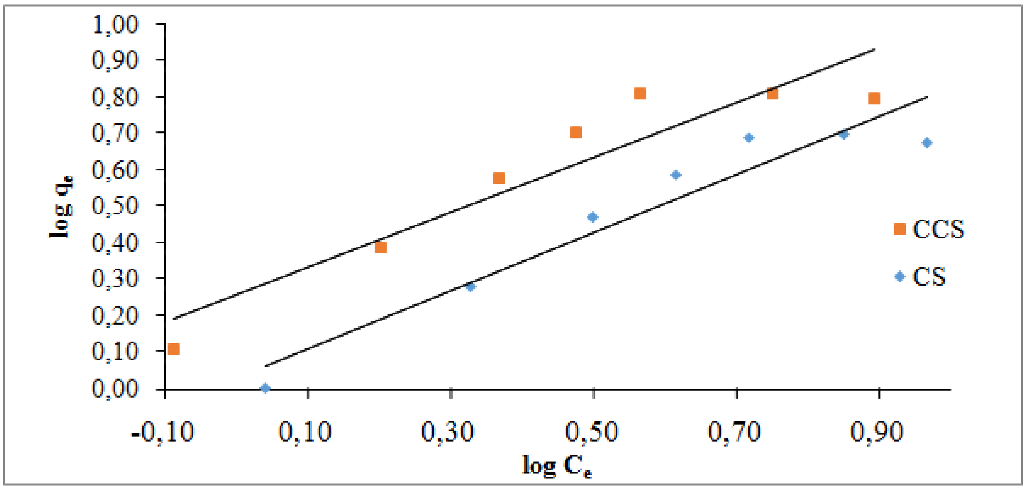


Figure 9: Linearization of the Freundlich equation for the adsorbent/adsorbate systems studied (pH = 6,70; V = 100 mL; m = 400 mg; stirring speed = 600 rpm; T = 26 ± 1 °C).

The linear representations of the experimental values of this adsorption process allowed us to determine the equilibrium parameters and the values of the Langmuir and Freundlich constants calculated by linear regression (table 2).

Table 2. Parameters of Freundlich and Langmuir isotherm.

	Freundlich isotherm			Langmuir isotherm		
Paramètres	n	K_f (L.g^{-1})	R^2	Q_m(mg/g)	K (L.mg^{-1})	R^2
CS	1.264	1.071	0.918	26.32	0.036	0.986
CCS	1.328	1.799	0.880	66.67	0.024	0.960

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

Study of adsorption kinetics

To study the adsorption kinetics of fluoride ions on chitosan and cross-linked chitosan, the experiments were carried out under the same operating conditions. A solution of fluoride (100 mL) containing 400 mg of the supports is stirred at 600 rpm. The results obtained are shown in figures 10 and 11. The first-order adsorption rate constant is deduced from the Lagergreen model [22]. The law of speed is written according to the following equation:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2{,}303} t \qquad \text{(Eq. 4)}$$

The pseudo-second order model makes it possible to deduce the adsorption kinetics. It takes into account the rapid fixing of the solutes at the most reactive sites according to the following equation [23]:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \qquad \text{(Eq. 5)}$$

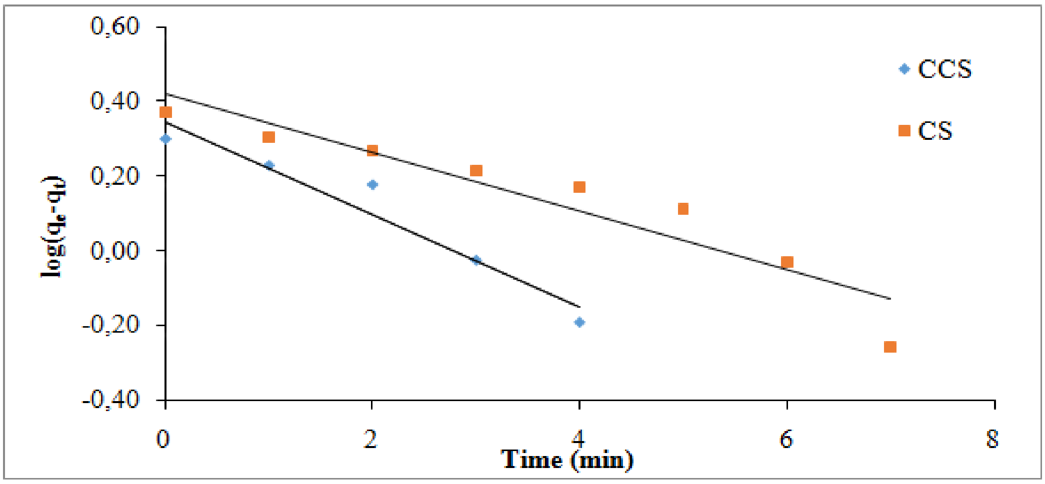


Figure 10: Pseudo-first order plot for the adsorption of fluoride ions onto chitosan (CS) and cross-linked chitosan (CCS).

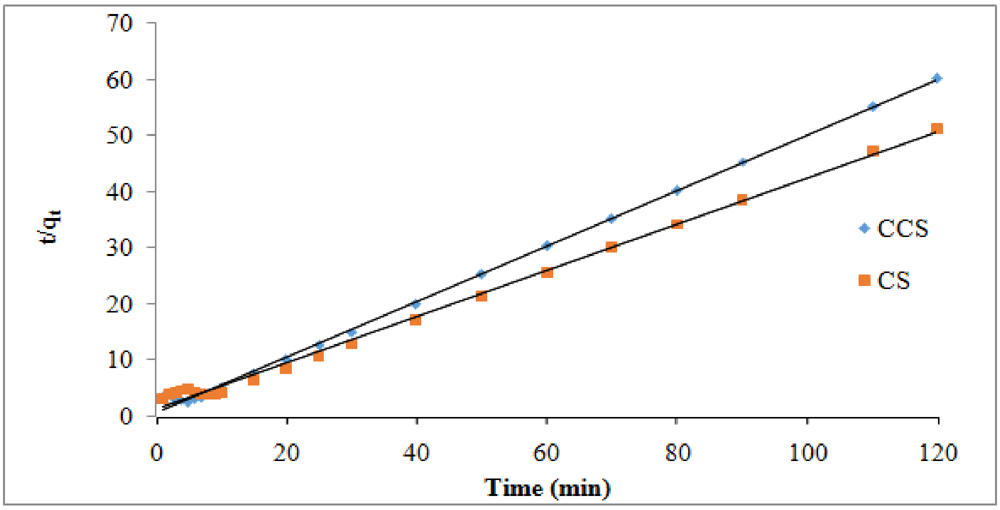


Figure 11: Pseudo-second order plot for the adsorption of fluoride ions onto chitosan (CS) and cross-linked chitosan (CCS)

The results obtained by applying the two kinetic models of the pseudo first order and pseudo second order are shown in table 3. These results show that the equilibrium adsorbed at the experimental level is closer to that calculated using the second order kinetic model but is different to that calculated using the first order kinetic model. The kinetics of adsorption of fluoride ions on the two materials is described by the pseudo-second order model.

Table 3. Kinetic parameters for the adsorption of fluoride ions onto chitosan and cross-linked chitosan on the pseudo-first and pseudo-second order equation

	Pseudo-first order			Pseudo-second order			
Paramètres	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)
CS	0.285	2.21	0.937	0.341	2.03	0.998	2.00
CCS	0.180	2.61	0.886	0.118	2.45	0.995	2.34

CONCLUSION

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

The adsorption efficiency of fluoride ions by chitosan and cross-linked chitosan depends on the contact time, pH solution, mass of the adsorbent and the initial concentration of the fluoride ions. The best adsorption of the fluoride ions was obtained by the cross-linked chitosan with a percentage of shrinkage fluoride ions of 60% whereas it was 50% for the chitosan at a pH of 6,7. Kinetic studies have shown that adsorption follows a pseudo-second order kinetic model. The study of the adsorbent systems adsorption showed that they are described by the mathematical model of Langmuir. This study showed that chitosan is an adsorbent effective for the adsorption of fluoride ions with superiority for chitosan cross-linked with glutaraldehyde.

REFERENCES

1. Z. Mandinic, M. Curcic, B. Antonijevic, M. Carevic, J. Mandic, D. Djukic-Cosic and C.P. Lekic, “Fluoride in drinking water and dental fluorosis”, Sci. Total Environ, vol.408, pp. 3507–3512, 2010.
2. N. Chen, Z. Zhang, C. Feng, M. Li, D. Zhu, R. Chen and N. Sugiura, “An excellent fluoride sorption behavior of ceramic adsorbent”, J. Hazard. Mater, vol.183, pp. 460–465, 2010.
3. A. Rafique, M.A. Awan, A. Wasti, I.A. Qazi and M. Arshad, “Removal of fluoride from drinking water using modified immobilized activated alumina”, J. Chem, pp. 1–7, 2013.
4. W. Pasanphan, T. Rattanawongwiboon, S. Choofong, O. Güven and K.K. Katti, “Irradiated chitosan nanoparticle as a water-based anti oxidant and reducing agent for a green synthesis of gold nanoplatforms”, Radiation physics and chemistry, vol. 106, pp. 306–370, 2015.
5. Y. Shigemasa, K. Saito, H. Sashiwa and H. Saimoto, “Enzymatic degradation of chitins and partially deacetylated chitins, ” J. Biol. Macromol, vol. 16, pp. 43–49, 1994.
6. M.V. Risbud and R.R. Bhonde, “Polyacrylamide chitosan hydrogels: In vitro biocompatibility and sustained antibiotic release studies drug delivery,” vol. 7, pp. 69–75, 2000.
7. M.N.V. Ravi Kumar, R.A.A. Muzzarelli, C. Muzzarelli, H. Sashiwa and A.J. Domb, “Chitosan Chemistry and Pharmaceutical Perspectives,” Chem. Rev, vol. 104, pp. 6017–6084,2004.
8. C.K.S. Pillai, W. Paul, C.P. Sharma, “Chitin and chitosan polymers: Chemistry, solubility and fiber formation,” Prog. Polym. Sci, vol. 34, pp. 641–678, 2009.
9. E. Guibal, “Interactions of metal ions with chitosan-based sorbents,” Separation and Purification Technology, vol. 38, pp. 43–74, 2004.
10. S. Vaezifar, M.A. Golozar, M. Morshed, S. Razavi, S. Karbasi and M. Kamali, “Effects of some parameters on particle size distribution of chitosan nanoparticles prepared by ionic gelation method,” J. Clust. Sci, Springer, 2013.

11. P. Bernabe, C. Peniche and W.A. Monal, "Swelling behavior of chitosan/pectin polyelectrolyte complex membranes. Effect of thermal cross-linking," Polymer Bulletin, vol. 55, pp. 367–375, 2005.
12. C. Zhang, Q. Ping, H. Zhang and J. Shen, "Synthesis and characterization of water soluble O-succinyl chitosan," European Polymer Journal, vol. 39, pp.1629–1634, 2003.
13. W. Wei, L.Y. Wang, L. Yuan, Q. Wei, X.D. Yang, Z.G. Su, and G. Hui, "Preparation and application of novel microspheres possessing autofluorescent properties," Adv. Funct. Mater, vol. 17, pp. 3153–3158, 2007.
14. A.C. Oyrton, J. Monteiro and C. Airoldi, "Some studies of crosslinking chitosan–glutaraldehyde interaction in a homogeneous system," International Journal of Biological Macromolecules, vol, 26, pp. 119–128, 1999.
15. W. Pasanphan, G.R. Buettner and S. Chirachanchai, "Chitosan conjugated with deoxycholic acid and gallic acid: A novel biopolymer-based additive antioxidant for polyethylene," Appl. polym. Sci, vol. 109, pp. 38-46, 2008.
16. E. Belamine, A. Domard and M. M. G. Guille, "Study of the solid-state hydrolysis of chitosan in presence of HCl water-soluble O-succinyl-chitosan," European Polymer Journal, vol. 39, pp. 1629–1634, 2003.
17. Thien DT, An NT and Hoa NT**,** "Preparation of fully deacetylated chitosan for adsorption of Hg(II) Ion from aqueous solution," Chem. Sci. J, vol. 6, 2015.
18. W. Zhang, J. Zhang, Q. Jiang, and W. Xia, "Physicochemical and structural characteristics of chitosan nanopowders prepared by ultrafine milling Carbohydrate Polymer," vol. 87, pp. 309–313, 2012.
19. R. J. Samuels, "Solid state characterization of the structure of chitosan films," J. Polym. Sci: Polym. Phys. Ed, vol.19, pp. 1081-1105, 1981.
20. H. Hu, J. H. Xin, H. Hu, A. Chan and L. He, Carbohydrate Polymer, vol. 91, pp. 305–313, 2013.
21. S. Jagtap, D. Thakre, S. Wanjari, S. Kamble, N. Labhsetwar and S. Rayalu, "New modified chitosan-based adsorbent for defluoridation of water," Journal of Colloid and Interface Science, vol. 332, pp. 280–290, 2009.
22. S. Langeren, Handlinger, vol. *24*, pp. 1-39, 1898.
23. Y.S. Ho and G. McKay, Process Biochemistry, vol. 34, pp. 451-465, 1999.