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FLUORIDE ADSORPTION CAPACITY OF COMPOSITES BASED ON CHITOSAN-ZEOLITE-ALGAE

EVALUACIÓN DE LA CAPACIDAD DE ADSORCIÓN DE FLUORURO EN COMPOSITOS A BASE DE QUITOSANO-ZEOLITA-ALGA MARINA

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Abstract

The objective of this study was to evaluate the adsorption capacity of fluoride in batch system at different pH on synthesized composites based in chitosan and low cost materials such as zeolite and seaweed. Both composites were compared: chitosan-zeolite (ch-z), chitosan-algae (ch-a). Adsorption experiments were individually conducted with these materials (chitosan, zeolite, and seaweed). The data of adsorption isotherms were a better fit to the Freundlich model. The adsorption capacity of these materials and composite is affected by the pH of the solution. At pH 5 the ch-z composite had 1.2 time higher fluoride adsorption than composite ch-a, which showed a higher capacity for fluoride removal to a pH 7. The characterization of these materials was performed with the infrared spectroscopy techniques with Transported Fourier (FTIR), thermal gravimetric analysis (TGA) and point of zero charge (PZC) to elucidate the possible fluoride adsorption mechanism. Finally according to our results both composites can be considered as efficient adsorbents for fluoride removal from water.

Keywords: fluoride, composites, seaweed, adsorption, chitosan.

Resumen

El objetivo de este trabajo fue evaluar la capacidad de adsorción de fluoruros en lotes a diferente pH sobre compositos sintetizados a base quitosano y materiales de bajo costo como la zeolita y las algas marinas, Se compararon ambos compositos: quitosano-zeolita (q-z), quitosano-alga marina (q-a). También se realizaron experimentos de adsorción con los materiales de manera individual (quitosano, zeolita, alga marina). Los datos de las isotermas de adsorción tuvieron un mejor ajuste al modelo de Freundlich. La capacidad de adsorción de todos los materiales y compositos se ve afectada por el pH de la solución. Se observó que el pH óptimo para el proceso de adsorción de fluoruro en el caso del composito q-z es a un pH de 5, ya que remueve 1.2 veces más fluoruro que el composito q-a, el cual mostro una mayor capacidad de remoción a un pH 7. La caracterización de estos materiales se realizó con las técnicas de espectroscopia Infrarroja con Transportada de Fourier (FTIR), análisis termogravimétrico (TGA) y punto de carga cero (PCC) con el fin de elucidar el posible mecanismo de adsorción de fluoruro. Finalmente de acuerdo con nuestros resultados ambos compositos pueden ser considerados como eficientes adsorbentes para la eliminación de fluoruro del agua.

Palabras clave: fluoruro, compositos, alga marina, adsorción, quitosano.

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1   Introduction

Fluoride is considered beneficial in drinking water at levels about 0.7 mg/L, but hazardous if it exceeds 1.5 mg/L which is the maximum permissible limit proposed by the World Health Organization (WHO, 1984). Some health damage caused by water intake with a high fluoride concentrations are: dental cavities, dental and skeletal fluorosis (Mohapatra *et al*., 2009). The methods used to remove excessive fluoride from drinking water are ion exchange resins, coagulation, electrochemical methods, unfortunately the high cost of these technologies make them unviable in developing countries (Miretzky and Cirelli, 2011).Many technologies have been developed to remove fluoride from water, that are based on the adsorption process using different adsorbents materials such as activated alumina, double layered hydroxides, carbon nanotubes, bone char, clays, among others (Leyva Ramos, *et al*, 2001; Medellin Castillo *et al*., 2007; Viswanathan and Meenakshi, 2010). In recent years, there has been special attention to adsorbents containing natural polymers such as chitosan, which is the second most abundant natural polymer on earth. Chitosan a cationic copolymer consisting of 2-glucosamine and N-acetyl-glucosamine-2 (Fig. 1), which is derived from chitin by demineralization processes, deproteinization and deacetylation (Navarro *et al*., 2010). This polymer is characterized by its high content of amino groups. Which are responsible of the interaction among metal ions by chelation mechanisms (Guibal *et al*., 1999; Kawamura *et al*., 1993). Chitosan can be found with the shape of flakes and powder, this has been a drawback for application in studies of columns, as it presents low mechanical strength. Thus, it has been looking for alternatives to overcome this disadvantage. Chitosan based microspheres have been prepared by using different type of support material that can give a greater mechanical strength. For example clay minerals, hydroxyapatite, and double layered hydroxide (Boddu *et al*., 2008; Dalida *et al*., 2011; Sairam Sundaram *et al*., 2008; Viswanathan and Meenakshi, 2010). Furthermore, chitosan has a pk $\approx$ 6.5, therefore, it is soluble in acid medium. Chitosan shows a tendency to form a gel in acetic acid and this gel may be precipitated in an alkaline solution to obtain microspheres (Salazar Leyva, 2014). The natural zeolites are microporous crystalline aluminosilicates, with structures formed by tetrahedrons of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ that are linked through oxygen atoms, which characteristics

provide high mechanical resistance. In addition to the property of having cation exchange because the surface is negatively charged (Leyva Ramos *et al*., 2001). There are many techniques that exist for the modification of zeolites and that make them more selective for anions such as fluoride. For example, it the surface of the zeolite can be modified by exchanging the Na^+ bound with Al^{3+} or La^{3+} ions, and these latter has an affinity with fluoride anions (Onyango *et al*., 2004). Furthermore, seaweed has also been used to study the removal of fluoride. Some species of the genus Ulva are considered as natural sources of alginate. Therefore, they are presented as functional carboxylic acid groups (Ghimire *et al*., 2007), and various amino groups, which are known to have affinity in the removal of fluoride (Paudyal *et al*., 2013). Seaweed is available in seas and oceans, especially in nutrient-rich waters. Sometimes the seaweed can begin to form massive algal blooms (Piñón Gimate *et al*., 2008), which cause an excessive seaweed which have been observed commonly on the beaches of the coastal areas causing an unpleasant appearance. This excessive of seaweed is consider as waste material. Seaweed has the tendency to disintegrate, causing operational problems, principally in adsorption columns; hence, the seaweed can be immobilized in various polymeric materials in order to increase stability and mechanical strength. Many studies have used some natural and synthetic polymers as polyvinyl alcohol and polyurethane (Chu and Hashim, 2007; Zhang and Banks, 2006). Furthermore, literature has reported studies on the removal of fluoride with different synthesized composites based in chitosan and different materials such as alumina composites, hydrotalcite (Viswanathan and Meenakshi, 2010), hydroxyapatite (Sairam Sundaram *et al*., 2008), mixed oxides (Muthu Prabhu and Meenakshi, 2014), bentonite (Zhang *et al*., 2013). The objective of this study is to synthesize composites based on a natural polymer such as chitosan and low cost materials such as zeolites and waste materials like seaweed and to evaluate their fluoride adsorption capacity.

2   Experimental

2.1   *Materials*

Zeolite-clinoptilolite samples $(Ca_3(Si_{30}Al_6)O_{72} \cdot 20H_2O)$ from Sonora Mexico and, seaweed *Ulva lactuca* samples from lagoon Santa Maria-La
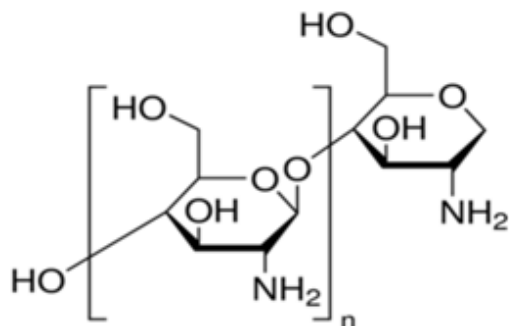
Fig. 1. Molecular structure of chitosan (Sigma-Aldrich).

Reforma, Sinaloa Mexico were used in the adsorption experiments.

All chemicals used were of analytical grade: chitosan (75-85% deacetylated) low molecular weight (Sigma-Aldrich), NaF (Fermont), acetic acid (J.T. Baker), 0.1 N NaOH (Hycel), 0.1 N HCl (Hycel), and NaCl (Caledon).

A fluoride stock solution of 100 mg L^{-1} was prepared by dissolving 221 mg of sodium fluoride in 1000 mL of deionized water. From the previous stock, solutions at different concentration in the range of 10 -100 mg L^{-1} were prepared for the adsorption experiments.

2.2 Seaweeds pretreatment

The seaweeds were washed with deionized water to remove impurities and were lyophilized at temperature of -36 °C. Then, they were ground to obtain a uniform particle size less than 100 microns. Subsequently, they were treated according to the methodology from Venkata Mohan, *et al.*, (2007) in a solution 0.1 N HCl for 8 hours. Finally, the seaweed was washed with deionized water and dried at 60 °C for 24 hours.

2.3 Synthesis of chitosan-zeolite and chitosan-algae composites

Two types of composites were synthesized with different proportions chitosan-zeolite (ch-z) and chitosan-algae (ch-a). For the preparation of ch-z and ch-a composites, 3.0 g of chitosan were dissolved in 50 mL of acetic acid 5% (v/v) and maintained under constant stirring, then 2.7 g of zeolite of the type clinoptilolite-Ca were added to 20 mL of deionized water, afterward it was incorporated into the chitosan

solution and maintained under stirring for 4 hours at 200 rpm. The formation of composites is obtained by supplying the chitosan-zeolite solution through a drip system in the solution of 25% NaOH, then washed with deionized water and, the pH was adjusted to neutral pH and dried at room temperature for 48 hours (Ennajih *et al.*, 2012; Fajardo *et al.*, 2005). The same methodology was followed to prepare ch-a composite, where the zeolite was replaced by pretreated seaweed with 0.1 N HCl.

2.4 Adsorption experiment

Adsorption experiments in batch were carried out to compare the fluoride adsorption capacity of the different materials (chitosan, zeolite, seaweeds, ch-z and ch-a composites) at different pH (5 and 7). Adsorption experiments were carried out as follows: 0.1 g of each material was added into polyethylene tubes that contained 50 ml of fluoride solution at different concentrations (10, 20, 40, 60, 80 and 100 mg L^{-1}). Subsequently, the samples were placed in an orbital incubator at 25 °C y 75 rpp, until equilibrium was reached. The pH was adjusted by adding 0.1N NaOH or HCl. Finally, the fluoride was determined by an ion selective electrode (SM 4500-F) and the amount of fluoride adsorbed was calculated using the following equation:

$$q_e = \frac{C(C_0 - C_e)}{w} \tag{1}$$

were: q_e is the adsorption capacity (mg g^{-1}) at equilibrium, C_0 and C_e are the initial and equilibrium fluoride concentrations (mg L^{-1}) respectively, V is the volume (L) of solution and w is the mass (g) of adsorbent.

2.5 Materials characterization

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was carried out to determine the percentage of chitosan present in the ch-z and ch-a composites with a Thermo Cahn Versa Therm at a temperature range of 30-800 °C with a temperature ramp of 10 °C/minute in air.

FT-IR analysis

FT-IR analysis were performed to identify the functional groups, which may be involved in the fluoride adsorption and thus to determine the

possible adsorption mechanisms with a Nicolet 67000 spectrophotometer (Thermo Scientific), using the ATR technique (Attenuated Total Reflection).

Point of zero charge

The point of zero charge of materials was performed by the method of Slurry pH: 0.1 g of sample was contacted with 5 mL of 0.1 M NaCl previously purged with nitrogen during 10 minutes to eliminate carbon dioxide from the solution. Subsequently, the solution was constantly stirred for 24 hours, finally the pH of each sample was recorded, being the point of zero charge (Davila *et al*, 2009).

3   Results and discussion

3.1   Characterization of the different materials and composites

Thermogravimetric Analysis (TGA)

The result of thermogravimetric analysis of 5 materials is shown in Fig. 2. The analysis of the derivative of the TGA in general for all materials showed a weight loss between 50 and 100°C corresponding water loss. In the case of chitosan, ch-z and ch-a may be seen a second range of temperatures between 200 and 400°C with a weight loss of 60% which is attributed to degradation of chitosan (Ge and Wang, 2014). As for the decomposition of algae the degradation of carbohydrates (loss 13% wt) occurred at temperatures between 180-270°C, while in a range of 270-390°C the cellulose is volatilized (Kebelmann *et al*., 2013). Finally the percentage of chitosan present in ch-z and ch-a was 43% and 20%, respectively.
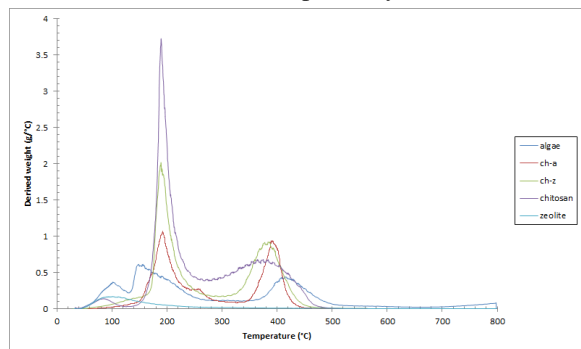

Fig. 2. Derivative thermogravimetric analysis of different materials.

Infrared Spectroscopy Fourier Transform analysis (FT-IR)

The FT-IR spectra resulting from analyzing the various materials before and after adsorption of fluoride is shown in Fig. 3 and Fig. 4. The spectra of chitosan (see Fig. 3b) showed a bond at 3368 cm^{-1} which is attributed to -NH$_2$ groups. This is because the principal groups in the chitosan are primary amino. The vibration of C-H bonds is reported at 2876 cm^{-1} and finally the bond 1053 cm^{-1} corresponds to the stretching vibration of C-O (Jagtap *et al*., 2011). The spectra of zeolite (see Fig. 3c) shows bands at 768, 1620 and 3600 cm^{-1}, which correspond to stretching vibrations of the Si-O, H-O and stretching -OH attached to aluminum, respectively (Corma *et al*., 2008; Karge, 1998; Quintero *et al*, 2012). Finally in the case of *U. lactuca*, bands at 1100 and 1200 cm^{-1} are due to vibrations of C-O bonds, while the band at 3290 cm^{-1} is attributed to the stretching vibrations of -OH and -NH (He and Chen, 2014). The spectra of ch-a composite (Fig. 4a) showed a bond at 1133 cm^{-1} which belongs to C-O vibrations, the bonds at 2861, 3645 and 3563 cm^{-1} are attributed to C-H, -OH and -NH vibrations, respectively (Ata *et al*., 2012). The presence of -NH$_2$ groups of chitosan and -OH and -NH groups of seaweed is due to the synthesizing of ch-a composite. When the fluoride was adsorbed in the ch-a composite (Fig. 4a) the bond attributed to C-H and -OH showed a lower intensity. In the ch-z composite peaks of 1367 cm^{-1} belongs to stretching -CH and -OH vibrations, 1645 cm^{-1} is attributed to -NH$_2$ groups vibrations, and finally the band of 2960 cm^{-1} corresponds to the stretching vibrations of type C-H (-CH and -CH$_2$). Also the absorption band 2960 cm^{-1} indicates the interaction of chitosan and zeolite by the CH groups, since this functional group is not present in zeolite.
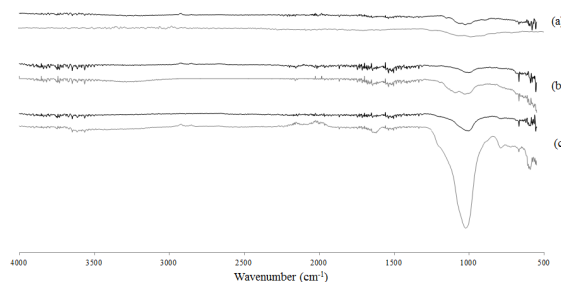

Fig. 3. FT-IR spectra for: (a) algae, (b) chitosan and (c) zeolite before and after the fluoride adsorption.
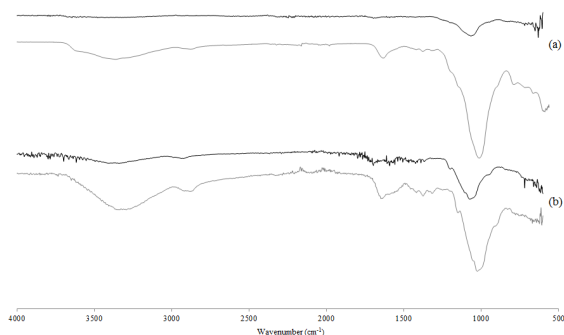
Fig. 4. FT-IR spectra of the (a) ch-a, (b) ch-z composites before and after fluoride adsorption.

3.2 Adsorption isotherms

Experimental data of fluoride adsorption isotherms for the different materials were fitted by using the Langmuir (1) and Freundlich (2) isotherm models, which are represented mathematically as:

$$q^* = \frac{q_m KC}{1 + KC} \qquad (2)$$

$$q^* = KC^{1/n} \qquad (3)$$

The constants values of both isotherms and the percentages of standard deviation are shown in Table 1. The experimental data of all materials were reasonably fitted by both Langmuir and Freundlich models, based on the correlation coefficient (r^2) and the standard deviation. This indicates that the materials presented a heterogeneous surface, and also the amount of adsorbed solute exponentially increased as the fluoride concentration increased.

3.3 Effect of pH and point of zero charge in the fluoride adsorption capacity in the different materials

The pH is considered one of the most important factors in the fluoride adsorption process, which depends on the specific characteristics of each adsorbent material. The F- adsorption isotherms at pH 5 and 7 are shown in Fig. 5 and 6. The results demonstrated that chitosan has a greater adsorption capacity compared to zeolite and algae. Moreover, the fluoride adsorption capacity for the chitosan adsorbents, zeolite and algae were of 1.62, 1.20 and 1.31 mg g^{-1}, respectively, at pH 5 and equilibrium concentration of 40 mg L^{-1}, when the pH was raised at pH 7 the adsorption capacity of chitosan, algae and zeolites decreases to 1.08, 1.06 and 1.01 mg g^{-1}, respectively. In both cases it can be seen that chitosan has a higher adsorption capacity than zeolite and algae, because it removes a 13% average of fluoride from water. However, we can observe that chitosan removed 1.5 times of fluorides at pH 5, respect to pH 7. The high adsorption capacity of chitosan can be attributed to its cationic behavior in acidic conditions, the protonation of amino groups promotes the adsorption anions such as fluoride, also according to the PZC (chitosan 7.7, zeolite 7.8 and algae 6.8) it is expected that the surface of the materials present positive charges at lower pH$_{PZC}$, which favors the adsorption of fluoride (Loganathan *et al.*, 2013). These results are comparable with those obtained by (Menkouchi *et al.*, 2007) in a study on natural chitosan, where they obtained a maximum adsorption capacity of 1.39 mg L^{-1}.

Table 1. Langmuir and Freundlich isotherm parameters

| Adsorbent	pH	PZC		Langmuir					Freundlich		
			q_{max}	k	R^2	% D	n	k	R^2	% D
chitosan	5	7.7	17.6	0.002	0.99	5.8	1.14	0.068	0.99	5.4
	7		129.3	0.0	0.91	20.4	0.72	0.005	0.95	22.4
zeolite	5	7.8	8.5	0.006	0.95	16.3	1.3	0.099	0.94	17.2
	7		70.9	0.4 e-3	0.97	8.4	0.89	0.016	0.98	8.5
algae	5	6.6	13.2	0.002	0.98	9.4	1.19	0.058	0.98	8.2
	7		1.8	0.044	0.65	17.5	2.57	0.266	0.7	15.4
ch-z	5	8.4	28.2	0.001	0.99	9.0	1.04	0.039	0.99	8.5
	7		4.8	0.015	0.95	12.8	1.66	0.18	0.93	12.5
ch-a	5	7	5.2	0.01	0.97	17	1.42	0.112	0.94	17.5
	7		11.2	0.004	0.89	31	1.2	0.072	0.89	30.0
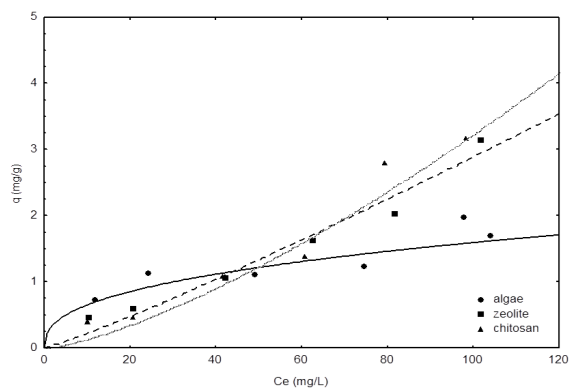
Fig. 5. Fluoride adsorption isotherm of different materials at pH 7 and 25°C. The lines represent the Freundlich model.
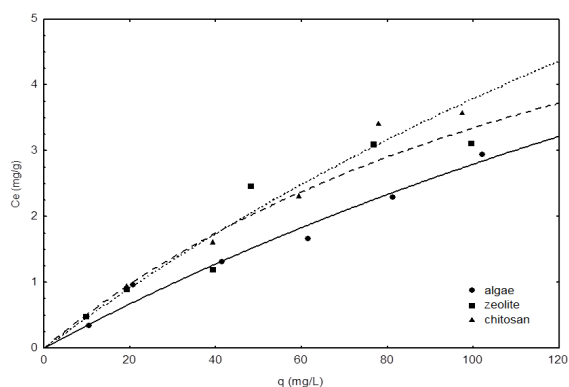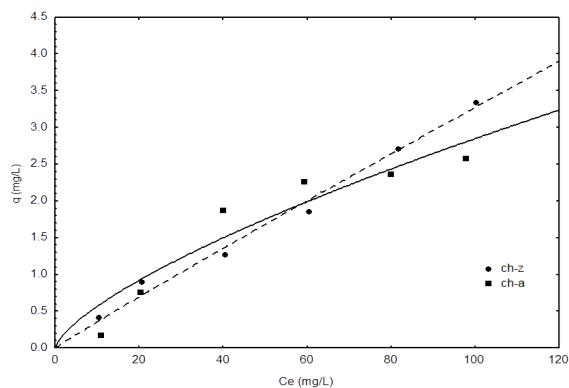

Fig. 7. Fluoride adsorption isotherm of different composites at pH 5 and 25°C. The lines represent the Freundlich model.

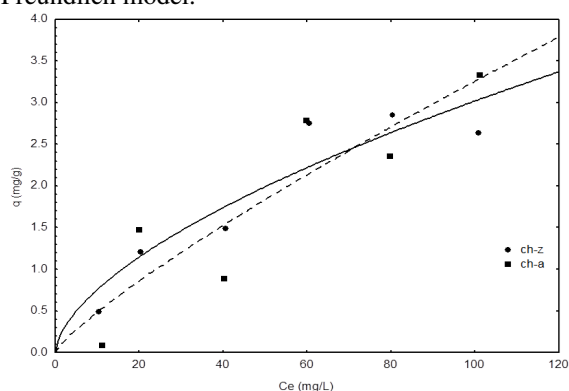Fig. 6. Fluoride adsorption isotherm of different materials at pH 5 and 25°C. The lines represent the Freundlich model.

Fig. 8. Fluoride adsorption isotherm of different composites at pH 7 and 25°C. The lines represent the Freundlich model.

Zeolite has a low adsorption capacity, because, it is an excellent cationic exchanger according to the literature, but it can have a low anions adsorption capacity (Bosch and Schifter, 1997). On the other hand, algae are known as excellent adsorbent material on removing cations and there are few studies on their use in the anions adsorption as fluorides. However, the functional groups that are present in their cell wall confer a negative surface charge, but when they are at low pH, the functional groups such as hydroxyls, carbonyls and amines confer positive charges to the surface due to the increased concentration of H^+ ions, thus increasing the capacity of anion exchange (Park *et al*., 2010). Although this capacity can be increased with various treatments for modifying the surface of adsorbents, as was performed in this study.

3.4 Effect of pH and point of zero charge in the adsorption capacity of fluoride in the ch-z and ch-a composites

Adsorption isotherms of fluoride at pH 5 and 7 on the two chitosan-zeolite (ch-z) and chitosan-algae (ch-a) composites are shown in Figures 7 and 8. In accordance to the results we can see that for a pH of 5 the ch-z composite shows a better adsorption capacity compared to the ch-a composite, since for low and high concentrations of fluoride, 20 and 100 mg L^{-1}, this removed 0.90 and 3.34 mg g^{-1}, respectively, while the ch-a composite had a removal capacity of 0.76 and 2.58 mg g^{-1} for the same equilibrium concentrations. This represents for both cases that the ch-z composite has an adsorption capacity of 1.2 times in contrast to the ch-a composite. Whereas for a pH of 7 the adsorption of fluorides is greater in the ch-a composite, because for these same concentrations (20 and 100

mg L^{-1}) this had an adsorption capacity of 1.47 and 3.33 mg g^{-1}: the ch-z composite removed only 1.21 and 2.64 mg g^{-1}. That is to say to a pH of 7 the ch-a composite removed 1.2 times more fluoride than ch-z composite. These results are comparable with those of other authors such as Sairam *et al.*, 2008 who synthesized a composite based on nanohidroxiapatite-chitosan which showed a capacity of 1.56 mg g^{-1} and a point of zero charge of 6.97. The pH$_{PZC}$ for both ch-z and ch-a composites was 8 and 7 respectively. Based on literature, pH 7 is optimized for the adsorption of fluorides on chitosan based composites (Viswanathan *et al.*, 2009).

3.5 Fluoride adsorption mechanism in composites

Through on FT-IR and PZC analysis we can elucidate the possible mechanism of adsorption of fluoride on the different composites. According to these results, the adsorption mechanism is accomplished by electrostatic interaction between the amino and hydroxyl groups present in the composite. This is because the working pH is below of the pH$_{PZC}$ of adsorbent material. Therefore, the surface of the absorbent material is positive, favoring the adsorption of fluoride ions.

Conclusions

With the exception of the zeolite, all the adsorption experimental data were best adjusted by the Freundlich adsorption isotherm. The adsorption capacity of all materials and composites is affected by the solution pH, so that the range of optimal performance of composites is at pH 5 in the case of ch-z composite, as this removes 1.2 times more fluoride respect to ch-a composite. In the case of ch-a composite, its optimum performance was observed at pH 7 as it increased its adsorption capacity 1.2 times compared to ch-z composite. The modified algae could be considered as an adsorbent material since showed the capacity to remove fluoride. The zeolite had a very low adsorption capacity, but its role in the composite is as a mechanical support for chitosan so that it could be used as an adsorbent material. The adsorption mechanism is by electrostatic attraction. Therefore both composites can be considered as good adsorbents for fluoride removal from water as well as being biodegradable and friendly with the environment.

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