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Removal of fluoride from drinking water by a chitin-based biocomposite in fixed-bed columns

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ABSTRACT

A detailed fluoride adsorption study in packed columns with chitin or a chitin-based biocomposite is reported. The biocomposite was preconditioned by an acidification process, which produced a suitable material to be used in a continuous fluoride adsorption process.

An empty bed contact time (EBCT) of 20 min was determined as adequate. The fluoride concentration of the artificially prepared influent was 5.1 mg/L. About 200 and 300 bed volumes of contaminated water were treated before saturation of packed columns with biocomposite or chitin, respectively. Fluoride was desorbed from the fluoride exhausted chitin and biocomposite by using a NaOH solution as eluent: the regeneration efficiencies were 85 and 84% for chitin and biocomposite, respectively. Finally, continuous fluoride adsorption experiments were carried out with natural fluoride contaminated water (3.9 $\text{mg}_{\text{fluoride}}$/L). The chitin and biocomposite fluoride selectivity was determined as follows: $SO_4^{2-} > HCO_3^- > F^- > Cl^- > NO_3^-$.

Results of this study confirmed the potential of chitin-based biocomposites as adsorbents materials of fluoride and other anions present in water. However, the preconditioning of the biocomposite should be considered.

1. Introduction

Chitin, the second natural polymer in abundance and its main derivative, chitosan, are known for their high capacity to remove either inorganic [1] or organic [2] contaminants from water. Such versatility is due to the presence of amine groups on their structure; these groups have great capacity to physically and chemically interact with other species, and they are highly sensitive to pH changes [2,3]. Most of the studies regarding inorganic species biosorption by chitin/chitosan have focused on removal of heavy metals and cations; however, some researchers have recently studied the capacity of such materials to remove inorganic anions e.g. fluoride from aqueous medium [4–15].

Fluoride, an inorganic anion, is one of the most important contaminants because of the great number of people exposed to its toxic effects [16]. At least 25 countries around the world possess groundwater naturally contaminated with fluoride as an endemic problem [17]. The effects on human health by the excessive fluoride ingestion range from dental fluorosis to serious skeletal fluorosis [16,18,19]. Fluoride ingestion could be related with other serious illnesses such as osteosarcoma and affectations of the immune and reproductive systems [18].

Adsorption onto activated alumina has been the most used method for fluoride removal from water, from the 1930s until nowadays [19–21]. However, the study of novel fluoride adsorbent materials of low cost and suitable sustainability is an important current scientific challenge. Chitin has turned in an attractive fluoride biosorbent, however, the use of this biopolymer in water treatment plants implies its application in continuous adsorption processes i.e. packed bed columns. In this sense, the main difficulty to use chitin as an adsorbent bed has been its low mechanical and chemical resistances compared to typical inorganic materials as silica. For this reason, diverse methods to support (or reinforce) chitin have been proposed [14,15,22–29], trying to preserve as much as possible the adsorption capacity of this biopolymer. The synthesis of biocomposites is a simple method to support/reinforce chitin, compared with other methods that use chemical substances to dissolve or chemically modify chitin. In addition, the chitin-based biocomposites can be molded to use them in packed bed columns. Among the materials that are useful to reinforce chitin, the synthetic polymers show advantages due to their easy handling and versatility. Besides, the biocomposites obtained can be homogeneous, porous and mechanically resistant. Polyurethane has demonstrated to be a suitable reinforcement medium for chitin [30] and its derivatives [31]. In fact, the sorption of fluoride in deionized water by chitin-based biocomposites in batch mode has been already proven by us [32]: chitin was mechanically reinforced by polyurethane and the fluoride adsorption capacity of

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chitin was kept even when the biopolymer was reinforced with polyurethane. Such results enable the possibility to apply the mentioned chitin-based biocomposites in a continuous adsorption process. Nevertheless, due to the characteristics of the chitin-based biocomposite, a conditioning step is required before its application in an adsorption column.

The aims of this study are: to develop a conditioning method of a previously reported chitin-based biocomposite [30], in order to use it in continuous fluoride adsorption experiments; to determine the most suitable operational conditions of packed columns; to determine the regeneration grade of saturated biocomposites; and to elucidate the biocomposites fluoride selectivity when treating a natural fluoride-contaminated water.

2. Experimental

2.1. Biopolymer

The Biotechnology Laboratory of the Universidad Autonoma Metropolitana Iztapalapa (UAMI) provided chitin. The biopolymer was provided as flakes with a particle size of around 1 mm, and a degree of acetylation (DA) of 79%.

2.2. Reagents

The following reactive grade chemicals were used as received: NaF (Fermont), NaCl (Fermont), HCl 0.01 N (J.T. Baker), NaOH 0.01 N (J.T. Baker), HNO_3 0.1 N (Sigma–Aldrich Inc.), fluoride standard solutions of 1, 10 and 100 mg/L (Thermo Electron Corp.) and TISAB II solution (Thermo Electron Corp.).

The polymeric matrix was based on a polyurethane prepolymer, provided by Bayer (Leverkusen, Germany), which has an isocyanate content of 14% by weight. No further purification or treatment was applied to this reagent. Moreover, as previously reported [30], tertiary amine provided by Clariant (Muttenz, Switzerland) was used as catalyst for the polyurethane polymerization.

Natural water was collected from a well (No. 58) located in San Luis Potosi, Mexico: the main characteristics were previously reported [33] and are shown in Table 1.

2.3. Biocomposite synthesis

The optimum biocomposite was obtained by mixing chitin and polyurethane prepolymer during the polymerization reaction as previously reported [30]. The composition of this biocomposite on weight bases was: 47% polymer, 53% chitin and 2% catalyst (polymer + chitin = 100%).

2.4. Instrumental methods

Fluoride analysis was conducted by an ion selective electrode (Thermo Electron). Dissolved carbon was analyzed by means of a Total Organic Carbon Analyzer (TOC-V_{CSN}, Shimadzu). According to the parameters shown in Table 1, bicarbonate (HCO_3^-) is the only source of inorganic carbon present in the studied groundwater. Hence, the inorganic carbon concentration reported by the TOC-V_{CSN} instrument was assumed associated to bicarbonate.

The concentration of sulfate (SO_4^{2-}), chloride (Cl^-) and nitrate (NO_3^-) was obtained by a capillary electrophoresis equipment Agilent CE system (Agilent Technologies).

Table 1
Main physicochemical parameters of natural water from well No. 58 in San Luis Potosí, Mexico [29]. Concentrations are reported in mg/L and the third column shows the determined values by authors.

Parameter	Reported value [29]	This study
pH	7.25	7.60
CO_3^{2-}	0	No determined
HCO_3^-	160.99	142.33
Cl^-	14.03	13.45
SO_4^{2-}	23.16	37.30
F^-	3.96	3.90
Organic C	No determined	1.85

2.5. Biocomposite conditioning

Preliminary biocomposite conditioning experiments were carried out, in order to evaluate the feasibility to carry out such process in situ, i.e. packing a column with the biocomposite. The most suitable conditioning method consisted on mixing the biocomposite with HNO_3 solution (initial pH of 3) at required mass/volume (m/v) ratio of biocomposite/solution. The m/v ratios studied in this work were 1, 2, 4, 8 and 16 $g_{biocomposite}/L_{solution}$. The suspension was shaken in an orbital agitator at 140 rpm for the required time (about 50 h) to reach constant pH. Finally, the biocomposite was separated by filtration with a nylon® mesh with 62 threads per square centimeter.

2.6. Continuous adsorption experiments

Fluoride adsorption experiments were carried out in laboratory-scale packed columns. Chitin and biocomposite were first conditioned as mentioned in Section 2.5, using batches of 5.3 and 10 g of the respective material. The conditioned material was packed in a chemically resistant borosilicate glass column of 2.5 cm of internal diameter and 20 cm height. The packed bed height was 4.8 cm (bed volume = 23.3 mL) for chitin and 9 cm (bed volume = 44.1 mL) for biocomposite. The approximated void volume was 0.262 cm^3 for chitin and 0.079 cm^3 for the biocomposite. The column influent consisted of artificially or naturally fluoride contaminated water, and was fed to the column by a variable speed peristaltic pump. The fluoride concentration for the artificial and natural influent was 5.1 mg/L and 3.9 mg/L, respectively (see Table 1).

The pH value of both influents (natural and artificial) was adjusted to 5 with 1 N HNO_3 solution. The feed flow was regulated base on the empty bed contact time (EBCT), i.e. the necessary time for an influent particle (ion/molecule) to cross the adsorbent bed, assuming that the column does not contain such solid medium [34]. In other words, EBCT is the ratio of adsorbent volume divided by the liquid volumetric flow. The column effluent was periodically sampled to determine the solution pH and ions concentration (F^-, SO_4^{2-}, Cl^-, NO_3^- and HCO_3^-).

2.7. Adsorbent regeneration experiments

Regeneration experiments of fluoride-saturated chitin/biocomposite (after continuous adsorption) were carried out. The desorption process conducted by feeding a 0.1 M NaOH solution to exhausted packed columns with an EBCT of 20 min. The effluent was sampled periodically for its subsequent fluoride concentration analysis.

3. Results and discussion

3.1. Biocomposite conditioning

As mentioned in Section 2.5, a mechanically agitated batch method was used to condition the biocomposite: Fig. 1 shows the monitoring of pH with time, and shows that the required equilibrium time for the biocomposite conditioning is independent of the m/v (biocomposite/solution) ratio. The equilibrium was

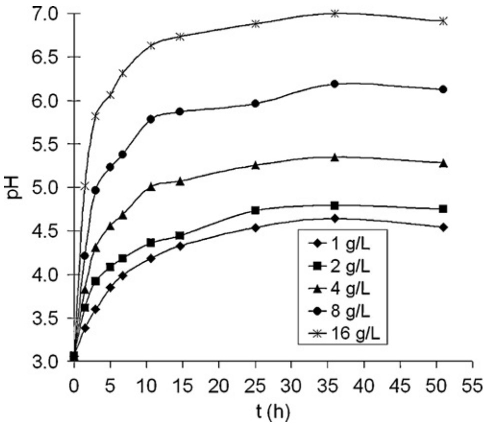

Fig. 1. pH vs time during the biocomposite conditioning at initial pH of 3 with diverse m/v (biocomposite/solution) ratios.

achieved in approximately 25 h for all the m/v ratios. As can be seen in Fig. 1, 16 and 8 g/L ratios achieved an equilibrium pH of about 7.0 and 6.1, respectively. Both pH values were relatively higher than the objective pH 5 or lower: conditions that were previously determined as the optimum to adsorb fluoride by the chitin-based biocomposite.

Besides, the m/v ratio of 4 g/L showed an equilibrium pH of about 5.3, which was much closer to 5. Nevertheless, the equilibrium pH of 4.8 by a m/v ratio of 2 g/L is more advisable in terms of protonation of the primary amine groups present in the biocomposite (pK_a = 6.5 [35]).

The m/v ratio of 1 g/L showed an equilibrium pH of 4.6 (see Fig. 1); however, this ratio represents a great use of acidified water. In addition, such m/v ratio would require a larger container size to carry out the conditioning process, and higher energy consumption to agitate the solid–liquid mixture. In other words, a m/v ratio of 2 g/L produces a conditioned biocomposite with the required pH by using the minimum acidified water. Hence, a m/v ratio of 2 g/L and 25 h were selected as the optimum for conditioning the chitin-based biocomposite. It is important to mention that the water used in the conditioning process can be reused and the batch conditioning method can be improved by using an automatic acid addition system to achieve a continuous pH control. This can accelerate the conditioning process and permit to use a greater m/v ratio to decrease the required water volume.

Regarding the concentration of dissolved organic carbon (DOC) in the supernatant after the conditioning process, the m/v ratio of 2 g/L showed 34 mg/L. However, when the conditioned biocomposite was contacted with fresh water at pH 5, a DOC concentration of only 1.1 mg/L was found. That is to say, the conditioning process eliminated the soluble portion of the biocomposite, probably composed of chitin of low crystallinity or low molecular weight. The weight loss and hydration of the conditioned biocomposite was 1.5% and 150%.

3.2. *Continuous fluoride adsorption*

3.2.1. *Optimum flow rate*

Experiments were carried out in order to determine the effect of EBCT on the fluoride breakthrough curves. Artificially fluoride contaminated water at pH 5 was fed into packed columns with conditioned biocomposite. The maximum permissible limit for fluoride in drinking water (MPL_F = 1.5 mg/L [16]) was used as the breakthrough point. As can be observed in Fig. 2, when the EBCT increased from 5 to 20 min the bed volumes treated to the MPL_F increased from about 28 to 46, which was due to a greater contact time (shorter mass transfer zone) between the liquid and solid phases. This permitted fluoride to diffuse into the biocomposite structure and to interact with the protonated primary amine sites of chitin. An EBCT of 30 min showed similar bed volumes treated, which means that an EBCT of at least 20 min is sufficient to allow the adsorption process to take place in full. Hence an EBCT of 20 min was used in the rest of the continuous adsorption experiments of this study. It is important to mention that the effluent pH in all the experiments shown in Fig. 2 was practically constant at 5 due to the previous biocomposite conditioning process.

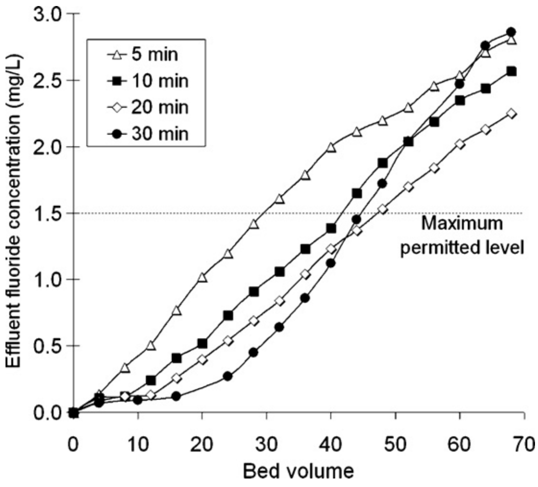

Fig. 2. Effect of EBCT on continuous fluoride adsorption on biocomposites. C_0 = 5.1 mg/L, influent pH = 4.8, T = 25 °C.

Fig. 3 shows the fluoride breakthrough curves for chitin and the biocomposite, both with an EBCT of 20 min and constant influent pH of 4.8. An equivalent chitin mass, between both experiments, was used. As can be seen in Fig. 3, the biocomposite processed about 50% less bed volumes than chitin (about 100 bed volumes). In addition, the biocomposite saturation point was achieved at about 200 bed volumes, while that for chitin was achieved at about 300 bed volumes. This fact can due to a restricted access of fluoride ions to the biocomposite adsorption sites compared to those of chitin. In fact, these results agree with those reported for batch fluoride adsorption on chitin and chitin-based biocomposites [32], where the biocomposite showed lower adsorption capacity compared to chitin at pH 5–8. This was corroborated in continuous fluoride adsorption experiments, since the biocomposite fluoride

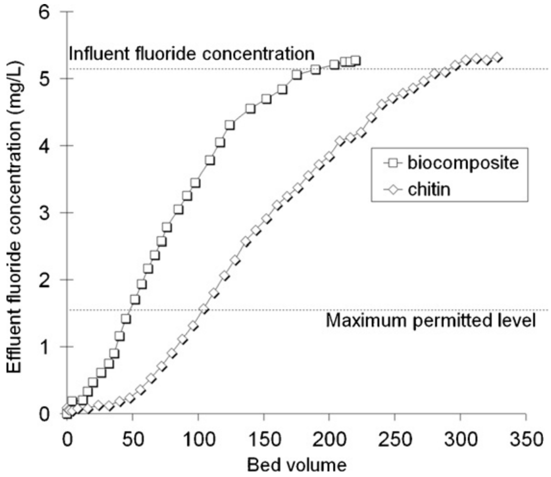

Fig. 3. Breakthrough curves for fluoride adsorption on chitin and the biocomposite. EBCT = 20 min, C_0 = 5.1 mg/L, influent pH = 4.8, T = 25 °C.

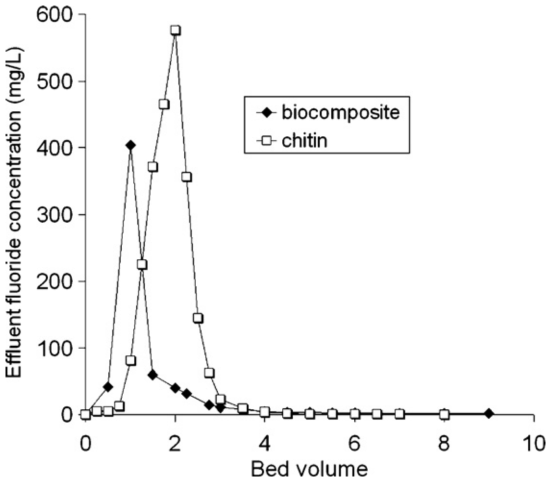

Fig. 4. Fluoride desorption curves for saturated chitin and biocomposite at an EBCT of 20 min and 25 °C by 0.1 M NaOH.

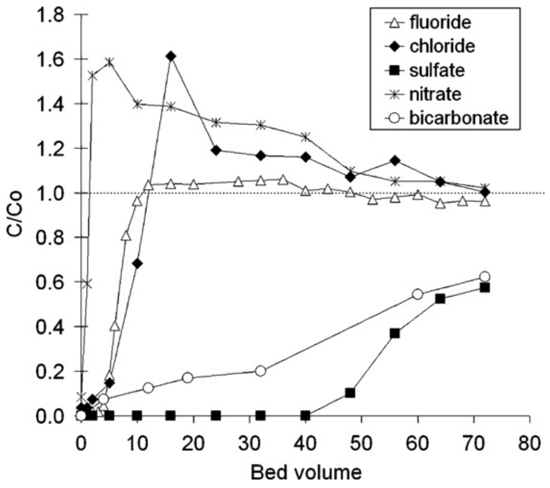

Fig. 5. Anions breakthrough curves when treating natural water by chitin at an influent pH of 4.8 and 25 °C. The initial concentrations of these anions are reported in Table 1.

adsorption capacity at the saturation point (i.e. 200 bed volumes) was 1.7 mg/g, while that for chitin (at 300 bed volumes) was 3.4 mg/g.

According to Fig. 3, it is evident that when saturation was achieved the fluoride concentration at the effluent was slightly greater than that in the influent, especially for chitin. This phenomenon can be due to a gradual desorption of fluoride once chitin reaches saturation.

3.2.2. *Fluoride desorption*

Once chitin and the biocomposite achieved the saturation point in the continuous fluoride adsorption experiments, they were regenerated. Sodium hydroxide was used to increase the solution pH inside the packed columns to deprotonate primary amine groups and to allow adsorbed fluoride ions to desorb ($NH_3^+F^- \rightarrow NH_2 + H^+ + F^-$).

Fig. 4 shows that only 4 bed volumes of eluent are needed to desorb pre-adsorbed fluoride. This eluent volume is much lower than that reported to regenerate a saturated biocomposite (composed by chitosan and ceramic alumina) with other ions as chromium (VI) (20 bed volumes [28]) and arsenic (III and V) (15 bed volumes [36]) with the same eluent at the same concentration.

It is important to mention that, although chitin processed 300 bed volumes, its fluoride desorption efficiency was 85%, very similar to that of the biocomposite (84%). Such efficiencies were very similar to those reported for fluoride desorption from chitosan, 85%, by using 0.1 M NaOH solution [5].

3.2.3. *Biocomposite selectivity for fluoride*

Breakthrough curves for fluoride and other anions present in natural water are reported in Fig. 5. It can be seen that chitin gets saturated with fluoride after 12 bed volumes, which is much lower than the 300 bed volumes processed when fluoride was dispersed in deionized water. This is explained by a great competition with other anions, especially with sulfate and bicarbonate. These results agree with those reported in previous equilibrium adsorption studies on chitinous materials, where bicarbonate and sulfate strongly competed with fluoride for active sites [6,8].

Fig. 5 also shows that chloride competed with fluoride in a lesser extent than sulfate and bicarbonate, and that chitin is more selective for fluoride than for chloride since this is 3.5 times more concentrated.

It must to be pointed out that the chloride breakthrough curve showed a roll-up, which is due to the exchange of a weakly adsorbed substance by other of higher adsorption force on the adsorbent surface [37]. This displacement is observed after 10 bed volumes to the end of the experiment, which could be due to nitrate since this breaks almost immediately, presents a roll-up and then start s to be adsorbed. It is to be noticed that nitrate it is not initially present in the water sample, however was found in the effluent since nitric acid was used to adjust the water pH, and also in the case of the biocomposite to precondition it. Moreover, nitrate, initially present in the previously conditioned material, was easily displaced by the rest of the anions contained in the influent, including fluoride. This phenomenon confirmed that nitrate barely competes with fluoride, sulfate and bicarbonate for the adsorption sites of chitinous materials, as it has been reported for equilibrium studies [6,8].

The roll-up effect was not perceptible in the fluoride breakthrough curve, which indicates that the fluoride adsorption forces are stronger than those for chloride and nitrate. This fact could be attributed to the electronegativity of these anions: $HCO_3^- \approx F^- > SO_4^{2-} > NO_3^- > Cl^-$ [38], which agrees in some extent with the breakthrough curves reported herein. Other parameters such as ion valence, size, and concentration definitely influence selectivity. For example, sulfate electronegativity is lower than that of fluoride or bicarbonate, but this has a negative valence of two, which enables it to be electrostatically attracted by two positive adsorption sites. Besides, chloride is the less electronegative anion among the anions studied. However, its size (atomic radius = 0.79 Å) could contribute to its greater adsorption compared to nitrate (ion radius ≈ 1.5 Å).

On the other hand, breakthrough curves for anions were obtained when treating natural water with conditioned biocomposite. It must be pointed out that the chitin mass contained in the biocomposite was the same as that used in the previous experiments. As can be seen in Fig. 6, the breakthrough curves are very similar to those showed by chitin experiment (Fig. 5). Nevertheless, some aspects must be highlighted.

The bed volumes treated by the biocomposite for fluoride were practically the same as those for chitin. However, the removal of sulfate and bicarbonate was less efficient than by using the biocomposite, which could be attributed to a restricted diffusivity of such anions due to the biocomposite polymeric matrix. In addition, the greater size of these anions compared to fluoride and chloride might contribute to maintain the fluoride adsorption capacity of chitin in the biocomposite. Additionally, as can be observed in Fig. 6, the chloride roll-up was delayed compared to the chitin experiment, since this occurred at 32 bed volumes

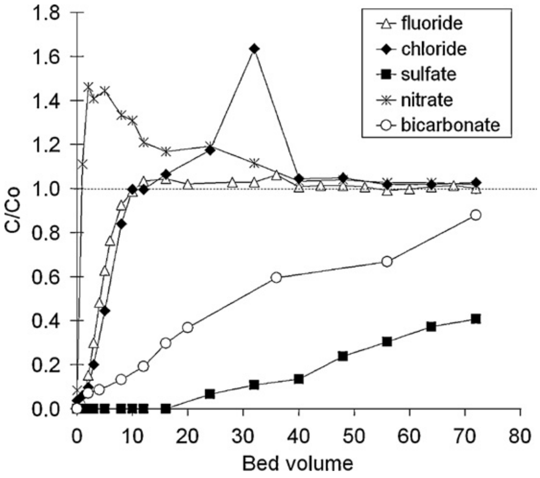

Fig. 6. Anions breakthrough curves when treating natural water by biocomposite at an influent pH of 4.8 and 25 °C. The initial concentrations of these anions are reported in Table 1.

instead of 16. This displacement was probably owing to a lesser adsorption of sulfate and bicarbonate.

Finally, the authors consider that since water contamination by fluoride is still of great concern in many places around the world, the development of low cost and efficient materials is needed. As a reference, it can be mentioned that the approximated cost of the biocomposite is 3.5 USD/kg, similar to the cost of commercial activated alumina (4 USD/kg). The results reported herein show the potential of a chitin-based biocomposite to remover fluoride from water, but more studies are still needed in order to improve adsorption capacity and selectivity.

4. Conclusions

The biocomposite has lower fluoride removal efficiency than chitin when this contaminant is present in deionized water. However, the performance of both materials, chitin and biocomposite, is similar when treating contaminated natural water, probably due to the different sizes of the anions adsorbed, which interacts in different ways with the materials.

An EBCT of 20 min allows the biocomposite to treat 50 bed volumes with a concentration under the maximum permissible limit recommended by the WHO, and a total of 200 bed volumes at the saturation point. Regeneration of the saturated biocomposite is possible by using only 4 bed volumes of a 0.1 M sodium hydroxide solution: the efficiency achieved is about 85%.

Sulfate and bicarbonate strongly compete with fluoride in the continuous adsorption process on chitin and biocomposite. Nevertheless, the affinity of such anions is lower for the biocomposite than for chitin. This fact modifies the breakthrough curves of both chloride and nitrate without affecting the fluoride one.

Both chloride and nitrate showed a roll-up effect when treating natural water with chitin and biocomposite, which demonstrates the lower affinity for such anions compared to the affinity of fluoride, bicarbonate and sulfate.

It should be mentioned that the preconditioning of the biocomposite needs to be considered in future improvements of this material: a chemical modification of chitin and polyurethane may be necessary. Finally, these results confirmed the potential of a chitin-based biocomposite as adsorbent of anions in aqueous medium. In addition, this study provides important basis to develop suitable adsorbent materials to remove fluoride and other anions from aqueous phase.

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