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Synthesis of a chitin-based biocomposite for water treatment: Optimization for fluoride removal

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ABSTRACT

The optimum composition of a chitin-based biocomposite was determined based on both its fluoride adsorption capacity and its chemical resistance in acid aqueous solution. Parameters such as the chitin content, additive content, catalyst content, chitin particle size, degree of acetylation of chitin and effect of pH on adsorption were evaluated. It was possible to chemically reinforce chitin while keeping an acceptable fluoride adsorption capacity onto the chitin-based biocomposites. Optimum chitin content (60%) was limited by the polymer–biopolymer anchoring capacity. An amine-based additive was used to improve the biocomposite adsorption capacity; however, its inclusion was not suitable in terms of biocomposite chemical resistance. The chitin particle size had no effect on adsorption capacity, and the degree of acetylation of chitin notably modified biocomposite adsorption capacity. On the other hand, the biocomposite chemical resistance was notably improved compared to pure chitin. The physicochemical properties of the optimum chitin-based biocomposite showed its potential for being used in continuous adsorption processes.

1. Introduction

Chitin and its most important derivative, chitosan, are two of the most studied biosorbents in the last decades for removal of metal cations in aqueous solution and, more recently, for removal of anions such as negative species of arsenic [1], molybdenum [2,3], vanadium [3], chromium [1,4], and fluoride [5]. Formation of metal–biopolymer complexes have been proposed by some authors as the mechanism for removal of cations [6–9], owing to the presence of free electronic pairs in the oxygen and nitrogen atoms of chitin and chitosan. In the case of removal of anions, which is carried out at acid pH, some researchers have proposed the electrostatic attraction between anions and primary amine groups of the biopolymer, protonated at such pH values, as the main sorption mechanism [8]. In fact, researchers have preferred partially desacetylated chitin, or chitosan in most cases, compared to fully acetylated chitin due to the higher presence of primary amine groups on its structure. This group is more reactive than the acetamide group [6], which is present in greater quantity on chitin, due to its lower steric impediments. In other words, the desacetylation process of chitin increases the density of anion adsorption sites; however, such a process also decreases the biopolymer crystallinity and in turn enhances its solubility, an undesirable effect for any adsorbent material. These and other properties of chitin, such as brittleness and flat morphology, are drawbacks to its application as an adsorbent material, especially in continuous processes due to its proved clogging effect and hydrodynamic limitations [6]. Due to these facts, some authors have studied several ways to support chitin and chitosan by means of synthetic materials such as polymers [9–11], or minerals [12,13]. Polymeric supports have advantages such as easy handling, versatility and possibility of obtaining homogeneous, porous, malleable and mechanically-chemically resistant biocomposites. Previous studies have proved that polyurethane is a suitable type of polymeric support for chitin and chitosan [14]. In summary, the resistance of chitin and chitosan can be improved if these are physicochemically reinforced; however, at the same time, their sorption capacity is reduced due to blockage of adsorption sites by the physical and chemical interactions between the supporting media and the biopolymer [10,15]. Such blockage could be reduced if the chemical interactions occur using the biopolymers' chemical groups that do not play an important roll in the adsorption process, e.g. hydroxyl groups. Another form to reduce blockage of sites might be by increasing the biopolymer content, which would increase the density of adsorption sites and reduce the blockage probability. In addition, it is possible to compensate such blockages by using additives containing chemical groups prone to adsorb the contaminant in question.

On the other hand, previous studies on different solutes reported disagreeing conclusions about the particle size effect of

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chitinous materials on their equilibrium adsorption capacity [16–19]; this effect has not been reported in regards to chitin–polymer biocomposites. The particle size variable is important because if chitin grinding is needed, it might mean a possible cost limitation in a real application.

Since the adsorption of anions on primary amine groups increases at low pH, where chitin solubility is enhanced, it is also important to measure the chemical resistance of the biosorbents at the same low pH.

Regarding water contamination, high fluoride concentration in drinking water, i.e. >1.5 mg/L [20], is still of significant concern in many countries, due to serious health consequences of its prolonged and systematic ingestion, even in minimal concentrations, i.e. parts per million [21]. Fluoride is classified by the World Health Organization as one of the human consumption water contaminant that most negatively affects water quality for human consumption, only comparable with arsenic and nitrate [20]. Removal of fluoride from water has been studied since 1930s; aluminum derivatives were mainly the first kind of compounds used for such a purpose [22]. Subsequently, different methods to eliminate fluoride from water have been developed, i.e. adsorption [23–25], chemical precipitation [25,26], reverse osmosis [25,27] and electrodialysis [28]; however, adsorption has remained as the most suitable technique [25]. Nowadays, adsorption on activated alumina is one of the most widely used methods for fluoride removal [20], due to its economical, operative and adsorption efficiency advantages. Nevertheless, there is an increasing necessity to produce more economical and environmentally sustainable adsorbents, thus promoting the increasing use of biosorbents. Supported biosorbents by synthetic materials show suitable properties for their use in high scale column adsorption processes. Therefore, the objective of this study is to determine the optimum composition parameters of a chitin-based biocomposite that enable its use in adsorption columns, and to explore its capability as an adsorbent material of contaminants present in water, such as fluoride.

2. Experimental

2.1. Biopolymers

Chitin was provided by the Biotechnology Laboratory of Universidad Autonoma Metropolitana, campus Iztapalapa (UAMI), in Mexico City. Two samples of the biopolymer were provided as flakes with a particle size of around 1 mm, and degree of acetylation (DA) of 99 and 79%.

2.2. Reagents

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

The polymeric matrix was a polyurethane prepolymer, provided by Bayer (Leverkusen, Germany), which has a NCO content of 14% by mass. No further purification or treatment was applied for this reagent.

Two catalysts based on amine compounds, named catalyst 1 (Ct1) and catalyst 2 (Ct2), were selected. Catalyst 1 is a hydroxyl substituted amine, provided by Clariant (Muttenz, Switzerland), while catalyst 2 is a tertiary amine provided also by Clariant (Muttenz, Switzerland). Both catalysts were used as received.

A polymeric amine was used as additive. This compound was provided by BASF (Ludwigshafen, Germany). This compound was used as received.

2.3. Polymeric matrix synthesis

The prepolymer was selected based on its chemical compatibility with chitin, chemical and physical resistance, and environmental suitability. Regarding catalysts, their selection was based on their capability to accelerate the polymerization reaction of the polymer.

Table 1 shows the percentages by mass of polymer, additive and catalyst (Ct1 or Ct2) that were used in the synthesis of the samples studied.

2.4. Materials characterization

Both chitin and the optimum biocomposite were physicochemically characterized. The surface area was determined by the BET method, using an ASAP 2020 (Micromeritics) nitrogen physisorption instrument, and elemental analysis was carried out by using an Elemental Combustion System (ECS 4010, Costech Instruments). X-ray diffraction patterns were obtained by means of an X-ray diffractometer D8 Advance (Bruker), at 35 kV, 25 mA and a scanning speed of 0.3 °/min within a range of 5–45°. Infrared spectra were recorded by using a Nicolet 6700 (Thermo Scientific) operating in the wavenumber range of 600–4000 cm^{-1}. Dissolved carbon was analyzed by means of a Total Organic Carbon Analyzer (TOC-V_{CSN}, Shimadzu).

The slurry pH of sample pHS was measured through the slurry pH method, which consisted of placing 0.1 g of biocomposite in 10 mL of a CO_2 free 0.1 M NaCl solution in an Erlenmeyer flask. Carbon dioxide was previously eliminated from the solution by sparging nitrogen into flask during 10 min. The mixture was stirred during 48 h at 150 rpm, and then the final pH, which was considered as the slurry pH, was measured.

2.5. Optimum composition of chitin-based biocomposite

Several experimental series were made to determine the optimum composition of a chitin-based biocomposite, at the same time able to adsorb fluoride and chemically resistant.

In the first stage, the adsorption capacity of the biocomposite was optimized, and was measured as either the ion exchange capacity (IEC, adsorption potential) or the fluoride adsorption capacity. For such purpose, a series of parameters were explored, such as chitin content, additive content and degree of acetylation of chitin, as well as chitin particle size and solution pH in the adsorption process. The biocomposites were obtained by mixing the biopolymer during the polymerization reaction of the polymeric matrix, in order to achieve a physical and chemical interaction between both materials.

In the second stage, the biocomposite chemical resistance was optimized, and was measured as the mass loss of the materials (chitin, polymeric matrix or biocomposite) when they were contacted with acidified water. A series of parameters such as catalyst type, catalyst content and additive content were studied.

Table 1 shows the mass percentages of each chemical component used to synthesize the studied samples of the 1st and 2nd optimization stage.

2.6. Ion exchange capacity (IEC)

The ion exchange capacity was evaluated as follows: 0.1 g of chitin or biocomposite was mixed with 50 mL of 0.01N HCl solution in Erlenmeyer flask. The mixture was shaken and kept at

Table 1
Chemical components of the synthesized biocomposites and polymeric matrix. The percentages are reported in mass base (chitin + polymer = 100%).

Stage	Target property	Studied parameter	Sample name	Component content					
				DA 99% chitin (%)	DA 79% chitin (%)	Polymer (%)	Additive (%)	Catalyst 1 (Ct1) (%)	Catalyst 2 (Ct2) (%)
1st	Adsorption capacity	Chitin content	CC1	19.9	–	78.6	–	0.9	–
			CC2	42.0	–	58.0	–	0.7	–
			CC3	61.8	–	38.2	–	0.4	–
		Additive content	Add1	38.0	–	62.0	0.7	1.3	–
			Add2	38.6	–	61.4	2.3	1.3	–
			Add3	38.9	–	61.1	3.9	1.4	–
		Adsorption pH	pHS	56.3	–	43.7	4.0	1.1	–
		Degree of acetylation	DA1	56.3	–	43.7	4.0	1.1	–
			DA2	–	56.3	43.7	4.1	1.1	–
		Chitin particle size	PS1	–	55.3	44.7	3.3	1.2	–
			PS2	–	55.6	44.4	4.1	0.9	–
			PS3	–	55.4	44.6	4.5	1.1	–
2nd	Chemical resistance	Catalyst type	CatT1	–	–	100.0	–	20.0	–
			CatT2	–	–	100.0	–	–	20.0
		Catalyst content	CatC0	–	–	100.0	–	–	–
			CatC1	–	–	100.0	–	–	0.2
			CatC2	–	–	100.0	–	–	0.4
			CatC3	–	–	100.0	–	–	1.1
			CatC4	–	–	100.0	–	–	2.0
			CatC5	–	–	100.0	–	–	4.1
			CatC6	–	–	100.0	–	–	8.2
			CatC7	–	–	100.0	–	–	15.8
			CatC8	–	–	100.0	–	–	20.0
		Additive content	AddC0	–	–	100.0	–	–	–
			AddC1	–	–	100.0	0.2	–	2.1
			AddC2	–	–	100.0	0.5	–	2.1
			AddC3	–	–	100.0	1.1	–	2.1
			AddC4	–	–	100.0	2.1	–	2.1
			AddC5	–	–	100.0	3.2	–	2.1

room temperature during 48 h, which was enough time to achieve equilibrium, since pH and chloride concentration did not change after 24 h of contact, according to different previous exploratory measurements (data not shown). The solid material was filtered and 10 mL of the solution were titrated with 0.01N NaOH solution. The ion exchange capacity was calculated from the difference between the initial and final HCl concentration, and it was reported in mmol of exchanged ions per gram of adsorbent material.

2.7. Adsorption experiments

A certain mass of biopolymer or biocomposite (0.5–2.5 g) was mixed with 50 mL of a 15 mg/L fluoride solution prepared from the stock solution, and the mixture was placed in a PET bottle. The pH was adjusted to the required value by adding 0.1N HNO_3 solution. Nitric acid was selected to adjust the solution pH because previous works have reported that nitrate is a low competitive ion in the fluoride adsorption process [29–31]. The mixture was stirred at 150 rpm and 25 °C during 72 h. This period was assumed as sufficient time to achieve equilibrium, according to previous kinetic studies with chitin/chitosan derivative materials, where maximum saturation times were around 5 h [9,30–34]. Adsorption experiments were carried out in duplicate and the reported data correspond to average values. The fluoride concentrations were determined by a selective ion electrode (Thermo Electron Corp.). The fluoride adsorption capacity (q [=] $\mathrm{mg}_{\text{adsorbed fluoride}}/\mathrm{g}_{\text{adsorbent material}}$) of each adsorbent material was calculated from the difference of fluoride concentrations ($C_{\text{initial}} - C_{\text{equilibrium}}$) in the solutions.

2.8. Chemical resistance

A certain dry mass of chitin or biocomposite was placed in contact with HNO_3 acidified water at a predetermined initial pH value, at an initial concentration of solids of 16 g/L. The mixture was shaken at 130 rpm while the pH was measured periodically (if necessary) until the equilibrium was reached, i.e. the pH was constant. Subsequently, solids were separated by filtration, dried at 70 °C during 48 h and the final mass was determined. Then, chemical resistance was evaluated by means of the percentage of mass loss caused by the contact of solids with acidified water.

3. Results and discussion

3.1. Chitin characterization

The surface area of 99 and 79% acetylated chitins was 5.76 and 0.32 m^2/g, respectively. Such values were similar to other reported values for chitinous materials [16,31,34]. This kind of materials has low surface areas, due to their nonporous structure. Both chitins were observed by scanning electron microscopy (images not shown), where their low porosity was corroborated due to its flat and laminar morphology. Nonetheless, an important density of potential adsorption sites in both chitins was determined. First, the nitrogen content measured by elemental analysis was 6.4 and 6.3% for 99 and 79% acetylated chitin, respectively. These contents represent 4.6 and 4.5 mmol of nitrogen per gram of chitin, respectively, i.e. an equal quantity of free nitrogen electron pairs that are prone to attract hydrogen ions from the aqueous medium. However, the ion exchange capacity (IEC) of 99 and 79% acetylated chitins was only 0.130 and 2.12 mmol/g, respectively. This difference between the IEC for the 99 and 79% acetylated chitins can be explained since, as the degree of acetylation (DA) decreased, the concentration of primary amine groups in chitin increased and, furthermore, the chitin crystallinity decreased.

On the other hand, the difference between nitrogen content and IEC can be explained since not all the ion exchange sites (i.e. nitrogen atoms) are located in accessible amorphous chitin zones;

some of them are located in inaccessible crystalline chitin zones, being the 99% acetylated chitin more crystalline than the 79% acetylated chitin. Nevertheless, considering that one adsorption site uptakes one fluoride ion, and based on the ion exchange capacity and the fluoride atomic weight, it is possible to calculate the maximum theoretical uptake capacity of fluoride adsorption onto both chitin samples, which is 2.47 and 40.3 mg/g, for 99 and 79% acetylated materials, respectively.

3.2. Biocomposite composition optimization, 1st stage

3.2.1. Effect of chitin content on the IEC

Three biocomposite samples containing 20, 40 and 60% of chitin and catalyst 1 (samples CC1, CC2 and CC3 from Table 1), were evaluated in terms of their IEC. The results are shown in Fig. 1.

As shown in Fig. 1, inasmuch as the biopolymer content increased in the biocomposite, the IEC also increased. This behavior was caused by an increasingly higher concentration of adsorption sites, i.e. primary amine and amide groups, as the chitin content was increased. In other words, when the chitin content was increased, the number of adsorption sites also increased and more of these groups were freed to interact with hydrogen ions. On the other hand, the physical interaction between chitin and the polymeric matrix is also important. As chitin content increased, the chitin flakes surface covered by the polymeric matrix and thickness of such a covering decreased. Hence the greater exposure of the chitin flakes improved the accessibility to the adsorption sites. It is important to mention that a content of chitin greater than 60% produced biocomposites with low chitin flakes anchorage on the polymeric matrix, since the mixing between these flakes and the polymeric matrix was inefficient. According to these results, 60% of chitin content was selected as the optimum to produce the biocomposite.

3.2.2. Effect of additive content on the IEC

Three biocomposite samples containing 1, 2 and 3% of additive (samples Add1, Add2 and Add3 from Table 1), were evaluated in terms of their IEC. It should be pointed out that no more than 3% of additive was used due to its high cost. The objectives to including such an additive were, on the one hand, to increase the quantity of potential adsorption sites on the biocomposite and, on the other hand, to supply functional groups able to act as reactive sites during the polymerization process, keeping the chitin adsorption sites intact.

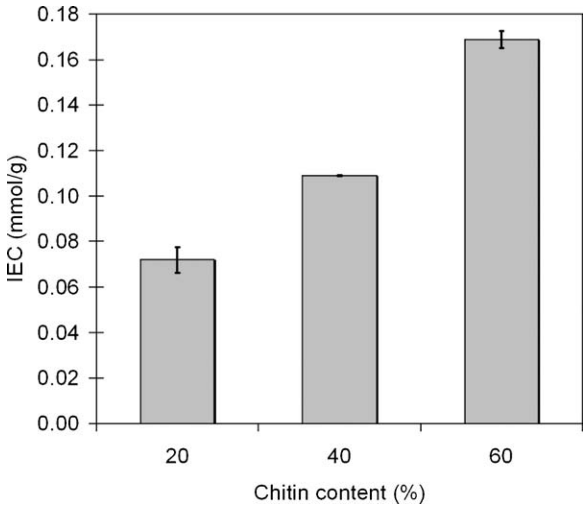

Fig. 1. Effect of chitin content on the IEC for chitin-based biocomposites.

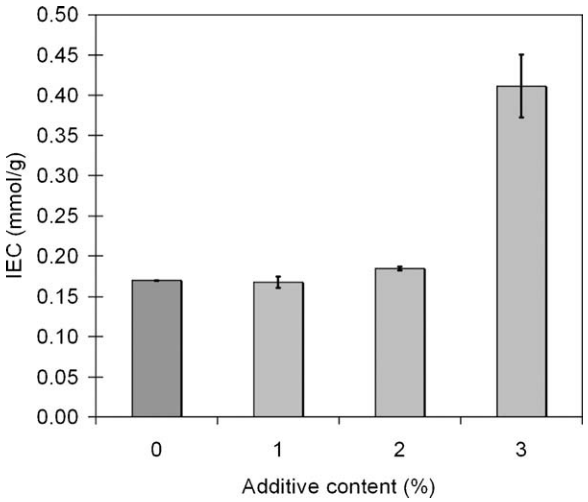

Fig. 2. Effect of additive content on the IEC of chitin-based biocomposites.

Fig. 2 shows that, in general, the IEC increased as the additive content increased, which was a consequence of a greater presence of functional groups. However, as can be observed from Fig. 2, when the additive content was 1 and 2% (w/w), the biocomposite IEC was only slightly improved. This was probably due to a chemical interaction between the additive and the polymer, causing the functional groups of the additive to disappear. However, an additive content of 3% (w/w) notably increased the IEC of the biocomposite, a fact which can be attributed to reactive functional groups (those that did not react with the functional groups of the polymer and are able to interact with fluoride). As a result, an additive content of 3% (w/w) was considered as optimum.

3.2.3. Effect of equilibrium pH on the fluoride adsorption capacity

Experiments were carried out in order to determine the influence of equilibrium pH on the fluoride adsorption capacity (q) of chitin-based biocomposites. Three fluoride adsorption experiments were performed using the biocomposite sample named pHS, according to the described adsorption method. Since primary amine groups are protonated as pH decreases from 8.5 to 4.5, the value at which they are fully protonated [3], an increase in the adsorption capacity was expected as the pH decreased between these values. The results obtained are shown in Fig. 3.

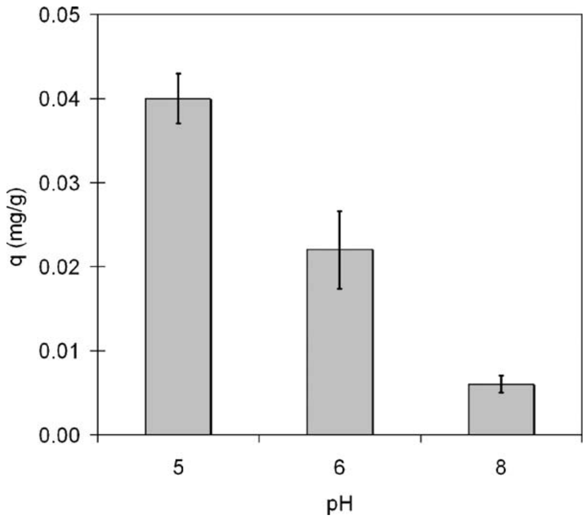

Fig. 3. Effect of equilibrium pH on fluoride adsorption capacity onto chitin-based biocomposite. $C_0 = 15$ mg/L and $T = 25$ °C.

The results reported in Fig. 3 corroborated the expected behavior of the adsorption capacity with respect to equilibrium pH, i.e. the lower the pH, the greater the fluoride adsorption capacity. These results agree with the slurry pH of sample pHS, which was 9.5. That is to say, at pH values lower than 9.5, the biocomposite surface was positively charged for the most part; thus, the fluoride sorption was induced. Nevertheless, pH values lower than 5 were not considered due to the adverse effect on the biocomposite chemical resistance. Besides, pH 5 could be achieved in a real continuous process.

3.2.4. Effect of biocomposites chitin degree of acetylation on the fluoride adsorption capacity

In this case, two biocomposites prepared with 99 and 79% acetylated chitin (samples DA1 and DA2 in Table 1) were evaluated in terms of their fluoride adsorption capacity; the results obtained are shown in Fig. 4.

Fig. 4 shows that the fluoride adsorption capacity increased as the degree of acetylation decreased, a fact that is directly associated with a greater concentration of primary amine group at a lower chitin acetylation. Furthermore, it is important to mention that the decrease in chitin crystallinity, related to its desacetylation degree, enhances the accessibility to adsorption sites [6]. In other words, chitin desacetylation progressively enhances the biocomposite adsorption capacity; however, both cost and solubility of the biopolymer also increased, which are drawbacks for chitin application in continuous adsorption processes. Based on these results, 79% acetylated chitin was selected as the best biopolymer option in this work.

3.2.5. Effect of chitin particle size on the fluoride adsorption capacity

Particle size of chitin was studied to determine its effect on the biocomposite adsorption capacity. Such knowledge would permit evaluation of the benefits of a grinding-classification of chitin flakes, before its use in the biocomposite synthesis. The received 79% acetylated chitin was classified into three particle size ranges: <1, 1–1.7, and >1.7 mm, which were used to synthesize biocomposites according to the thereafter optimum characteristics (samples PS1–PS3 in Table 1). Results of fluoride adsorption experiments onto such biocomposites are shown in Fig. 5.

As shown in Fig. 5, the biocomposite fluoride adsorption capacity was not affected by chitin particle size. This was because of similar density and accessibility of adsorption sites among different chitin particle sizes. On the one hand, the density of sites depends only on chitin chemical composition, which is the same among different chitin particle sizes, since all fractions came from the same chitin source. On the other hand, the accessibility to chitin sites does not depend on its surface area, as occurs with porous adsorbents, but rather depends on the chitin swelling capacity. Desacetylated chitin swells when it is in acid aqueous medium, i.e. primary amine groups protonation causes hydrogen bridges between chitin chains to be disrupted and, in turn, access of water molecules to the structure [35,36]. Such swelling modifies the chitin structure by opening channels to which other dissolved species can access the chitin adsorption sites. This phenomenon mainly occurs at the chitin amorphous regions; however, it has been proposed that chitin crystalline regions also can be modified by the swelling effect [35]. Since different particle sizes came from the same chitin source in this study, it is reasonable to say that their chemical structure and crystallinity degree were the same. Hence, it can be also expected that the swelling capacity among different particle sizes was similar and for this reason the accessibility to the chitin adsorption sites was also the same. Due to these results, it was determined that 79% acetylated chitin could be used as received.

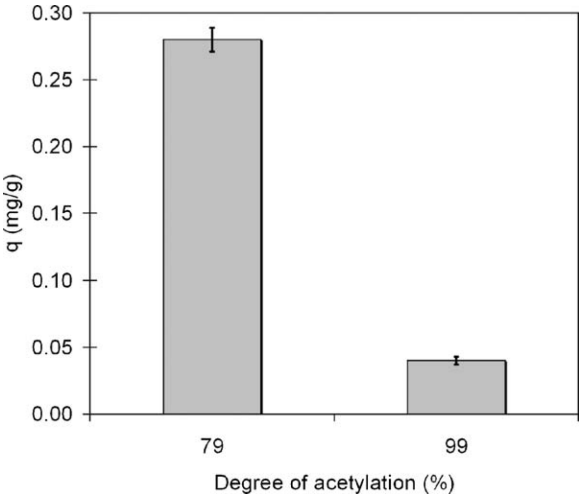

Fig. 4. Effect of degree of acetylation of chitin on the fluoride adsorption capacity of the biocomposite. C_0 = 15 mg/L, pH 5 and T = 25 °C.

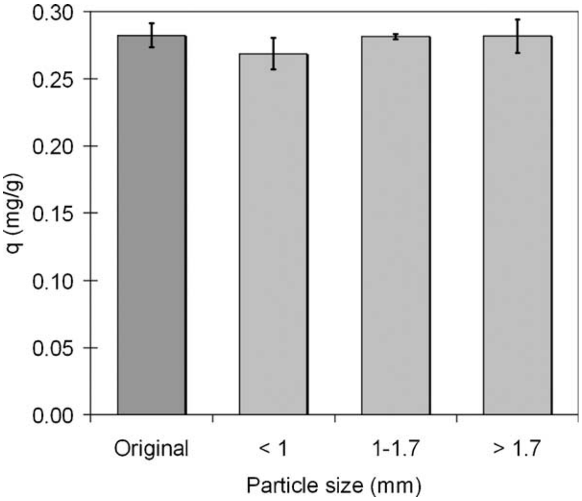

Fig. 5. Effect of chitin particle size on the biocomposites fluoride adsorption capacity. C_0 = 15 mg/L, pH 5 and T = 25 °C.

So far, the composition of the optimum biocomposite based on the adsorption capacity (named OBAC) included 60% (w/w) of 79% acetylated chitin and 3% (w/w) of additive, adding 1% of catalyst 1. Furthermore, pH 5 was determined to be an acceptable value for fluoride adsorption and, finally, the original particle size of chitin was determined to be suitable for synthesizing the biocomposites.

3.3. Biocomposite composition optimization; 2nd stage

3.3.1. Chemical reinforcement of chitin by the polymer

The chitin chemical reinforcement was tested by measuring its mass loss after being placed in contact with water at pH 5. Fig. 6 shows that, indeed, chitin biocomposite (OBAC) was more chemically resistant than pure chitin due to the physical and chemical interaction between both polymer and chitin.

The physical support occurred by an adhesion effect between chitin flakes and polymer, because of attractive forces between polymeric and biopolymeric chains. But also, the chemical support occurred by chitin–matrix interactions caused by chemical reactions between functional groups of both biopolymer and polymer during the polymerization process.

The polymeric matrix covered chitin flakes, thus decreasing the chitin exposure to the acid aqueous medium. However, such

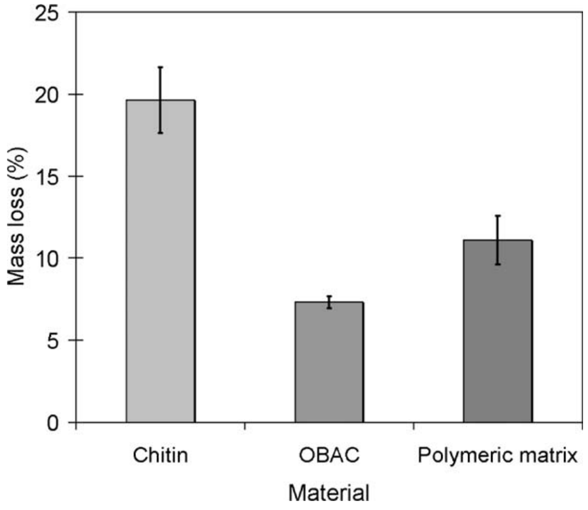

Fig. 6. Chemical resistance (measured as mass loss) of pure chitin, optimum biocomposite based on adsorption capacity (OBAC) and polymeric matrix when contacted with water at pH 5.

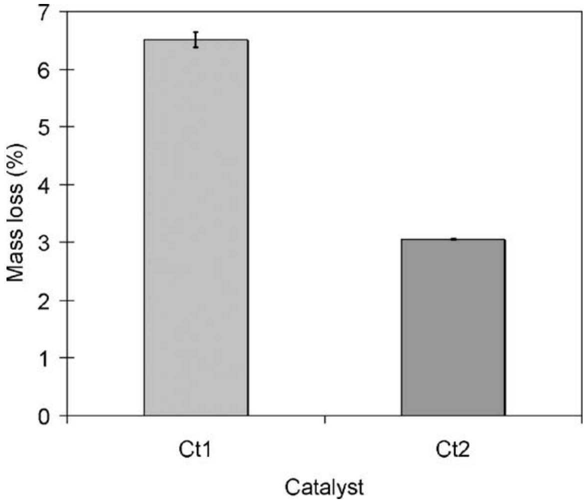

Fig. 7. Effect of the catalyst type on the chemical resistance (measured as mass loss) of the polymeric matrix at pH 5.

exposure was enough to keep the chitin swelling which is, as mentioned above, an important phenomenon to promote ion diffusion into chitin flakes. Based on these results, it can be said that the optimum chitin content on the OBAC balanced both support and exposure of chitin flakes.

Moreover, Fig. 6 shows that the polymeric matrix mass loss was also greater than that of the OBAC (around 11 and 7%, respectively). This could be understood since the polymeric matrix was also reinforced by the biocomposite, due to the aforementioned physical and chemical interactions between the polymeric and biopolymeric phases. Nevertheless, the OBAC mass loss of around 7% was still high. These results motivated optimization of the polymeric matrix composition, for which experiments were carried out to study the replacement of catalyst 1 for catalyst 2, and the advantage of the additive inclusion in terms of chemical resistance.

3.3.2. *Effect of catalyst type and its content on the chemical resistance*

Catalyst 2 (Ct2) was tested in order to improve the chemical resistance of the polymeric matrix, besides the catalyst 1 (Ct1). Polymeric matrix samples including only polymer and catalyst, either Ct1 or Ct2, were prepared (samples CatT1 and CatT2 in Table 1) and subjected to the chemical resistance test.

The polymeric matrixes containing either Ct1 or Ct2 are compared in terms of mass loss in Fig. 7. It can be observed that Ct2 improved the chemical resistance of the polymer, which could be attributed to a higher polymerization reaction conversion. Another reason for such improvement could be a greater entanglement of Ct2 inside the polymer structure. Ct2 has both a longer and more linear chemical structure than Ct1, which could produce such physical interaction. Due to these results, it was decided to use Ct2 instead of Ct1 in the synthesis of the following composites.

In order to optimize the Ct2 content, a series of experiments were conducted with different amounts of this catalyst (see Fig. 8). As it can be observed in Fig. 8, a practically constant mass loss of about 1.2% was produced with less than 10% of Ct2. However, according to *in situ* observations (reaction time and foam volume), 2% provided both fast and efficient polymerization and this is why this amount was selected as optimum. The observed mass loss of around 1.1% with Ct2 content of 0% may be due to an unavoidable loss of polymer when it was contacted with an acid aqueous medium for the first time. Additional experiments (data not shown) obtained data on mass losses of polymeric matrixes of only 0.5% when these were subjected to a second contact with acidified water. The observed mass loss of just 1.1% was much lower compared to the mass loss of 11% of the separated polymeric matrix (used for synthesis of the OBAC).

3.3.3. *Effect of additive content on the chemical resistance*

Since previously proposed additive has high affinity for water, it was assumed that such a component could be dissolved when contacted with water during the adsorption process. As a consequence, the additive content was studied to determine its effect on the chemical resistance of biocomposites. Polymeric matrix samples including polymer, catalyst 2 and the additive were prepared (samples CatC0 through CatC8 in Table 1) and subjected to the chemical resistance test. Results of such experiments are shown in Fig. 9, where it is possible to observe that the mass loss of the matrix increased in a semi-linear way with respect to additive content. This effect may be explained because the additive was weakly bonded to the polymer. Although its inclusion in the biocomposites improved the adsorption potential (measured by IEC in Fig. 2) its effect on chemical resistance was not advantageous for the purposes of this study. For example, the previous determined optimum additive content (3%) produced almost 5% of matrix mass loss, and when the additive content was lower than 1% the mass loss was decreased to just around 1%.

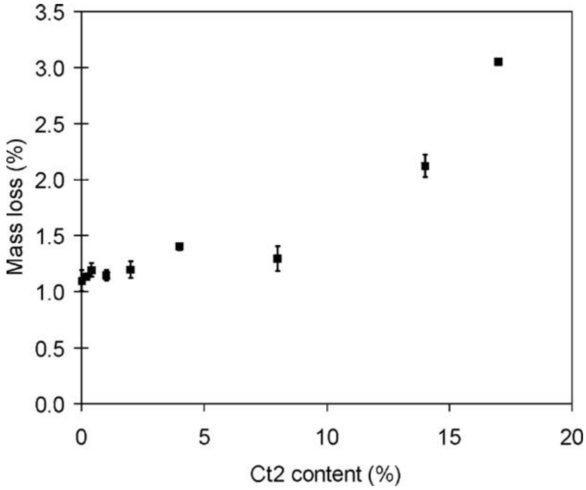

Fig. 8. Effect of the catalyst content on the chemical resistance (measured as mass loss) of the polymeric matrix at pH 5.

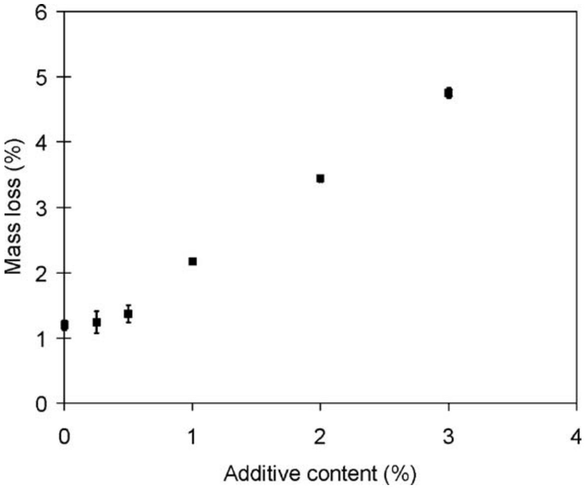

Fig. 9. Effect of the additive content on the chemical resistance (measured as mass loss) of the polymeric matrix at pH 5.

However, an additive content lower than 3% did not enhance the biocomposite adsorption potential in any significant way (see Fig. 2). Hence, in terms of adsorption capacity, it was not advantageous to include the additive in a percentage lower than 3%, but in terms of chemical resistance, it was not beneficial to add more than 1% of additive. Based on this analysis, it was decided to eliminate the additive from the final biocomposite chemical composition.

3.4. Final composition of optimized chitin-based biocomposite

Table 2 shows the final composition parameters of the optimum chitin-based biocomposite based on both adsorption capacity and chemical resistance (named OBACCR). It is important to mention that the adsorption capacity of OBACCR, under the same experimental conditions used in the experiments of the first optimization stage, was 0.29 mg/g, a similar value to the one previously achieved with the first optimization stage (see Fig. 5). Previous studies of chitosan-based sorbents have reported fluoride sorption capacities in the range of 1–6 mg/g, under similar experimental conditions to those considered as optimum in this work [5,29–31]. Such a difference can be mainly attributed to the high DA (79%) of the chitin used to obtain the OBACCR. Besides, the chemical resistance of those sorbents has not been reported and, thus, it is not totally valid to make a direct comparison of such materials with OBACCR. The OBACCR mass loss when it was placed in acidified water (pH 5) was just 1.5%, which was slightly greater than the achieved value with the polymeric matrix without the additive (1.1%). It is important to say that the total organic carbon dissolved in supernatant water after mass loss test of the OBACCR was 32 mg/L. Nevertheless, once the same OBACCR sample was again contacted with water at initial pH 5, the total organic carbon was only 1.2 mg/L. These results may mean the necessity of an acid conditioning step of the OBACCR before its use in the continuous adsorption process.

Table 2
Optimum composition parameters for the chitin-based biocomposite based on both adsorption capacity and chemical resistance (OBACCR). The values are reported in mass percent.

Parameter	Value
Polymer content	40%
Catalyst content	2%
Additive content	0%
Chitin content	60%
Degree of acetylation of chitin	79%
Chitin particle size	~1 mm

3.5. Characterization of the OBACCR

3.5.1. Surface area

The surface area of the OBACCR was 0.08 m^2/g, a much lower value than the 79% acetylated chitin one, 0.32 m^2/g. Such a decrease was due to the presence of the polymeric matrix on the biocomposite. This matrix covered the chitin flakes surface, filling the pores and cracks of such flakes. This was corroborated when the biocomposites were observed through scanning electron microscopy (images not shown); composites were smoother than the surface of the original chitin.

3.5.2. Ion exchange capacity (IEC)

The IEC of the OBACCR was 0.38 mmol/g, 80% lower than the 79% acetylated chitin value (2.12 mmol/g). Such decrease was an effect of the polymeric support, which decreased the chitin exposure to the aqueous medium and, in turn, reduced the extent of hydrogen ion uptaking during the IEC experiment. However, such lower exposure enhanced the chemical resistance of the biocomposite compared with the pure chitin (see Fig. 6). These results confirmed the inevitable compromise between adsorption capacity and chemical resistance of the chitin-based biocomposites; this compromise is controlled by the exposure level of chitin flakes.

3.5.3. Elemental analysis

The nitrogen content of the OBACCR determined by elemental analysis was 6.6%. This result was practically equal to the pure chitin one (6.3%), which means that the polymeric matrix contributed with a quantity of nitrogen atoms sufficient to keep the nitrogen content on the biocomposite in a similar value to the received chitin. However, the nitrogen atoms in the polymeric matrix were not in the form of primary amine groups, but rather as secondary amine groups which are part of the urethane groups. Such nitrogen atoms exhibit a higher resistance to protonation owing to steric effects, as occurs with acetamide groups of chitin, whit a pKa of 3.5 [8]. In other words, a very low pH would be required in order to protonate such secondary amine groups. These findings and the proposed adsorption pH caused the potential anions adsorption sites of the OBACCR to be less than in the raw chitin. In addition, both chemical and physical interactions between chitin and polymeric matrix caused blockage of adsorption sites. All this caused the OBACCR fluoride adsorption capacity to be 70% lower than that of the original 79% acetylated chitin (0.29 and 0.95 mg/g, respectively). This fact reconfirmed the blockage of the chitin adsorption sites when the biopolymer was mixed with polymeric matrix.

3.5.4. X-ray diffraction (XRD)

The XRD spectra of chitin (79% acetylated), optimum biocomposite and final polymeric matrix were obtained (see Fig. 10). These spectra show that chitin exhibits a narrow high peak, at $2\theta = 20^\circ$, and a wide lower peak at $2\theta = 11^\circ$, which is a typical pattern of a chitinous material. It is also clear that the polymeric matrix structure is mainly amorphous, which is revealed by the absence of peaks on its XRD spectrum.

The OBACCR XRD spectrum revealed the mixture of chitin and polymeric matrix, showing an intermediate behavior between both phases, due to a dilution effect by the polymeric matrix onto chitin in the biocomposite. Nevertheless, chitin crystallinity was even kept in the biocomposite, which is important in terms of chemical resistance.

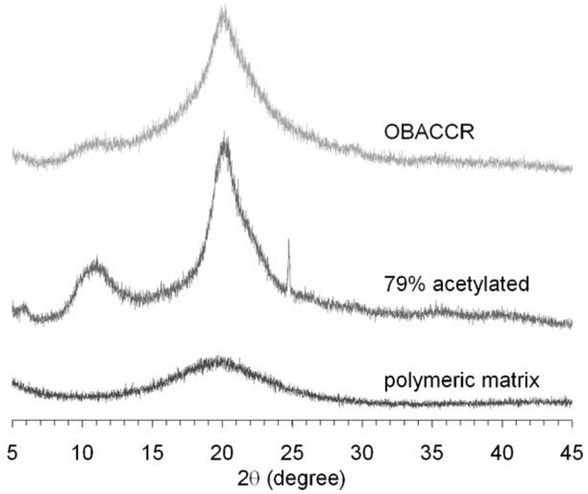

Fig. 10. XRD spectra of the optimum biocomposite (OBACCR), 79% acetylated chitin and the optimized polymeric matrix.

Previous studies have proposed that part of the chitin crystallinity is lost when the material is placed in an acid aqueous medium [35], due to the progressive protonation of primary amine groups. Such protonation generates repulsive forces that open spaces between neighbor chitin chains [14], which causes chitin swelling, by entering both water molecules and other dissolved species (e.g. anions), enhancing the chitin diffusional properties. In this study, the optimum biocomposite swelling was evident after it was equilibrated with an aqueous medium at pH 5. Once the supernatant solution was separated, the biocomposite wet mass was around three times greater than its dry mass.

Finally, it is important to say that brittleness (caused by the high crystallinity) is a chitin's drawback if it is applied in a continuous adsorption process. In this work, the problem was overcome by using an amorphous polymeric matrix; this condition produced higher capacity to absorb and dissipate mechanical stress. Hence, the inclusion of such a polymer in the biocomposite composition enhanced the mechanical resistance of the OBACCR. This enhancement is important in terms of the application of the material in a continuous adsorption process, when it is under relatively high hydrostatic pressures.

3.5.5. Fourier transform infrared spectroscopy (FTIR)

The main IR bands of 79% acetylated chitin spectrum were retained once chitin was mixed with the optimized polymeric matrix, especially those related to primary amine group, located at 1595 and 3295 cm^{-1} (see Fig. 11). The retention of bands confirmed the preponderant physical interaction between chitin and polymeric matrix over the chemical interaction. Primary amine groups are able to react chemically with the polymer functional groups; however, such a reaction did not occur to a large extent owing to the low achievability of amine groups resulting from the high chitin crystallinity. Nevertheless, a small portion of the total primary amine groups located on the chitin flakes surface could react, contributing to the chitin–matrix anchorage.

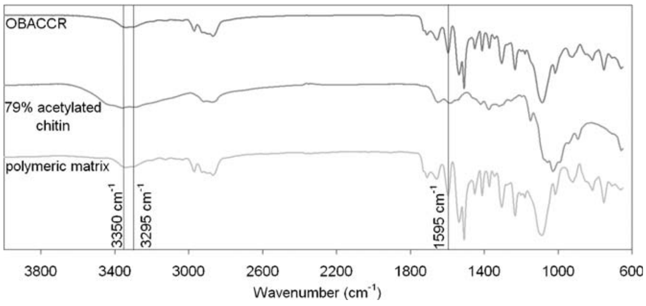

Fig. 11. FTIR spectra of 79% acetylated chitin, optimum biocomposite (OBACCR) and the optimized polymeric matrix.

Regarding the hydroxyl groups, their band (3350 cm^{-1}) slightly decreased when chitin was mixed with the polymeric matrix (see Fig. 11). Thus, the hydroxyl groups on the chitin surface could also participate in the chemical interaction between chitin and polymeric matrix, since these groups are also prone to react with the polymer functional groups.

The results reported herein suggest that the OBACCR properties make it a promising adsorbent material to remove fluoride and other anions in aqueous medium. It is evident that, in order to complete this research, future work should include the study of adsorption at equilibrium, adsorption kinetics, and the application of the biocomposites in continuous adsorption processes.

Finally, it is important to mention that diverse studies have proved that chitin/chitosan derivatives are excellent adsorbent materials of metal cations and organic contaminants [6,37]. Hence, it is likely that the optimized chitin-based biocomposite, produced in this study, work as an efficient adsorbent of such substances, making it a versatile adsorbent material.

4. Conclusions

A biocomposite based on chitin and a polymeric matrix was obtained, capable of adsorbing fluoride from aqueous solutions.

The exposure level of chitin decreases by both chemical and physical interactions with the polymeric matrix when these two are mixed to produce biocomposites. However, the chitin adsorption properties were retained and optimized by improving the biocomposite composition.

A decrease in the degree of acetylation of chitin promotes a higher fluoride adsorption capacity. In addition, the solution pH is a critical fluoride adsorption parameter, since fluoride adsorption notably increases as pH decreases from 8 to 5.

Although chitin crystallinity is not affected when mixed with the polymeric matrix, part of crystallinity is lost when the biocomposite is placed in aqueous medium due to the chitin swelling capacity.

The optimum composition of the chitin-based biocomposite contains 60% biopolymer, 40% polymer and 2% catalyst 2. Moreover, the particle size of chitin contained in the biocomposites does not have any effect on the adsorption capacity, and the biocomposites chemical resistance is notably enhanced (mass loss of 1.5%) compared to pure chitin (mass loss of 19%).

The optimized biocomposite is able to adsorb 0.29 mg of fluoride per gram of material at an initial concentration of 15 mg/L and pH 5.

Finally, according to the physicochemical characteristics of the optimum chitin-based biocomposite (OBACCR), it is a promising adsorbent material that can be used in continuous processes to remove a wide range of contaminants present in the aqueous phase.

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References

[1] S.N. Kartal, Y. Imamura, Bioresour. Technol. 96 (2005) 389–392.
[2] L. Dambies, T. Vincent, E. Guibal, Water Res. 36 (2002) 3699–3710.
[3] R. Navarro, J. Guzman, I. Saucedo, J. Revilla, E. Guibal, Macromol. Biosci. 3 (2003) 552–561.
[4] R.S. Bai, T.E. Abraham, Bioresour. Technol. 87 (2003) 17–26.
[5] W. Ma, F.Q. Ya, M. Han, R. Wang, J. Hazard. Mater. 143 (2007) 296–302.
[6] E. Guibal, Sep. Purif. Technol. 38 (2004) 43–74.
[7] N. Li, R.B. Bai, C.K. Liu, Langmuir 21 (2005) 11780–11787.
[8] C.H. Niu, B. Volesky, D. Cleiman, Water Res. 41 (2007) 2473–2478.
[9] D. Zhou, L.N. Zhang, J.P. Zhou, S.L. Guo, Water Res. 38 (2004) 2643–2650.
[10] J.A.R. Filho, E.E. Bach, R.R. Vargas, D.A.W. Soares, A.A.A. de Queiroz, J. Appl. Polym. Sci. 92 (2004) 1310–1318.
[11] W.S.W. Ngah, A. Kamari, Y. Koay, Int. J. Biol. Macromol. 34 (2004) 155–161.
[12] V.M. Boddu, K. Abburi, J.L. Talbott, E.D. Smith, R. Haasch, Water Res. 42 (2008) 633–642.
[13] S. Hasan, T.K. Ghosh, D.S. Viswanath, V.M. Boddu, J. Hazard. Mater. 152 (2008) 826–837.
[14] S.S. Silva, S.M.C. Menezes, R.B. Garcia, Eur. Polym. J. 39 (2003) 1515–1519.
[15] C. Jeon, W.H. Holl, Water Res. 37 (2003) 4770–4780.
[16] G. Annadurai, L.Y. Ling, J.F. Lee, J. Hazard. Mater. 152 (2008) 337–346.
[17] J.R. Evans, W.G. Davids, J.D. MacRae, A. Amirbahman, Water Res. 36 (2002) 3219–3226.
[18] E. Guibal, M. Jansson-Charrier, I. Saucedo, P.L. Cloirec, Langmuir 11 (1995) 591–598.
[19] G. Rojas, J. Silva, J.A. Flores, A. Rodriguez, M. Ly, H. Maldonado, Sep. Purif. Technol. 44 (2005) 31–36.
[20] WHO, Guidelines for Drinking-Water Quality [Electronic Resource]: Incorporating First Addendum, vol. 1, Recommendations, 2006, pp. 375–377.
[21] P.T.C. Harrison, J. Fluorine Chem. 126 (2005) 1448–1456.
[22] C.S. Boruff, Ind. Eng. Chem. 26 (1934) 69–71.
[23] P.L. Bishop, G. Sansoucy, J. Am. Water Works Assoc. 70 (1978) 554–559.
[24] F.J. Maier, Am. J. Public Health 37 (1947) 1559–1565.
[25] D. Clifford, S. Subramonian, T.J. Sorg, Environ. Sci. Technol. 20 (1986) 1072–1080.
[26] T.J. Sorg, J. Am. Water Works Assoc. 70 (1978) 105–112.
[27] D. Cohen, H.M. Conrad, Desalination 117 (1998) 19–35.
[28] S. Annouar, M. Mountadar, A. Soufiane, A. Elmidaoui, M.A. Menkouchi Sahli, Desalination 165 (2004) 437.
[29] S.P. Kamble, S. Jagtap, N.K. Labhsetwar, D. Thakare, S. Godfrey, S. Devotta, S.S. Rayalu, Chem. Eng. J. 129 (2007) 173–180.
[30] N. Viswanathan, S. Meenakshi, J. Fluorine Chem. 129 (2008) 503–509.
[31] N. Viswanathan, C.S. Sundaram, S. Meenakshi, J. Hazard. Mater. 161 (2009) 423–430.
[32] L. Furlan, V.T. de Fávere, M.C.M. Laranjeira, Polymer 37 (1996) 843–846.
[33] E. Guibal, A. Larkin, T. Vincent, J.M. Tobin, Ind. Eng. Chem. Res. 38 (1999) 4011–4022.
[34] W.S.W. Ngah, S. Fatinathan, Chem. Eng. J. 143 (2008) 62–72.
[35] Z. Cui, Y. Xiang, J.J. Si, M. Yang, Q. Zhang, T. Zhang, Carbohydr. Polym. 73 (2008) 111–116.
[36] R. Seoudi, A.M.A. Nada, Carbohydr. Polym. 68 (2007) 728–733.
[37] G. Crini, P.-M. Badot, Prog. Polym. Sci. 33 (2008) 399–447.