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# Chitin Based Biocomposites for Removal of Contaminants from Water: A Case Study of Fluoride Adsorption

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## 1. Introduction

Around the world, safe water for human consumption and use is more and more scarce, due to its increasing demand and to the natural or anthropogenic contamination of the water resources (Jackson et al., 2001). World population grew 15% only in a decade from 1990 to 2000, that is to say 789 million people, which means an equal quantity of new water consumers (WHO, 2000). In addition, an annual mortality rate of 2.2 million of people associated to contaminated water consumption was reported by the World Health Organization (WHO) in 2000 (WHO, 2000). Such contamination, either natural or anthropogenic, affects lakes, rivers or groundwater; from these reservoirs, the last represents one of the most important water sources for human consumption.

On one hand, the natural contamination of groundwater occurs due to geochemical phenomena, which take place during the natural cycle of water, when this comes into contact with underground rocks, reaching chemical equilibrium which causes in turn dissolution of part of such rocks. Due to these facts, groundwater contains diverse chemical species, and some of them can be considered as contaminants, based on the negative effects of each substance in water on the human health and the integrity of other living beings.

On the other hand, the anthropogenic contamination of groundwater is mainly due to emissions of some industries e.g. mining, textile and metal-mechanic. Other human activities as agriculture are also sources of water contamination with fluoride due to the intensive use of fertilizers.

People from arid regions around the world use groundwater as main source to satisfy their water necessities. In Mexico, for example, 37% of the total water consumption is groundwater, according to data generated in 2008 (CONAGUA, 2010). Nevertheless, the use of groundwater for human consumption in humid regions is also important, due to the increasing contamination of surface water. These facts have increased the need to eliminate contaminants from water before its use by human beings, which can be achieved by means of diverse methods.

## 2. Typical methods to remove contaminants from water

The selection of the method to remove a specific water contaminant depends on: chemical speciation of such contaminant, concentration, presence of suspended solids, required

system size, influent flow variability, etc. (Clifford et al., 1986). Also, the treatment cost must be evaluated in order to minimize it and have a good cost-benefice balance. The most used methods for water contaminants removal are chemical precipitation, membrane separation, ion exchange, electrochemical methods and adsorption (Clifford et al., 1986). One of the preferred methods, especially at low concentrations of contaminants, is adsorption, due to its low cost, easy operation and little use of chemical additives, as well as the possibility of reusing the adsorbent materials. At industrial scale, the adsorption process is carried out in packed columns. Figure 1 shows a typical scheme of an adsorption system, as well as an example of a real adsorption system that uses activated carbon as adsorbent.

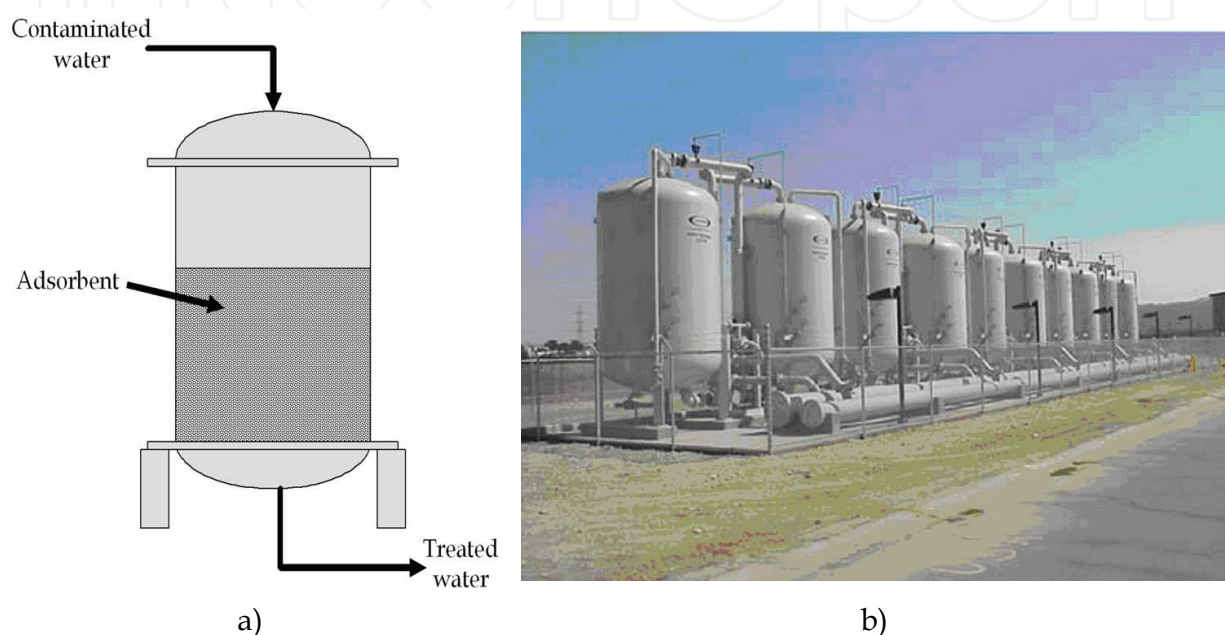


Fig. 1. a) Scheme of a continuous adsorption system (USEPA, 2002). b) Example of an adsorption system consisting of activated carbon columns (Alcan, 2005).

### 3. Biosorption

The list of typical adsorbent media includes materials produced by means of processes which consume great quantities of energy and/or chemical substances (e.g. activated carbon) involving high environmental costs. Therefore, there is a need of cheaper and more sustainable materials. This need has promoted the increasingly scientific study of biosorbents during the last decades. Biosorbents are adsorbent materials obtained from biomass by relatively simple processes that use considerably lower quantities of chemical substances and energy, compared to the production of typical adsorbents. Besides, most biosorbents are obtained from materials typically considered like byproducts or wastes.

The biomass is naturally composed by very diverse substances as proteins, polysaccharides, pigments, carboxylic acids, etc., which have many functional groups as hydroxyl, carboxyl, carbonyl, tiol, sulfhydryl, sulfonate, phosphonate, amine, amide, etc. (Volesky, 2003). Under determined conditions, such groups can interact physically or chemically with contaminants present in water, which causes their retention on the surface of the biosorbent, that is to say, the biosorption occurs (AWWA, 1999; Volesky, 2003).

4. Biosorbents

4.1 Sources and applications

Only certain types of biomass have the capacity and selectivity to remove an appreciable quantity of a contaminant from an aqueous medium and, thus, can be considered for use in high scale biosorption processes. Nevertheless, at present, many biomass-derived materials have been studied as biosorbents, as it can be seen in Table 1.

Source	Examples
Vegetable matter	Aquatic plants, canola, moss, peat moss, cellulosic materials, seaweed.
Agricultural residues	Apple residues, banana residues, coconut husk, palm fiber, corncob, olive residues, peanut husk, rice husk, tea leafs, coffee residues, beet residues.
Other	Starch, human hair, eggshell, residual water sludge, scallop shell, crustaceans' residues, chitin, chitosan.

Table 1. Example of the variety of sources from which have been obtained the biosorbents studied at present (Volesky, 2003).

Biosorbents have been studied as ion removers, being heavy metal (cations) or anions. The removal of cations by biosorbents from water has been considered as more viable than the removal of anions, since most chemical groups of biomass act as ligands, i.e. as electron donors, which enable them to form coordination complexes with heavy metals. Only some chemical groups, specifically amine groups (primary, secondary and tertiary) are capable to acquire positive electrical charge at acid pH values, because the protonation phenomenon takes place. Protonation occurs due to the chemical nature of amine groups, which act as Brönsted-Lowry bases regarding that these accept hydrogen ions, or as Lewis bases regarding they donate their nitrogen free electron pair to the hydrogen ions. Hence, nitrogen acquires positive charge and the amine group becomes an anion adsorption site. Two of the biosorbents that have high density of amine groups are chitin and its main byproduct, chitosan.

4.2 Chitin and chitosan

4.2.1 Nature and purification

Chitin is the second natural polymer in abundance, exceeded only by cellulose, and it is found in nature mainly as constituent of invertebrates' exoskeleton (Pastor, 2004). This biopolymer was discovered in 1811 by H. Braconnot, who purified it from fungi. In 1823, A. Odier obtained the chitin from beetles and named the biopolymer from the greek word "χιτῶν", which means cover or wrapper. In 1859, C. Rouget obtained "modified chitin" from alkaline chitin treatment with sodium hydroxide. However, in 1894 F. Hoppe-Seyler (who ignored Rouget's studies) subjected chitin to a new alkaline treatment with potassium hydroxide at 180°C; the product was very soluble in acetic and hydrochloric acids and Hoppe-Seyler named it "chitosan" (Pastor, 2004).

The chemical name of chitin is poly-[β-(1-4)-2-acetamide-2-deoxy-D-glucopyranose], which is conformed by repetitive units of saccharide rings linked by β-(1-4) bonds, with presence

of an acetamide group jointed at C2 position (Figure 2a), composed in turn by acetyl and secondary amine groups.

Chitin is obtained by alkaline deproteinization, acid demineralization and decoloration by organic solvents contact of crustaceans' wastes (Pastor, 2004). Although this chemical method is the most known and used, a more sustainable method has been recently developed in Mexico, specifically in the Universidad Autonoma Metropolitana Iztapalapa (UAMI). Such method consists of a biological step, where crustacean wastes are partially demineralized and deproteinized by lactic fermentation. The second step consists of chemical elimination of residual pigments, minerals and proteins from the solid produced in the first step (Cira et al., 2002). This novel process produces chitin with similar composition compared to the chitin obtained by the purely-chemical method, but with considerable savings of chemical substances and energy. The developed technology at the UAMI has been transferred to a local company, which will allow to exploit the high potential of Mexico as chitin producer. This country produces, for example, about 100,000 tons of shrimp per year (CONAPESCA, 2007), from which around 40% are chitinous wastes (Cira et al., 2002). At present, only 5% of such wastes are used in farming activities. The rest of the chitinous wastes from shrimp are discarded and represent an important environmental problem (Cira et al., 2002).

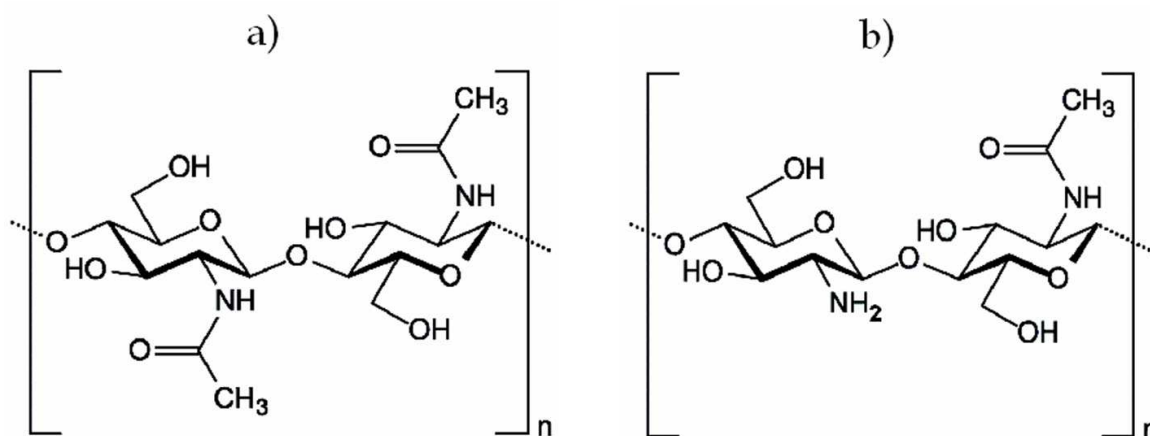


Fig. 2. Chemical structures of a) chitin and b) chitosan.

Chitosan, poly- $[\beta$ -(1-4)-2-amino-2-deoxy-D-glucopyranose], has a very similar chemical structure to that of chitin (Figure 2b). However, a part of its repetitive units does not have the acetyl group or, in other words, such units have primary amine groups. Thus, chitosan is a product of the deacetylation process of chitin, which can be partially or totally deacetylated. In fact, the typical process to obtain chitosan consists on the chitin deacetylation by contacting the biopolymer with a concentrated alkaline solution at temperatures over  $60^\circ\text{C}$  (Pastor, 2004). Nevertheless, the degree of deacetylation (DD) of chitin is variable and depends on the process conditions (alkali concentration, contact time, temperature, etc.), which produces degree of deacetylation values from 0 to 100%. Because of this, chitin is known as the biopolymer which has a DD from 0 to 60%; likewise, when chitin has been deacetylated over 60%, the biopolymer is named chitosan. It is important to say that such convention is still in debate in the scientific community; in fact, some researchers consider chitin only between 0 and 50% of deacetylation (Sengupta, 2007). Besides, the use of the degree of acetylation (DA) rather than the degree of deacetylation as a way to distinguish between chitin and chitosan is common. Both parameters, DD and DA,



are complementary, since a DD of 0% is equivalent to a DA of 100% and a DD of 100% is equivalent to a DA of 0%. However, owing to its greater use in cited literature, only DA will be used hereafter.

The importance to know the DA is based on the great difference of chitin and chitosan properties, which are evident by the greater reactivity and, in general, greater sensibility of chitosan to the variability of environment physicochemical conditions, especially the pH. Such sensibility is due to the higher density of primary amine groups of chitosan respect to that of the chitin.

Other important difference between chitin and chitosan is the greater crystallinity of the former. The lower crystallinity of chitosan increases the accessibility to the adsorption sites of the biopolymer. A chitin with DA of 100% has a highly crystalline structure, which is arranged in one of three molecular forms, named  $\alpha$ ,  $\beta$  y  $\gamma$ -chitin, respectively (Pastor, 2004). The  $\alpha$ -chitin is the most common form of this biopolymer (Carlstrom, 1957), present in crustaceans as shrimp, from which nowadays is obtained the most commercial chitin (Peesan et al., 2003). The  $\alpha$ -chitin is characterized by an antiparallel arrange of its chains; in other words, adjoining chitin chains run in opposite directions (Pastor, 2004). This type of arrange produces a greater union between biopolymeric chains due to created forces by hydrogen bonds, which causes in turn the formation of orthorhombic units (Peesan et al., 2003; Pastor, 2004; Zhou et al., 2005), with axis longitude of 0.5, 1.0 and 1.8 nm, respectively (Carlstrom, 1957), and right angles between each pair of axis. Such crystallinity is decreased during the deacetylation process, due to the removal of a portion of the acetyl groups from the chitin structure and, thus, to the greater presence of primary amine groups. These facts change the intra and intermolecular interactions, conformed mainly by hydrogen bonds (Ramírez-Coutiño et al., 2006), and generate amorphous zones in the biopolymer, with swelling capacity higher than that of crystalline zones, owing in part to the great affinity of primary amine groups to water. Summarizing, chitosan has a lower crystallinity than chitin and, therefore, is more susceptible to hydration and dissolution in aqueous medium, especially at low pH values.

#### **4.2.2 Application of chitin and chitosan in water treatment**

Since chitin was discovered, it has been object of numerous studies in order to understand its properties and find its application in very diverse fields. Nowadays, chitin and chitosan have application in pharmaceutical, biomedical, food, agricultural, paper, cosmetic and textile industries, as well as in chromatography and water treatment (Pastor, 2004). At present, the application of chitin and chitosan in water treatment focuses mainly in coagulation-flocculation processes to remove organic residues, suspended solids, amino acids and dyes (Pastor, 2004). Nevertheless, this way of application of the biopolymers implies the loss of the material, because the added material to the process is not reused, which contributes to the generation of sludge which must be after processed or confined. Due to this disadvantage, scientific studies have focused on other applications of chitin and chitosan in water treatment, especially as biosorbents in continuous adsorption processes, where these materials can be regenerated and reused.

#### **4.2.3 Biosorption onto chitin and chitosan**

Chitin and chitosan have been widely studied as biosorbents of cations (mainly heavy metals) and to a lesser extent as biosorbents of anions (metals, metalloids and organics) and organic compounds. Table 2 shows a series of examples of studies regarding this.

Chitin has been little studied as biosorbent compared to chitosan, due to the concentration of primary amine groups in chitosan. Such chemical groups are the main responsible of adsorption either of cations (by chelation), or anions (by electrostatic attraction) or polar molecules (by interactions as ion-dipole, dipole-dipole, van der Waals forces, etc.). However, chitin also can have a considerable density of primary amine groups even at high DA values; such density can be enough to make chitin a competitive biosorbent compared to other materials. Theoretically, 100% acetylated chitin has about 5 mmol/g of nitrogen. For example, if a certain mass of chitin is 20% deacetylated, the density of primary amine groups would be 1 mmol/g, which would be equivalent to a lead removal potential of 207 mg/g, value greater than the greatest reported capacity for typical adsorbents as activated carbon, around 100 mg/g (Sekar et al., 2004; Issabayeva et al., 2006). Besides, chitin has advantages compared to chitosan as a lower solubility in acid medium and lower cost.

Removed species	Contaminant / biopolymer	Reference
cation	Al/ Qs	(Septhum et al., 2007)
cation	Cd / Qs	(Evans et al., 2002)
cation	Co / Qs	(Minamisawa et al., 1999)
anion	As / Qs	(Kwok et al., 2009)
anion	Au, Se, Cr, V / Q	(Niu & Volesky, 2003)
anion	Remazol black 13 reactive / Qs	(Annadurai et al., 2008)
anion and polar molecule	palm oil residues / Qs	(Ahmad et al., 2005)

Table 2. Examples of contaminants removal studies by biosorption onto chitin and chitosan. The abbreviations Q and Qs mean chitin and chitosan, respectively.

4.3 Advantages and disadvantages of biosorbents

Some of the advantages of the biosorbentes are the following: (Volesky, 2003):

- Their obtaining sources are abundant in most of cases.
- Their cost is low, due to the use of byproducts or wastes.
- Their adsorption capacities can be competitive with commercial grade absorbents.
- The improvement of their adsorption capacity by diverse treatments is feasible.
- Their regeneration and reuse is possible.

The main disadvantages of the biosorbents are the following:

- Extreme variation of pH and temperature denaturalize them.
- Their physical and morphological properties restrict their application in packed columns, since the obstruction of these is possible.

The first of these disadvantages can be overcome in an adsorption process because pH and temperature are controllable variables that can be set at not extreme values, especially in water treatment for human consumption.

Finally, both of the mentioned disadvantages of the biosorbents can be overcome by supporting and/or reinforcing them.

4.4 Biocomposites

The physical and chemical resistance of the biosorbents can be improved by producing biocomposites i.e. the addition or mixing of the biosorbents into or with a supporting and/or reinforcing matrix. In addition, the morphological drawbacks of the biosorbents can

be also overcome by producing biocomposites, since during their obtaining process it is possible to give hydrodynamic shapes to the particles of the material. In other words, the biocomposites can be produced in such way that, when they are placed inside of an adsorption column, a porous bed is obtained. Such bed must allow water to flow through it. However, despite the great quantity of scientific studies about the biosorbents-based biocomposites, at present there is not commercial biocomposites for water treatment. This situation can be mainly attributed to the low physical and chemical stability of the produced materials, which does not allow their application under real process conditions.

The biosorbents are supported/reinforced by means of matrixes which are frequently of synthetic nature (organic or inorganic) such as polymers and minerals, or the biosorbents are crosslinked with itself, by adding adequate chemicals. Table 3 shows the major methods to produce biocomposites, their description, and the most important drawbacks.

It is important to stand out that the adsorption capacity and the intraparticle diffusion of the biocomposites are lower than that of the pure biosorbents, regardless the method used to support/reinforce the biosorbents. Therefore, one of the most important aims of the study of the biocomposites is to maximize the reinforcing of the biosorbents and keeping, at the same time, their original adsorption capacity as much as possible.

One of the methods that have been used to overcome the loss of adsorption capacity of the biocomposites with regard to the biosorbents is the use of additives. An additive should be physically or chemically affine to the biosorbent and, at the same time, should have chemical groups that can act as adsorption sites of the contaminant of interest, or remains inert toward the biosorbent, at least.

#### **4.5 Biosorption onto chitin/chitosan-based biocomposites**

As the rest of the biosorbents, chitin and chitosan show the typical aforementioned disadvantages of its nature. Thus, the support/reinforcement of both biopolymers by means of biocomposites synthesis has been a matter of many studies. Table 4 shows a series of examples on the biosorption onto chitin/chitosan-based biocomposites. As can be seen in Table 4 and as it was aforementioned for the pure biosorbent, chitosan has also been preferred by researchers in order to obtain biocomposites to remove contaminants from water. Nevertheless, chitin has a great potential as biosorbent, above all if it is considered its greater chemical resistance compared to chitosan.

One reason used to justify the use of chitosan instead of chitin is its greater solubility, especially because many of researchers look for the maximum adsorption potential of these biopolymers by separating and spreading out the polymeric chains by dissolution processes. Such processes are expected to enhance the accessibility toward the adsorption sites and make more easy-to-use the chitin/chitosan. However, the dissolution eliminates the original crystallinity of the biopolymer, which decreases its physical and chemical resistance and, thus, the support/reinforcement of the biopolymer becomes essential. These facts make necessary to use additional chemical substances which represent an increase of the economic and environmental cost to produce the chitin/chitosan-based biocomposites.

Consequently, the study of novel ways to support/reinforce of chitin and chitosan that does not necessarily depend of their dissolution is important. In this manner, the inherent physical and chemical resistance of both biopolymers, particularly chitin, could be utilized. A possible way to synthesize chitin/chitosan-based biocomposites without the need of dissolving the biopolymer is by mixing of chitin with the support/reinforcement matrix.



Method	Description	Restrictions
Entrapment	The biosorbent particles keep fixed by means of other material e.g. a gel in which they are inserted.	<ul style="list-style-type: none"><li>• The matrix causes problems of mass transport of the contaminants towards inside of the biosorbent particles.</li><li>• Part of the effective treatment volume of the biosorbent is lost.</li><li>• If the proportion of biosorbent is excessive, the biocomposite becomes fragile.</li></ul>
Encapsulation	The biosorbent particles are confined inside of a wrapper conformed by a permeable membrane.	<ul style="list-style-type: none"><li>• The development of adequate membranes for this application is still incipient. For example, the existent membranes at the present are easily broken.</li></ul>
Adhesion	The biosorbent particles are joined by means of a sticky substance.	<ul style="list-style-type: none"><li>• The sticky substance can be an additional limitation to the contaminants diffusion.</li><li>• The adhesive could deteriorate the mechanical properties of the biocomposite compared to the pure biosorbent.</li></ul>
Crosslinking	A crosslinker chemically reinforce the biosorbent, by creating bonds between adjoining molecules or polymeric chains of the biosorbent.	<ul style="list-style-type: none"><li>• Macro-particles are not produced.</li><li>• Part of the potential adsorption sites is obstructed.</li><li>• Additional costs by the crosslinking process.</li><li>• Possible generation of undesirable residues.</li></ul>
Anchorage	The biosorbent chemically adhere on a pre-conditioned surface.	<ul style="list-style-type: none"><li>• Chemical substances are used intensively.</li><li>• Dissolution of the biosorbent is required.</li><li>• The biosorbent loss its original properties, which decreases its mechanical and chemical resistance.</li></ul>
Grafting	The biosorbent is reinforced by means of compounds that are inserted in the original chemical structure of the biosorbent.	<ul style="list-style-type: none"><li>• Chemical substances are used intensively.</li><li>• Dissolution of the biosorbent is required.</li><li>• The biosorbent loss its original properties, which decreases its mechanical and chemical resistance.</li></ul>

Table 3. Common methods, their description and restrictions reported in literature for support/reinforcement of the biosorbents (Volesky, 2003).

The mixture of chitin and the supporting/reinforcement matrix permits the union of both phases in terms of their exposed surface. Such matrix should allow the diffusion of the contaminants towards the supported biopolymer particles and, at the same time, chemically and physically stabilize the biopolymer. In fact, the most studied supporting/reinforcement mediums of chitin/chitosan are organic compounds and polymers (see Table 4).

Contaminant / biopolymer	Method of support and/or reinforcement	Medium of support and/or reinforcement	Additive	Reference
Ag/Qs	crosslinking	TU <sup>1</sup> , glutaraldehyde	Fe <sub>3</sub> O <sub>4</sub>	(Donia et al., 2007)
Cd, Cr (III)/Qs	crosslinking	silicate	-----	(Copello et al., 2008)
Cd, Ni/Q	grafting	poly-vinylpyrrolidone	-----	(Filho et al., 2004)
Cu/Qs	crosslinking	tripolyphosphate	-----	(Lee et al., 2001)
Cu/Qs	crosslinking	polyvinyl alcohol	-----	(Wan Ngah et al., 2004)
Cu/Qs	anchorage	perlite	-----	(Hasan et al., 2008)
Cu, Ni/Qs	-----	-----	alginate	(Huang et al., 1996)
Hg/Qs	crosslinking	glutaraldehyde	-----	(Jeon & Höll, 2003)
Hg/Qs	grafting	polyacrylamide	-----	(Li et al., 2005)
Hg/Qs	crosslinking	EDGE <sup>2</sup>	PEI <sup>3</sup>	(Kawamura et al., 1997)
Ni/Qs	anchorage	alginate, silica	-----	(Vijaya et al., 2008)
Pb/Q	crosslinking	thiourea, cellulose	-----	(Zhou et al., 2004)
U/Qs	grafting	glutaric acid	-----	(Guibal et al., 2002)
As/Qs	-----	-----	MoO <sub>4</sub> <sup>2-</sup>	(Dambies et al., 2002)
As/Qs	anchorage	alumina	-----	(Boddu et al., 2008)
As/Q, Qs	crosslinking	glutaraldehyde	-----	(Elson et al., 1980)
F/Qs (1.7 mg/g)*	crosslinking	glutaraldehyde	-----	(Viswanathan et al., 2009)
F/Q, Qs (3.8 mg/g)*	-----	-----	La	(Kamble et al., 2007)
F/Qs (4.2 mg/g)*	crosslinking	glutaraldehyde	HClAc <sup>4</sup> , Fe	(Viswanathan & Meenakshi, 2008)
Mo, V/Qs	crosslinking	glutaraldehyde	-----	(Guibal et al., 1998)
humic acid/Qs	anchorage	PET <sup>5</sup>	-----	(Zhang & Bai, 2003)
dyes: PaMX <sup>6</sup> , Rvbr <sup>7</sup> , ArH5G <sup>8</sup> /Qs	grafting	poly methylmethacrylate	-----	(Singh et al., 2009)
phenol, chlorophenol/Qs	-----	-----	alginate	(Nadavala et al., 2009)

<sup>1</sup> thiourea; <sup>2</sup> ethyleneglycoldiglycidylether; <sup>3</sup> polyethylenimine; <sup>4</sup> chloroacetic acid;  
<sup>5</sup> polyethyleneterephthalate; <sup>6</sup> Procion Yellow MX; <sup>7</sup> Remazol Brilliant Violet;  
<sup>8</sup> Reactive Blue H5G

\* Maximum reported adsorption capacity

Table 4. Examples of the study of contaminants removal by biosorption onto chitin/chitosan-based biocomposites. The abbreviations Q and Qs mean chitin and chitosan, respectively.

This preference can be attributed to the affinity of such substances to the biopolymers i.e. the formation of stable chemical links (covalent bonds) and/or physical interactions (electrostatic attraction) between the chitin/chitosan and such substances. The use of polymers as supporting/reinforcement matrix has given encouraging results with biosorbents as seaweed, moss, sunflower waste and maize plant mixed with polyurethane (Alhakawati & Banks, 2004; Zhang & Banks, 2006).

Polymers as polyurethane show advantages as: easy handling, versatility and the possibility to obtain homogeneous, porous, malleable and resistant biocomposites. The polyurethane includes a group of polymers derived from the isocyanates, organic compounds which are very reactive. When chemical reaction between the isocyanate and a primary amine group occur, the urea group is produced; on the other hand, when the reaction occurs with hydroxyl group instead of amine, the urethane group is constituted. Both urea and urethane are very stable chemical groups, which make the polyurethane a very useful polymer in applications that must resist extreme conditions of temperature, friction and UV radiation (Hepburn, 1982). Figure 3 shows the main steps of the polyurethane polymerization from its precursors (polyol and diisocyanate) to the stable polymer. Due to the high reactivity of the isocyanate with the primary amine and hydroxyl groups, it would be possible to suppose that the polyurethane establish strong unions with a partial or totally deacetylated chitin, particularly over the contact surface of both phases during polyurethane polymerization, since chitin and chitosan have the mentioned groups on its structure.

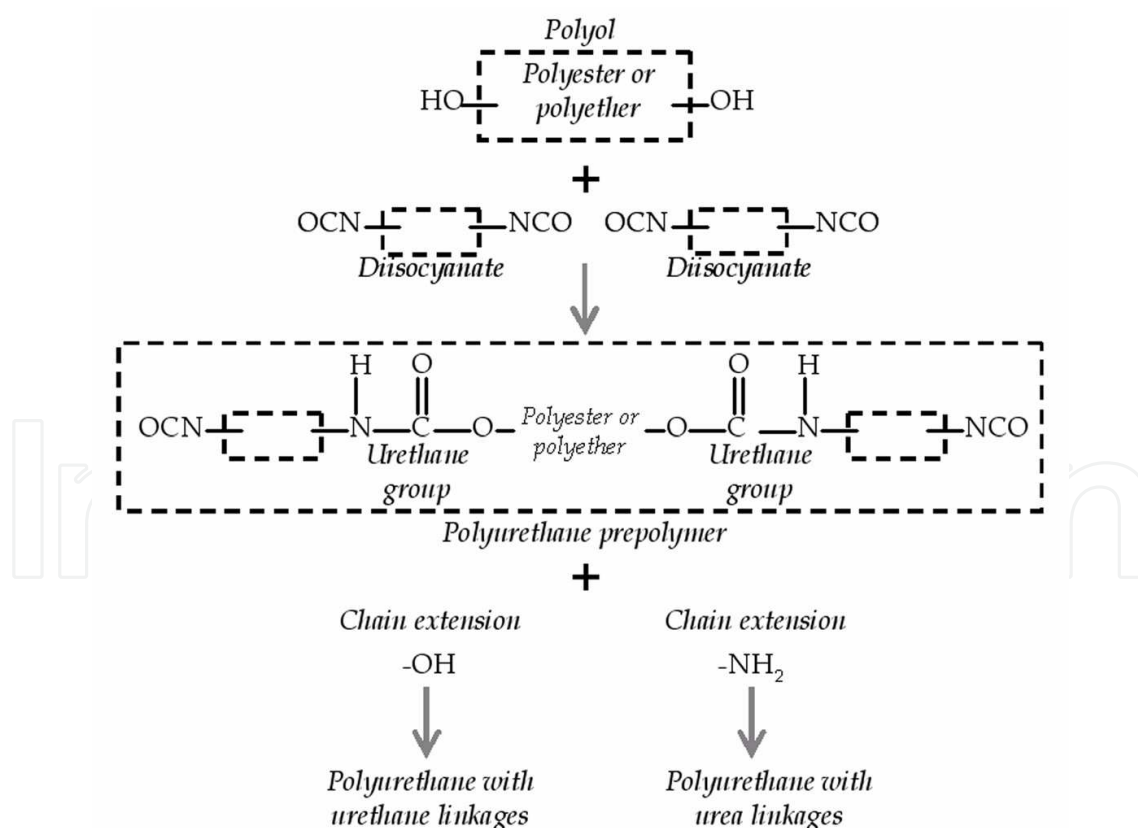


Fig. 3. Schematic representation of polyurethane synthesis (Hepburn, 1982).

In addition, Table 4 shows that the use of additives in the production of chitin/chitosan-based biocomposites has been little studied, particularly during cations biosorption. As

mentioned, an additive should establish chemical or physical links with either the biopolymer or the support/reinforcement matrix, as well as to provide adequate adsorption sites. For example, a molybdenum oxyanion (molybdate) has been used as additive of chitosan for arsenic removal from water (Dambies et al., 2002); such oxyanion establishes covalent bonds with the nitrogen and oxygen of the biopolymer and, at the same time, has a strong affinity for arsenic anions. Nevertheless, in studies where molybdate has been applied, it has been demonstrated that this oxyanion is desorbed during the arsenic removal (Dambies et al., 2000), which is a serious technical drawback.

Regarding the regeneration of the chitin/chitosan-based biocomposites, some studies reported its feasibility by chemical processes which are based on a sudden pH change. For example, citric acid, tartaric acid and phosphate ions were studied to desorb arsenic (V) previously adsorbed onto molybdate impregnated chitosan (Dambies et al., 2000). In batch tests, phosphate was the best eluent, achieving regeneration values over 95% with a 0.1 M phosphate solution. In other work, hexavalent chromium previously adsorbed onto a chitosan-alumina biocomposite was desorbed in a packed column, using a 0.1 M NaOH solution as eluent (Boddu et al., 2003); the total desorption was carried out using 15 bed volumes, without appreciable decrease of the adsorption capacity of the biocomposite during the first operation cycles. In other study, desorption of 85% of fluoride initially adsorbed onto chitosan spheres by means of a 0.1 M NaOH solution was reported (Viswanathan et al., 2009). Therefore, the regeneration of chitin/chitosan-based materials is feasible, which is suitable in terms of a lower operation cost.

Finally, it is important to point out that, since a few years ago, the study of chitin and chitosan as biosorbents has been focused towards the inorganic anions removal. Among these anions, the arsenic oxyanions have been the most studied in the last decade, due to the reduction of the maximum permitted level in water for human consumption (from 50 to 10  $\mu\text{g}_{\text{arsenic}}/\text{L}$ ), established in many countries from the WHO recommendations in 1993 (WHO, 2006). It is important to mention that other inorganic anions e.g. fluoride, are also considered by the WHO as relevant water contaminants, since these affect the health of million of people around the world (WHO, 2006). That is why in recent years fluoride biosorption has started to be studied in a more intense manner.

## 5. Fluoride

### 5.1 Nature and removal methods

Fluoride ( $\text{F}^-$ ) is one of the most ubiquitous inorganic water contaminants in groundwater around the world, due to its easy dissolution from underground rocks that contain it; consequently, fluoride can be found in natural water in concentrations that reach 25 mg/L (AWWA, 1999). Presence of fluoride in groundwater is considered an endemic problem in at least 25 countries including México (Gupta et al., 2007).

Besides, there are also anthropogenic sources of water contamination by fluoride around the world, as superphosphate industry, aluminum and zinc smelters, brickworks, ceramic works, uranium enrichment facilities, coal fired power plants, and oil refineries (Gupta et al., 2007). Fluoride ingestion in low concentration (between 0.5 and 1.5 mg/L) is recommended as prevention of dental caries. However, when fluoride is ingested in quantities that exceeds the recommendation of the WHO i.e. >1.5 mg/L (WHO, 2006) it permanently deposits on teeth and bones, which causes calcium deficiency and abnormal growth of bones. The most frequent diseases due to the excessive ingestion of fluoride are

dental fluorosis (ingestion of water containing 1.5 to 4 mg/L) and skeletal fluorosis (ingestion of water containing > 4 mg/L) (BGS, 2000). However, the possible relationship between fluoride ingestion, and other health problems such as osteosarcoma, and damages to the immune and reproductive systems has been discussed by researchers for the last decades (Harrison, 2005).

Regarding chemical aspects, fluoride is the reduced state of fluorine, which is the most electronegative and reactive of the chemical elements. Due to these properties, fluoride is the only natural form of fluorine. In the solid state, fluoride is always associated with metals; in aqueous solution, fluoride can be found as either free ion or joined to metals/metalloids in complexes forms. At pH values lower than 5, fluoride associates with the hydrogen ion ( $H^+$ ) to form the HF molecule and the complex  $HF_2^-$ . The relative proportion of each of these chemical species in pure water is showed in Figure 4.

The study of fluoride removal from water started in the 30's, by means of coagulation and batch adsorption processes, using diverse aluminum-based compounds (Boruff, 1934). Subsequently different methods as chemical precipitation (Maier, 1947; Sorg, 1978; Clifford et al., 1986), inverse osmosis (Clifford et al., 1986; Cohen & Conrad, 1998) and electrodialysis (Annouar et al., 2004) were implemented. However, adsorption has remained as the most used technique (Maier, 1947; Bishop & Sansoucy, 1978; Clifford et al., 1986; WHO, 2006) due to its operative and cost advantages. The most used fluoride adsorbent at present is the activated alumina, with a maximum adsorption capacity that can vary between 1 and 3 mg/g (Ghorai & Pant, 2004; Medellín, 2006), depending of the type of alumina and the experimental conditions, particularly pH.

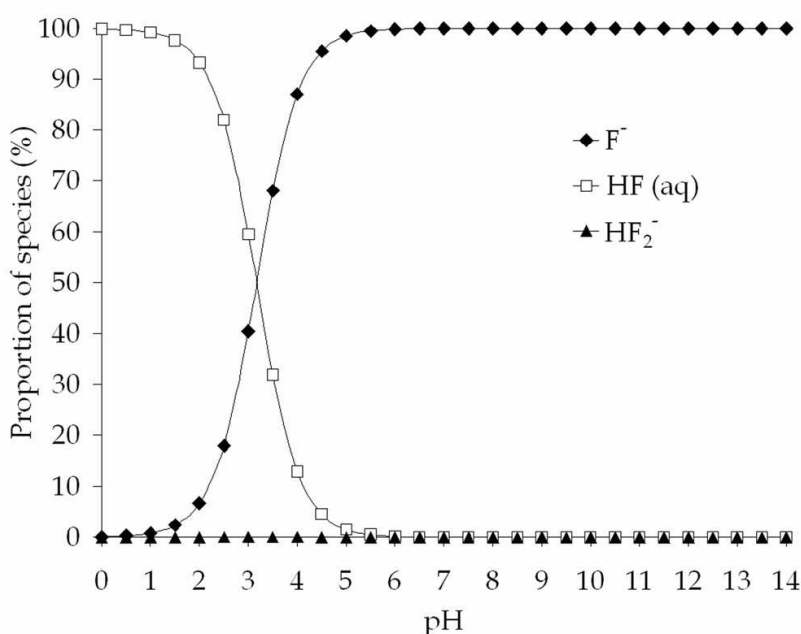


Fig. 4. Diagram of chemical species of fluoride in aqueous solution.

## 5.2 Fluoride biosorption

The biosorption of fluoride has been recently explored. In fact, only since 2007 the biosorption of fluoride has been reported; fluoride has been adsorbed on algae (Venkata Mohan et al., 2007), fungus (Ramanaiah et al., 2007), pure chitosan (Viswanathan et al., 2009)



and added with iron (Viswanathan & Meenakshi, 2008), lanthanum (Kamble et al., 2007; Bansawal et al., 2009), neodymium (Yao et al., 2009), titanium (Jagtap et al., 2009), hydroxyapatite (Sairam-Sundaram et al., 2008) and magnesium oxide (Sairam-Sundaram et al., 2009). The reported results are encouraging, since the maximum fluoride adsorption capacities has been reported around 20 mg/g, which is in agreement with the high density of amine groups contained on the biological structures, especially due to the presence of proteins. Amine groups work as either adsorption sites or anchorage sites of the substances used as additives. Nevertheless, the biocomposites chemical resistance has not been reported, which is a very important aspect of adsorbent materials in order to be used in real adsorption processes. In addition, some of the additives used in the aforementioned studies would considerably increase the biocomposites production cost.

Chitin has been little studied as biosorbent, and fluoride biosorption is not an exception; however, properties of chitin as chemical resistance and lower cost compared to other biosorbents, particularly to chitosan, could represent important advantages to its application in adsorption processes of fluoride or other contaminants. Based on these advantages, a biocomposite based on chitin and a polymeric matrix was recently obtained (Davila-Rodriguez et al., 2009), capable of adsorbing fluoride from aqueous solutions. Such biocomposite was composed mainly by chitin and polyurethane, which were mixed during the polymerization reaction of the last. This method promoted the formation of physical and chemical interactions between both polymers, which caused in turn a decrease of the exposure level of chitin (surface area decreased from 0.32 to 0.08 m<sup>2</sup>/g). Such decrease was due to a lower accessibility to the adsorption sites measured as a decrease of the ion exchange capacity (IEC) of the biocomposite compared to pure chitin (from 2.12 to 0.38 mmol/g). However, the biocomposite showed a greater chemical resistance, measured as a decrease of around 10 times in the loss of mass when the material was submerged in an acid aqueous medium at pH 5 (from 19.6 to 1.5%). Besides, the chitin adsorption properties were retained and optimized by improving the biocomposite composition. The optimum composition of the chitin-based biocomposite was: 58% chitin (DA=79%), 40% polymer and 2% catalyst. Such biocomposite had a fluoride adsorption capacity of 0.29 mg/g at pH 5, being the initial fluoride concentration of 15 mg/L at 25°C, which was around 2 times lower than that of pure chitin (0.70 mg/g) at the same experimental conditions. Although such decrease of the adsorption capacity was considerable, the aforementioned increase of the chemical resistance was even more important.

The study of chitin/polyurethane biocomposite showed that a decrease in the degree of acetylation of chitin promoted a greater fluoride adsorption capacity, which was due to the greater availability of adsorption sites (primary amine groups) as the degree of acetylation of chitin decreased. Besides, the pH of the aqueous medium was a critical fluoride adsorption parameter, since fluoride adsorption notably increased as pH decreased from 8 to 5. This fact was caused by the greater protonation of the primary amine groups as pH decreased.

In addition, chitin crystallinity was not affected when mixed with the polymeric matrix, since the interaction chitin-polyurethane was mainly on the contact surface. In fact, the X-ray diffraction pattern of the chitin-based biocomposite showed an intermediate behavior between chitin and polyurethane diffraction patterns, due to the dilution effect of the mixture biopolymer-polymer.

Additional work has shown that the optimum chitin-based biocomposite has a swelling capacity which permits that the fluoride ions can enter to the hydrated structure of the

material and, thus, access to the adsorption sites contained mainly on the chitin structure. Besides, the fluoride adsorption capacity of both chitin and biocomposite is considerably great, if they are compared to other chitinous materials, as reported in Table 4.

The authors consider that future work should include studies about the adsorption kinetics of the fluoride adsorption process, as well as packed columns tests in order to determine the behavior of the respective breakthrough curves. Such knowledge would permit to scale the fluoride biosorption process to real processes and so achieve the application of the chitin-based biocomposites, which in turn would contribute to resolve one of the most important water contamination problems around the world, by means of more sustainable technologies.

## 6. Conclusion

Although chitin is an abundant biopolymer in nature, its utilization in the daily activities of people is even little. Chitin and chitosan have a great potential to be used in many fields because of the particular properties of these biopolymers. In fact, the possibility to use chitin and chitosan as biosorbents has been widely demonstrated; however, the low mechanical and chemical resistance of both biopolymers is a disadvantage which restricts their application in real scale adsorption processes. The production of chitin/chitosan-based biocomposites has shown encouraging results in terms of improved adsorption capacity and resistance. Regarding chitin, this has been studied as biosorbent to a lesser extent than chitosan; however, the natural greater resistance of the former compared to the last, due to its greater crystallinity, could mean a great advantage. Besides, the possibility to control the degree of acetylation of chitin permits to enhance its adsorption potential by increasing its primary amine group density. Recent studies regarding the production of chitin-based biocomposites and its application as fluoride biosorbents have demonstrated the potential of these materials to be used in continuous adsorption processes. Moreover, these biocomposites could remove many different contaminants, including cations, organic compounds and anions. Future work will permit to advance towards the application of biosorption processes, especially those based on the use of chitin and its derivatives.

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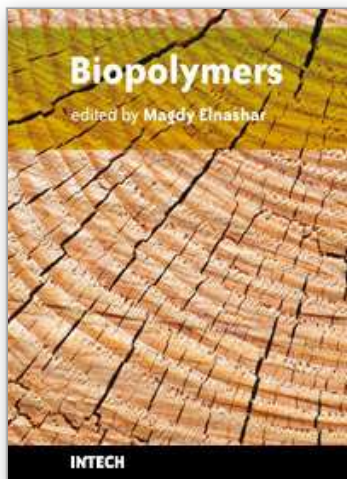
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## **Biopolymers**

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