OBTAINING AN ORGANIC FLOCCULANT OF SHRIMP FOR USE AS COPPER CHELATING

OBTENÇÃO DE UM FLOCULANTE ORGÂNICO DE CAMARÃO PARA APLICAÇÃO COMO QUELANTE DE COBRE

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Recebido em: 24/07/2017, Aceito em: 11/10/2017, Publicado em: 07/11/2017
DOI: 10.22407/1984-5693.2017.v9.p.80-89

ABSTRACT

The increasing development in the industrial use of heavy metals in mining, batteries, fertilizers, tanneries and installations of plastics with metals on their surface, led to an increase of emissions of metals in the aquatic environment. This is a major concern, given that some metals are extremely toxic, even in low concentrations. The project in question aims to reduce copper of the aquatic environment, using as chelating the chitosan. This is a cationic polysaccharide which acts as a flocculant and it is obtained by deacetylation of chitin in alkaline solutions. Prior to the deacetylation process is the process of obtaining the chitin, which follows the steps of deproteinization, demineralization and depigmentation of the carapace of shrimps. Through the ion exchange method, the chitosan has shown to be effective by providing a percentage of approximately 99 % of extraction of the copper in water, in 2 minutes of stirring, using 0.08 g of chitosan, with the squared correlation coefficient (R^2) equal to 0.9996.

Keywords: chelating, copper, chitosan, shrimp.

RESUMO

O crescente desenvolvimento do uso industrial de metais pesados em mineração, baterias, fertilizantes, curtumes e instalações galvanoplásticas levaram ao aumento de emissões de metais em ambiente aquáticos. Isso representa uma grande preocupação visto que, alguns metais são extremamente tóxicos, mesmo em baixas concentrações. O projeto em questão visa a redução de cobre no meio aquático, utilizando como quelante a quitosana. Esta é um polissacarídeo catiônico que age como floculante e é obtida através da reação de desacetilação da quitina em soluções alcalinas. Anteriormente ao processo de desacetilação, ocorre a obtenção da quitina, que segue as etapas de desproteinização, desmineralização e despigmentação da carapaça do camarão. Através do método de troca iônica, a quitosana se mostrou eficaz ao apresentar uma porcentagem de aproximadamente 99 % de extração de cobre da água, em 2 minutos sobre agitação, utilizando 0,08 g de quitosana, com o coeficiente de correlação ao quadrado (R^2) igual a 0,9996.

Palavras-chave: quelante, cobre, quitosana, camarão.

INTRODUCTION

Water is one of the basic needs for subsistence and the continuity of life. Therefore, it is important that it has good quality and that it is available for human consumption and for the accomplishment of their activities. With the increase of chemical industries, environmental issues that covers the products that are generated by this sector, are being debated in Brazil and the world, because of its high rate of pollution emitted (LIMA, 2010).

The treatment of the effluents of these industries is needed because these effluents contains heavy metal ions, and when they are not properly treated and are improperly disposed in the rivers, because they are not biodegradable, they tend to accumulate (JANEGITZ *et al*, 2007). In Brazil, the National Environmental Council - CONAMA is the consultative and deliberative organ of the National Environmental System - SISNAMA.

Copper ions are found in the partial decomposition of chemicals that are present in some pesticides and fungicides, and in solubilized products resulting from the decomposition of electrodeposited materials and electronic drums, respectively (ROSA, 2008).

Some procedures can be used to remove the copper of the water, including hydroxides precipitation, ion exchange, adsorption, among others (JANEGITZ *et al*, 2007). Chitosan is an adsorbent that combines low cost production, easy regeneration and higher selectivity concerning heavy metal ions (FONSECA *et al*, 2005). It has proved to be effective as a chelating agent of the copper ions, especially on the powder form, presenting better performance than other comercial chelating agents (NGAH & ISA, 1997).

The chitosan is obtained from the deacetylation of chitin in alkaline solutions. Chitin is an extremely abundant polysaccharide in nature, staying behind only to the cellulose in availability. This is found in many organisms such as insects and crustaceans, being the main constituent of shrimp shells and crab shells. Regarding the production of crustaceans, the “Sete-barbas” shrimp andthe “Pink” shrimp were the species that were most captured in the country on 2010, about 15.276 T and 10.237 T, respectively. These figures represent 26.7 % and 17.9% of the total composition of the production of marine crustaceans in Brazil (NETO, 2011).

Generally, the waste generated by the production of shrimps are clandestinely buried or thrown into the sea, causing ecological imbalance of the marine species in the region, and also providing the proliferation of insects that are attracted by the stench, causing the spread of diseases (CARVALHO, 2006). The production of chitosan from chitin is an alternative to the reuse of such waste (ROSA, 2008).

Therefore, the main objective of this article is obtaining chitosan from the shell of the schrimp and use it as copper chelating.

LITERATURE REVIEW

Copper (Cu) is abundant in nature in the form of sulfides, arsenite, chlorides and carbonates. It is an essential element for living organisms in small quantities, but the ingestion of water containing high metal concentrations may produce nausea, vomiting, abdominal pain and diarrhea. Children are more sensitive to the effects of the exposure to copper, and when this exposure is prolonged, can cause liver damages (CETESB, 2016).

The chitosan has become an important natural polymer because of its combination of characteristics like biodegradability, biocompatibility, nontoxicity, hydrophilicity, bioactivity, and interesting physical and mechanicalproperties (WANG *et al*, 2013).

For having natural, renewable and abundant source, chitosan can be used for many diferent goals. It can be used as a metal chelating agent, a flocculant, a dye adsorbent, anadsorbent of metal anions and others (CARVALHO, 2006).

Chitosan is obtained from the deacetylation of chitin in alkaline solutions. During the deacetylation reaction, the acetamido groups (-$NHCOCH_3$) of chitin are transformed in amino groups (-NH_2) to give chitosan, as seen in Figure 1. Therefore, chitin is a linear polysaccharide containing waste streams *β*- (1-4) -2-acetamide-2-deoxy-*D*-glucose. The difference of the chitosan from the chitin is that the deacetylation occurs at the carbon-2 position of each glucoside unit with amino groups (ANTONINO, 2007). Since chitosan has these free amino groups on its chain, its adsorption capacity is higher when compared to chitin´s capacity (CHEN *et al*, 2008).

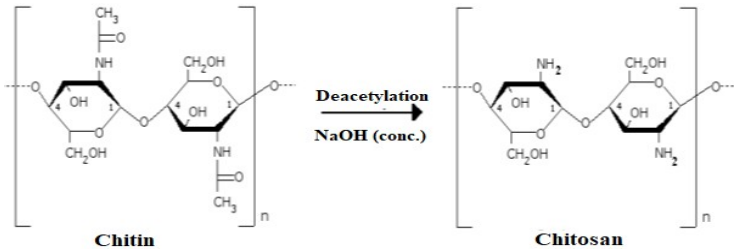


Figure 1. Representation of the chitin and the chitosan (ANTONINO, 2007).

Chitosan´s high adsorption capacity and selectivity regarding metal ions can be explained for three factors: (1) the high hydrophilicity of chitosan with a large number of hydroxyl groups; (2) the large number of primary amino groups content with high activity; and (3) the flexible structure of the polymer chains of chitosan, which enables a suitable configuration for complexation with metals ions INOUE et al, 1993).

Some models have been proposed to explain the formation of the complexes between the chitosan and metals. The first one is called “pendant model”, which considers the metal ion is bonded to an amino group as a pendant. The second model, “the bridge” one, assumes that the metal ion is linked to a lot of nitrogen atoms of the same or different chains (CARVALHO, 2006). The models can be seen in Figure 2.

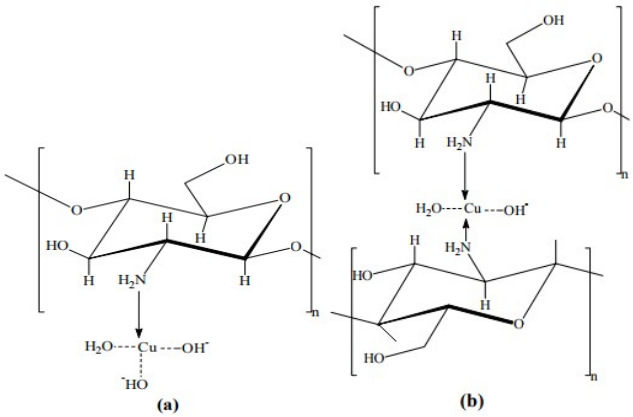


Figure 2. Proposed structures for the complexes of Cu (II) and chitosan: (a) Pendent model; (b) Brigde model (CARVALHO, 2006).

METHODS

Process for obtaining the chitosan

Step 1 - Manual separation of the "heavy" material of the shrimp shell, such as meat, eggs, vegetables, organic materials and others, that can eventually go along with the waste. This procedure is performed with the aid of gloves, with subsequent rinsing in running water, proceeded to a process of sun drying and oven during a period of 4 hours at 80 ºC (MOURA *et al*, 2006).

Step 2 - The already pretreated husks are ground with the aid of a slicer or domestic multiprocessor. These are organized according to meshes, where according to the literature and some laboratory tests, the interval was set between the mesh passage from 60 to 100 meshes (MOURA *et al*, 2006).

Step 3 - In order to reduce the ash present in the raw material, the demineralization step is performed, which runs from the addition of HCl 2.0 $mol.L^{-1}$. The procedure is performed at room temperature, where the beaker should contain sufficient volume for the mixing of the husks and HCl, which comes from a 40 mL addition, for each of these grams. After 2 hours, under constant agitation (magnetic or mechanical stirrer) the solution goes through a washing process with distilled water until neutrality. Later, undergoes to vacuum filtration with subsequent drying in a stove for 1 hour and 25 minutes at 80 ºC, and then a desiccator until a constant weight (ANTONINO, 2007; MOURA *et al*, 2006; NEVES *et al*, 2013; FERREIRA *et al*, 2009).

Step 4 - The deproteinization step is performed in order to reduce the protein nitrogen content. This comes from the addition of 10 % KOH in constant stirring for 3 hours at 50 ºC. Subsequently, the material undergoes to a washing procedure with distilled water, vacuum filtration and drying in the oven for 4 hours at 80 ºC (ANTONINO, 2007; MOURA et al, 2006; NEVES et al, 2013; FERREIRA et al, 2009).

Step 5 - In order to remove odor and pigments the step of deodorization and depigmentation is realized. This works with the addition of 1% NaClO for 8 hours at 40 ºC. The resulting solid is washed with distilled water until pH 7, and is then filtered on a vacuum system. After deodorization is required the drying of the obtained product (wet chitin). This drying is performed at a temperature of 80 ºC for 4 hours, so that the entry into the reactor deacetylation does not alter the concentration of the solution of KOH 50 % (ANTONINO, 2007; MOURA et al, 2006; NEVES et al, 2013; FERREIRA *et al*, 2009).

Step 6 – Now the step of obtaining the chitosan starts. The deacetylation consists of adding a concentrated solution of KOH 50 %. The reaction time may be 5 hours at 100 ºC, under constant agitation, or using a jacketed reactor with circulation thermostatic bath at 115 ºC for 6 hours. After reaching the room temperature, the solid is washed with distilled water until neutrality, with subsequent vacuum filtration with the solid being washed again with ethanol, vacuum filtered and placed in the greenhouse for 12 hours at 40 ºC (ANTONINO, 2007; MOURA *et al*, 2006; NEVES *et al*, 2013; FERREIRA *et al*, 2009).

Step 7 - The purification step (in order to remove the remaining salts of the other steps). It proceeds with the addition of acetic acid 0.5 $mol.L^{-1}$, where the chitosan will dissolve, because it is soluble on organic acids (to approximately pH 6.0). The solution is then brought to a centrifuge, so that it is possible to remove the material that was not dissolved, and obtain a solution with less impurity.

Finally, precipitated chitosan with alkaline solution (to pH 12.5) with subsequent filtration and washing process until neutrality, having the dried material at room temperature for 2 hours (FERREIRA *et al*, 2009; ANDRADE *et al*, 2010; ANDRADE, 2012).

Step 8 - Finally, the last step consists in analyzing the chitosan produced by two methods. Thefirts step is the analysis by spectroscopy in the infrared region, which allows the determination of the functional groups present on the chitosan produced. The second one is the analysis of the degree of deacetylation, where the higher the value, the better the property. (FERREIRA *et al*, 2009; ANDRADE *et al*, 2010; ANDRADE, 2012).

Process of removing the metal ions of Cu^{2+}

Analyzes of the removal of metal ions of Cu^{2+} from differents solutions and concentrations were made, using the chitosan with the higher average degree of deacetylation.

By the standard solution of Cu, a solution of Cu^{2+} with molarity of 20 $mg.L^{-1}$ and pH 5.5 is prepared. This is split into four volumetric flasks, yielding four solutions of the same concentration. In each flask is added 0.2 grams of chitosan, initially. The solutions are maintained in volumetric flasks under constant agitation, and, after a period of thirty minutes, the solution of the first balloon is removed by filtration of the solid and liquid portion. After another thirty minutes, the second balloon is removed using the same method and so on. Later, different masses of chitosan were placed in the volumetric flasks, ranging from 0.04 to 0.16 g, keeping them in agitation for fixed periods of one and two minutes. The resulting solutions were analyzed in "Flame Atomic Absorption Spectrometer (FAAS)."

RESULTS AND DISCUSSION

Process for obtaining the chitosan

Initially 19.5 g of shrimp shells were ground with the aid of molecular sieves, the shells were selected with sizes between 60 and 100 mesh. In the demineralization stage, the skins were left in contact with the solution of 40 mL of hydrochloric acid 2 $mol.L^{-1}$ for 2 hours, with consequent neutralization using of distilled water, vacuum filtration and heating for 48 hours. A change not very expressive in color, which became rosier, could be noticed.

In the deproteinization step, the demineralized material was brought into contact with 10 % potassium hydroxide (amount added to submerge the material under study), and after washing procedures with distilled water, filtration and heating, a significant change was not seen in the coloring, but a reduction in the characteristic odor of the organic material could already be seen.

The next step was referring to the deodorizing and depigmentation, with the action of sodium hypochlorite (1 % added to submerge the material), having at the end, a color already whitened, with no shrimp odor. The output of this step is chitin, which was carried on infrared analysis, generating the comparative graphs for identification of chitosan.

Finally, it was added KOH 50 % (up to submerge the chitin, so that its evaporation during the heating does not compromise the ultimate dissolution), after washing with water and alcohol, and finally obtaining the chitosan. The chitosan was also taken for infrared analysis, by plotting its graphics with the chitin in order to obtain a replacement of the analysis of the acetamido groups to amino groups. The final color is whitish, with no odor, having a considerable mass loss during the process in which, at the end, was obtained only 4.3 g of chitosan. This characterizes a loss of approximately 78 % by weight.

The step, that would be the last one, which consisted on the addition of acetic acid, was removed from the experiment, because, at the time, it was favoring the production of biofilms nanoporous structure. The contact of chitosan with dilute organic acid, promotes the production of viscous solutions capable of forming films, which is not in accordance with the ideal of application of the project, which would be more focused on acting as a metal chelator.

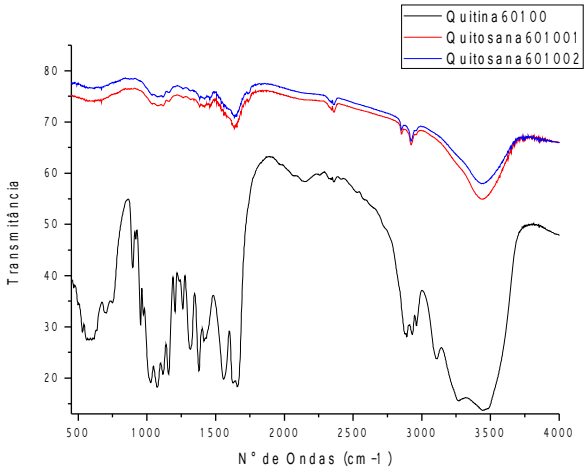


Figure 3. Characterization of chitin and chitosan on infrared analysis.

Spectroscopy technique is useful for checking the hydrolysis of the acetyl groups of the chitin structure by the reduction of the amide carbonyl stretching band in the region of 1655 cm^{-1}. The main advantage of using infrared is the ease of obtaining the analysis that can be made in the form of film or KBr tablet (CANELLA; GARCIA, 2001).

In the FTIR spectrum in Figure 3, for the chitosan obtained from the shrimp shell, characteristic bands were observed, such as: OH axial stretch band between 3440 to 3580 cm^{-1}, wich appears overlapping the N-H stretchband; Axial deformation of C = O amide I (from 1600 to 1700 cm^{-1}); angular deformation of N-H (between 1583 to 1594 cm^{-1}); symmetric angular deformationof CH_3 (1380 to 1383 cm^{-1}); Axial deformation of amide -CN (at 1425 cm^{-1}), bands of polysaccharide structures in the region from 890 to 1156 cm^{-1}, bands that can be compared with those described by Santos *et al*., 2003.

The difference between chitin and chitosan bands can be noteced in the region of 2800 to 3600 cm-1, where there is an overlap of the stretching bands of OH and NH. In the chitin spectrum, two bands can be seen at about 3000 and 3200 cm-1 assigned respectively to the NH group of amide and the hydrogen bonds involving the amide groups, which disappear completely in the chitosan spectrum. This is an evidence of an occurrence of the expected deacetylation from the chitin to the chitosan, in which the amide groups are transformed into amine groups (ASSIS, BRITTO, 2008).

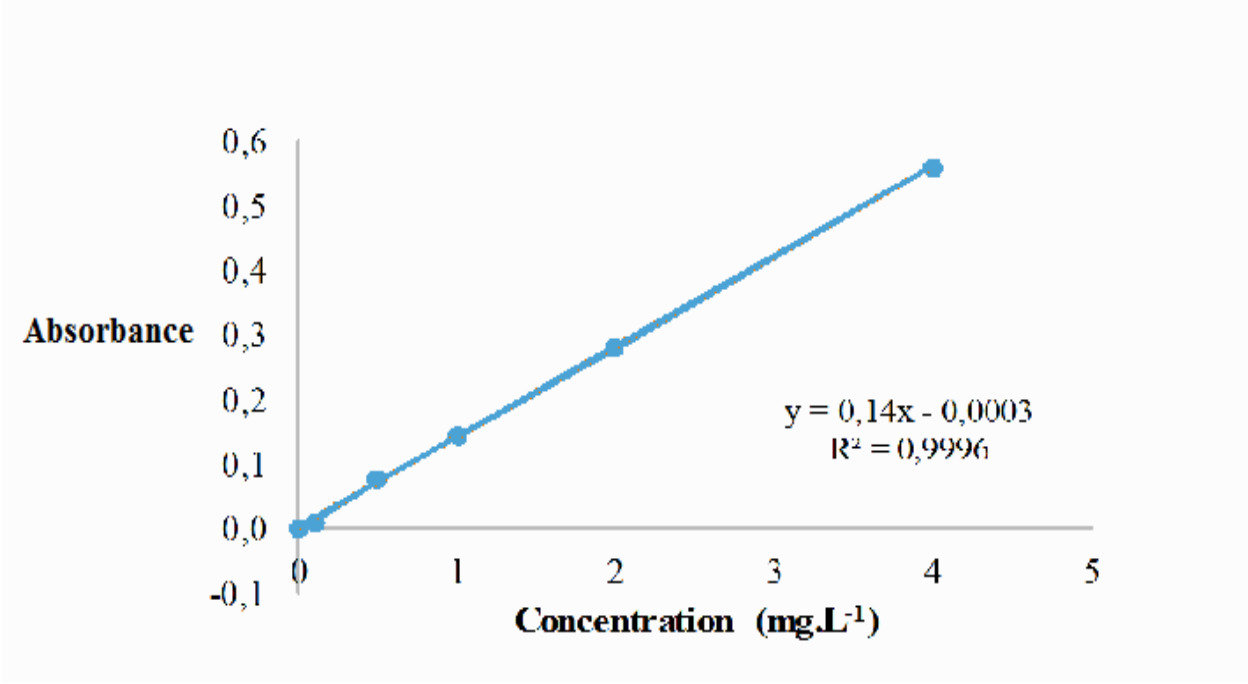
The deacetylation analysis was done qualitatively, only to identify that chitin was transformed into chitosan, and, for that reason, the FTIR analysis was sufficient to prove this change.

Process of removing the metal ions of Cu^{2+}

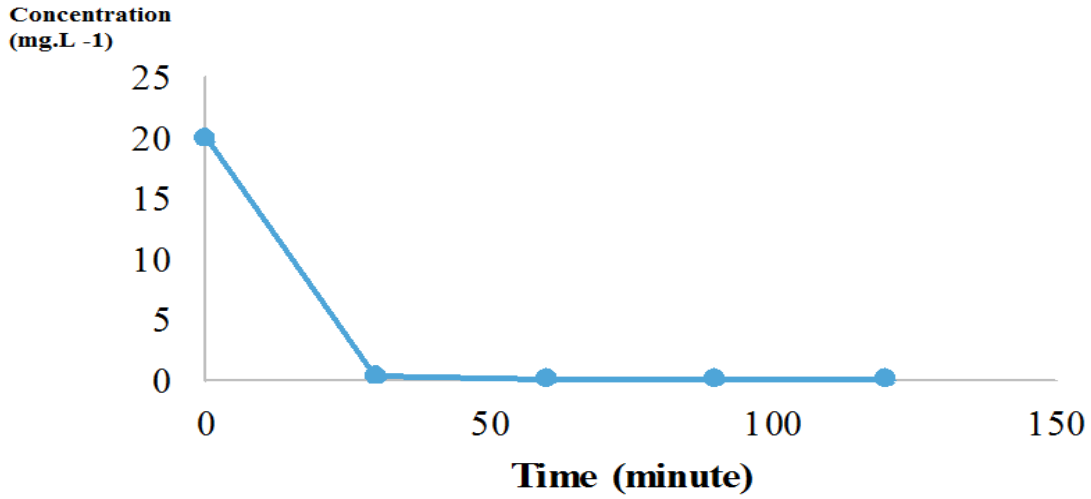
The tests were made using a 50 mL solution with concentration of 20 $mg.L^{-1}$ to evaluate the efficiency of the extraction of copper ions from the water, using chitosan as a chelate of these ions. Calibration was done using standards of known concentrations of copper for determination by FAAS.

The analyses for copper determination of the tests were made from the calibration curve which is shown in Figure 4, whose equation is: y = 0,14x - 0.0003, with the squared correlation coefficient (R^2) equal to 0.9996 and relative standard deviation (RSD) less than 5 %.

Graphic 1. Calibration curve for the determination of the copper concentration after extraction. Equation of the curve: y = 0,14x - 0.0003, with R^2 = 0.9996.



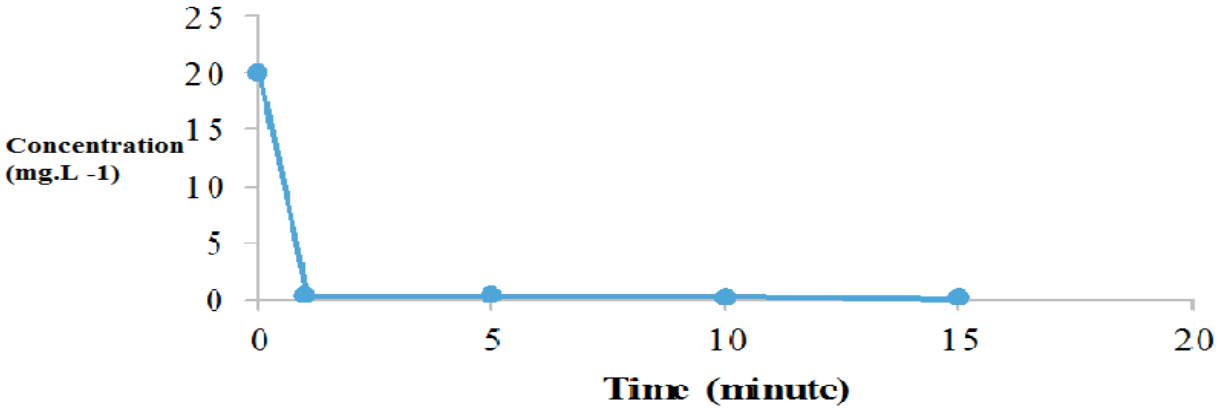
The first test was performed to check the ideal time for the agitation of the volumetric flasks containing the copper solution and the chitosan. They were weighed masses of nearly 0.200 g of chitosan in four balloons of 50 mL. Then, it was added to each of these flasks, 50 mL of the copper solution, which has a concentration of 20$mg.L^{-1}$. For the balloons 1, 2, 3 and 4, it was waited 30, 60, 90 and 120 minutes of extraction, respectively. The concentration of the copper on the solution after 30, 60, 90 and 120 minutes was 0.316, 0.141, 0,104 and 0.109 $mg.L^{-1}$, which represents an extraction of copper of 98.4%, 99.3%, 99.4% and 99.4% respectively, as seen in Figure 5.



Graphic 2. Evaluation of the copper concentration *versus* the time of exposure of the copper to the chitosan.

After obtaining a satisfactory percentage of extraction of the copper from the water with the mixture being stirred for 30 minutes, further tests were made to verify if the extraction would still be efficient with a less waiting time. The 50 mL solution with concentration of 20 $mg.L^{-1}$ was maintained. Again, the calibration was made using as a parameter standards of known concentrations of copper for determination by FAAS.

The methodology used in the previous tests was retained. Therefore, 0.200 g of chitosan was weighed in 4 volumetric flasks of 50 mL and then was added to each of the flasks 50 mL of the copper solution ($20mg.L^{-1}$). The waiting time for extraction was 1, 5, 10 and 15 minutes for the balloons 1, 2, 3 and 4, respectively. The results obtained were a final concentration of copper of 0.316, 0.326, 0.246, 0.179 $mg.L^{-1}$, which means that the extration of copper of the solution was 98.4%, 98.4%, 98.8% and 99.1% for 1, 5, 10 and 15 minutes, respectively, as shown in Figure 6.



Graphic 3. Evaluation of the copper concentration *versus* the time of exposure of the copper to the chitosan.

Since the amount of copper that was extracted using 0.200 g of chitosan was highly satisfactory, the tests were repeated now using the same stirring time, but different masses of chitosan present in the volumetric flasks. Again, the method of the previous tests was maintained, including the inicial concentration of copper in the flasks (20 $mg.L^{-1}$).

Eight solutions were prepared, using masses of chitosan from 0.0423 g to 0.2031 g. The stirring time was initially 1 minute for the first four flasks. Then, similar masses were used, but the stirring time was 2 minutes. The results obtained are seen in Table 1.

Table 1. Evaluation of the percentage of the extraction of the copper from the water using as the extruder phase the Chitosan, analyzing the mass quantity.

Test	**Chitosan mass (g)**	**Time (min.)**	**Final conc.** ($mg.L^{-1}$)	**%Extraction**
1	0,0800	1	8,1351	59.3
2	0,1211	1	5,9176	70.4
3	0,1649	1	4,0834	79.6
4	0,2031	1	3,0806	84.6
5	0.0423	2	3.1074	84.5
6	0.0805	2	0.5423	97.3
7	0.1208	2	0.0516	99.7
8	0.1643	2	0.3113	98.4

This test showed that both time and mass have a large influence on the percentage of extraction. The stirring time of 1 minute was insufficient to obtain an efficient extraction, while 2 minutes of stirring proved to be an excellent time to extract a great amount of copper. Regarding the mass of chitosan present on the solution, the masses from 0.08 g demonstrated to be capable of providing an effective extraction of copper using chitosan as a chelating.

CONCLUSIONS

Based on the results, the methodology used to obtain the chitosan is effective, the method had positive results in the tests and the sample material showed specific characteristics, such as color density, satisfactory smell and characteristic bands on the infrared analysis.

Chitosan proved to be a good alternative to act as chelator of the copper, showing to be effective by providing a percentage of approximately 99 % of extraction of the metal from the water. The extraction was influenced by both stirring time and chitosan mass present in the solution. The time of 2 minutes of stirring in volumetric flasks, and the mass of 0.08 g of chitosan proved to be sufficient for a satisfactory extraction of the metal present in the solution, with the squared correlation coefficient (R^2) equal to 0.9996.

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