

Chitosan Microspheres Applied for Removal of Oil from Produced Water in the Oil Industry

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Abstract: The discharge of oily wastewaters in the environment is steadily increasing, causing serious damages. Among various treatment methods, adsorption is generally considered the most appropriate, since it can remove both organic and inorganic pollutants. Adsorption using low-cost alternative biopolymers for removal of contaminants from wastewater has been widely investigated. In this context, chitosan has been drawing particular attention because, among its many applications, it can be used in the treatment of aqueous effluents. In this study, microspheres were prepared by reticulation of chitosan with sodium triphosphate (STP) and studied for the treatment of water containing crude oil. The microspheres were regular and had surface pores. These microspheres were packed in treatment columns and their ability to remove oil was measured with a fluorometer, by the difference in the oil concentration before and after passing through the column. The microspheres that presented porosity about 80 % were highly efficient in oil removal, with rates above 90%.

Keywords: Chitosan, microspheres, sorption, oily water, wastewater.

Introduction

A large amount of water is extracted along with petroleum. Much of this oilfield wastewater is not emulsified, but a significant portion is emulsified with oil (w/o), requiring physical and chemical treatment methods. The discharge or even reinjection of this oilfield wastewater is only permitted after removal of the oil and suspended solids to reduce them to acceptable levels^[1].

The purification of the wastewater from various industrial processes is an important global problem, mainly due to the restricted quantities of water that can be safely used directly and the high cost of purification installations^[2]. In recent years suitable technologies for treatment of wastewaters and other effluents has attracted great interest, due to more rigorous laws and regulations.

The literature reports a variety of processes for cleaning contaminated wastewaters and other effluents^[3]. Different technologies and processes are currently used for this purpose^[4,1]. Among these treatment methods, adsorption stands out for being effective, efficient and cheap^[5]. Adsorbents can be of mineral, organic or biological origin^[6]. Polymeric adsorbents have been widely used to remove organic pollutants from industrial wastewaters and natural waters^[7].

Derivatives of chitin and chitosan have been attracting a good deal of attention as effective biosorbents due to their low cost and high concentration of amino and hydroxyl functional groups, which have significant adsorption potential to remove various pollutants from water^[8]. It has been widely used due to its characteristics such as nontoxicity, abundance in nature, biocompatibility and biodegradability^[9].

Chitosan is a linear polysaccharide resulting from the partial substitution of the N-acetyl groups present in

chitin when in the presence of an alkaline solution^[10]. Its chemical structure is formed by repeating constitutional units of 2-amino-2-deoxy- β -(1,4)-D-glucose and 2-acetamide-2-deoxy- β -(1,4)-D-glucose^[11].

When chitosan is used in its natural form, it tends to agglomerate and form gels^[9], as well as presenting other disadvantages in adsorption processes, such as solubility in acid media, which prevents it from being recycled. Besides this, its low internal surface area limits the access to unexposed adsorption sites (amino groups), thus diminishing the maximum capacity and speed of the adsorption process. These problems can be minimized by chemical modification of the polymer with substances, such as reticulating agents that increase the performance of chitosan as an adsorbent^[12].

Another advantage of the chitosan is the possibility of being shaped into different forms with the morphology chosen to best suit the particular application. The spherical form is preferred because it allows better surface characterization, enabling the establishment of useful geometric parameters for reproducibility of the process and for comparisons, as well as permitting optimal packing in reactors and filtration devices^[13].

One of the reticulating agents that can be used to obtain chitosan particles is sodium triphosphate (STP). It is a multivalent anionic salt which has an advantage over chemical agents that promote cross-linkage because it is nontoxic^[14]. The large number of negative charges of STP results in its facility to reticulate ionically with chitosan^[15].

Chitosan is being widely used in water treatment, especially in removing metals, dyes, phenols, and there are also few studies using the chitosan in the remotion

of oil. In respect to oil removal, a study shows its use compared to other natural adsorbents (bentonite and activated carbon) in a jar-test, where chitosan showed better results in removal of a residual oil mill effluent from palm oil^[16]. In other study the use of chitosan flakes as adsorbent for the removal of pollutants from biodiesel wastewater had an adsorption capacity that corresponds to a reduction in the initial oil and grease level of around 67%^[17]. In other work, the authors compared the adsorption of residue oil from palm oil mill effluent using chitosan powder and flake, and observed that powder chitosan had better results due to its larger surface area^[18].

Despite the chitosan has been studied in water treatment, their use as microspheres crosslinked with sodium tripolyphosphate in packed columns for removing crude oil from oily waters has not been studied yet.

The main components of the crude oil are saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes. Saturated hydrocarbons constitute the largest group, consisting of normal alkanes (n-paraffins), iso-alkanes (isoparaffins) and cycloalkanes (naphthenes). Aromatic hydrocarbons comprise aromatic compounds, the naftenoaromatics, and benzothiophenes and their derivatives (sulfur-containing heterocycles). The asphaltenes and resins are present in the heaviest fraction of crude oil and these fractions present higher molar mass, polarity and aromaticity than another compounds present in the crude oil^[19].

The purpose of this work of using the chitosan-based compound in the recovery of water contaminated with crude oil is due to its chemical structure that has a cyclic conformation of carbons in the main chain, which gives low polarity and may attract by Vander Waals interactions similar structures such as hydrocarbons compounds (included the aromatics compounds) present in the medium, having the same mechanism than divinylbenzene-based resins shown in previously studies^[20].

Additionally, the polar NH and OH groups, pending in the carbon chain of chitosan, give to the structure a certain polarity that can directly influence the adsorption of slightly polar molecules (groups with heteroatoms and functional groups with pairs of free electrons in its structure) present in the crude oil composition. This interaction, which could be via covalent bonds, can be direct or by chemical modification of its structure (either by simple variation of pH, either via chemical reactions fast and direct)^[21].

So, in this work, a chitosan microsphere was produced and applied as polymeric resin to pack column treatment for removal of oil from oily wastewater through adsorption. The main objective was to evaluate if this chitosan microsphere could be used in column treatment, presenting good efficiency and flow resistance.

Experimental

Materials

The following reagents were used in this work: Sodium hydroxide P.A., obtained from B. Herzog,

Hydrochloric acid P.A., Ethyl alcohol P.A. and Acetone P.A. from Vetec, Sodium Borohydride from Tedia Brazil and Sodium tripolyphosphate 85% from Sigma Aldrich. The crude oil used was donated by the Petrobras Research Center. It had the following characteristics: °API = 19.7; asphaltenes content = 2.45%; paraffins content = 4.17%. This composition indicates that this sample is regarded as heavy oil^[21].

Synthesis and characterization of chitosan

The chitosan was obtained by deacetylation of chitin extracted from the shrimp shells. This method is known and can be found in the literature^[11,22] and it was used in this work in order to obtain the chitosan sample with high mass molar, characteristic that is very important in the microspheres formation.

Determination of the acetylation degree of the chitosan

The ¹H-NMR technique was used to determine the acetylation degree of the chitosan. The spectra were obtained with a Varian Mercury VX 300 spectrometer (300 MHz for ¹H) (Palo Alto, USA), equipped with 5-mm inverse detection probes.

Approximately 10 mg of chitosan was dissolved in 1mL of a 1% (v/v) HCl/D₂O solution and waited for 24 hours for complete solubilization of the sample. The analysis was carried out in a test tube with diameter of 5 mm at 70 °C.

The average acetylation degree was determined according to Equation 1 below.

$$DA (\%) = (I_{\text{CH}_3}/3) / (I_{\text{H}_2\text{-H}_6}/6) \quad (1)$$

In the equation, I_{CH_3} corresponds to the intensity of the signal from the hydrogen atoms of the methyl group of the β -(1,4)-2- acetamido-2-deoxy-D glucose residues, and $I_{\text{H}_2\text{-H}_6}$ is the sum of the intensities of the H-2 signal from the deacetylated residue and the H-2 to H-6' signals from both the deacetylated residue and acetylated residues^[23].

Determination of the chitosan molar mass

The viscosimetry method was used to determine the molar mass of the chitosan, based on the intrinsic viscosity of the solution^[23].

To determine the intrinsic viscosity $[\eta]$, a stock solution was prepared of 0.5%, where the chitosan was dissolved in a solution of acetic acid (0.1 mol.L⁻¹)/ sodium chloride (0.2 mol.L⁻¹) under constant stirring for 24 hours. Five dilutions were prepared from the stock solution with the purpose of obtaining six chitosan solutions.

The absolute viscosities (η) of the solvent and chitosan solutions were measured in a Haake Mars II rheometer, with Z-20 geometry and shear rate interval ($\dot{\gamma}$) between 1-500s⁻¹, to determine the region of Newtonian behavior. To obtain the absolute viscosity values of the solutions and solvent, the shear rate selected was 490 s⁻¹.

The mean viscosimetric molar mass (\bar{M}_v) was determined using the Mark-Houwink-Sakurada equation – Equation 2^[24].

$$[\eta] = K (\bar{M}_v)^a \quad (2)$$

For the rheological assay, the chitosan samples were dissolved in an acetic acid/sodium chloride solution at 25 °C, under conditions in which the values of the constants were $K=1.81 \times 10^{-3}$ and $a=0.93$ ^[25].

Preparation of the solutions of chitosan and sodium triphosphate (STP)

A 1% (p/v) solution of chitosan was prepared, because above this concentration the solution is too viscous to produce microspheres. For this purpose, 1 g of chitosan was dissolved in 100 mL of a 2% acetic acid solution. The pH of the solution is 3.8 and in this pH the chitosan molecules are positively charged.

The STP solution was prepared by dissolving 5 g of this reticulating agent in 100 mL of distilled water. The pH of the solution was 8.6. And, in this pH the STP molecules are negatively charged.

In these pH values of chitosan and STP solutions, intere intramolecules bonds between the phosphate groups of STP and amino groups of chitosan are formed^[26].

Obtaining and characterization of chitosan microspheres

To obtain the chitosan microspheres, the chitosan solution was slowly dropped into a beaker containing a 5% STP solution in an ultrasound bath. After the addition of all the chitosan solution, the system was kept in the ultrasound bath for 2 hours.

The chitosan microspheres (wet and dried) were examined and photographed with an Olympus SZH 10 optical stereomicroscope coupled to a Nikon Coolpix 5400 digital camera to observe their morphological characteristics, such as sphericity.

The dried microspheres were also analyzed under a Jeol JSM 5610LV Scanning Electron Microscope to observe their surface structure, particularly their porosity.

Determination of microspheres porosity

The porosity can be estimated using Zeng and Ruckenstein method^[27], based only on the water amount that fills the pores. The porosity can be calculated by weighing the wet chitosan microspheres before and after water extraction, by vacuum (approximately 250 mmHg) for 30 min. Vacuum is applied to the microspheres until constant weight to allowing only free water and not bound water to be removed from the structure. The porosity (ϵ) can be estimated by Equation 3, where m_1 and m_2 are the masses of the microspheres before and after water extraction of the pores, respectively, (ρ_w) is the specific density of water at 20 °C and (v) is the volume of wet microspheres. The procedure was performed in triplicate.

$$\epsilon = \{[(m_1 - m_2) / (\rho_w \cdot v)]\} * 100(\%) \quad (3)$$

Preparation of synthetic oily water

Since crude oil is the main contaminant in the produced water from oil wells, this was chosen as the contaminant for this study.

The oily water was prepared according to a known procedure that can be found in the literature^[20]. A 200 ppm

of synthetic oily water was prepared for subsequent studies.

Packing the column with chitosan microspheres and eluting the oily water

Stainless steel columns were filled with the chitosan microspheres, according to the packing method described by Queirós et al.^[20]. The flows used were 3.0 and 7.0 mL/min. The contaminated water permeates the column filled with the polymer and three aliquots of 45 mL of eluted water were collected for analysis of the contaminant concentration for each 300 mL that passes through the column.

Analysis of the contaminant concentration in the oily water

The level of contaminants present in oily wastewaters in general is expressed in terms of total oil and grease (TOG). The TOG was measured by fluorescence using a Turner Designs TD-3100 bench fluorimeter. For this reading it is necessary to extract the organic phase from the aqueous phase using a hydrocarbon solvent, which in this experiment was n-hexane.

To extract the oil phase, a 45 mL aliquot of the oily water was placed in a 50 mL test tube and 5 mL of n-hexane was added. The tube was then shaken vigorously so that the n-hexane could extract the maximum amount of oil. After complete separation of the phases, the organic phase, isolated at the top of the tube, and was retrieved.

The extracted samples were then immediately analyzed with the fluorimeter.

Results and Discussion

Characterization of the chitosan sample

From the ¹H-NMR spectrum the areas were obtained of the chemical shifts related to the H atoms of the methyl group ($I_{CH_3} = 0.17$) and the areas of the chemical shifts related to the sum of the intensities of the H₂ signal from the deacetylated residue ($I_{H_2} = 1.03$) and the H₂ to H₆ signals from the deacetylated and acetylated residues ($I_{H_2-H_6} = 4.45$). From the area of these chemical shifts and Equation 1, the chitosan's degree of deacetylation was calculated and the value is 93.79.

To calculate the viscosimetric molar mass of the chitosan, we analyzed the graphs of viscosity *versus* shear rate of all solutions to determine the shear rate at which these solutions present Newtonian behavior. We chose a shear rate of 490 s⁻¹. The solvent's viscosity was 2.295 cP.

To calculate the intrinsic viscosity $[\eta]$ we plotted a graph of viscosity reduction *versus* chitosan concentration in the solution (Figure 1). The value of $[\eta]$ is equal to the linear coefficient of the graph obtained^[24].

Based on the $[\eta]$ obtained, and the values of K e a , the viscosimetric molar mass of the chitosan was 8.31×10^5 g/mol.

Scanning electron microscopy

The SEM photographs of chitosan microspheres was shown in Figure 2.

The chitosan microspheres shows a very clear and bumpy layer of pores which are arranged homogeneously.

According to the microscopic examination, the microspheres had diameters of approximately 500 μm , with the surface and interior presenting high porosity.

Porosity values

The microspheres showed porosity values about $80\% \pm 3$. This value is considerably higher, however in other studies^[27], chitosan microspheres with different crosslinking agents already showed values close to those obtained in this study.

Column elution

Brazilian environmental legislation (CONAMA)^[28] establishes the limits of contaminants in effluents for discharge. According to its Resolution, the maximum TOG limit in wastewater is 29 mg/L (monthly average), with daily peaks of up to 42 mg/L allowable.

The Figure 3 shows the efficiency of the chitosan microspheres in removing the oil.

Figure 3a shows the result obtained from elution of the oily water in the adsorption column containing chitosan microspheres, at flow of 7.0 mL/min.

At the end of the test 28 liters of oily water was eluted in the column. The black line represents the oil concentrations before elution. We intended to prepare a 200 ppm oily water, but the difficult of dispersion the oil in the salt water and operator mistakes cause a variation

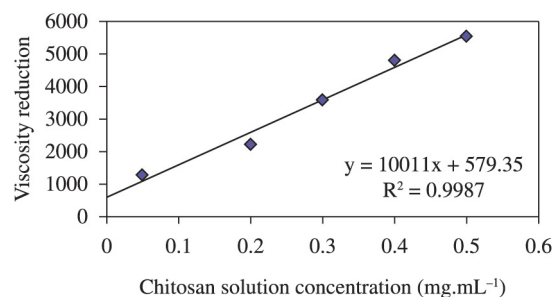


Figure 1. Viscosity reduction vs. chitosan solution concentrations.

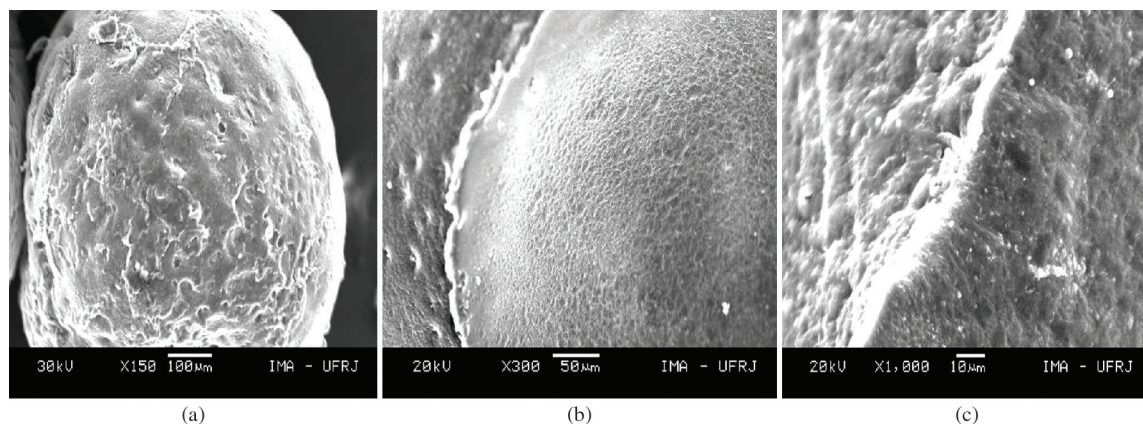


Figure 2. Scanning electron micrographs of: (a) whole sphere, without any cut, where the surface can be observed; (b) cut sphere, what allows a better observation of the interior and (c) an expansion of this image.

of these concentrations. The gray line represents the oil concentrations in the water after elution, i.e, the TOG values for the aliquotes. Finally, the dotted black line indicates a fixed concentration of 29 ppm, that indicates a maximum monthly average accepted for TOG concentration by CONAMA Resolution 393/07.

As can be seen in the Figure 3a the efficiency was greater than 90% even in the beginning of the test. The gray lines became to appear more frequently above the limit after the passage of the 16th liter of oily water. From the 20th liter can be seen a decrease in this values what indicates that are within the established until the 25th liter when is seen a further increase. This fluctuation of efficiency is related, probably, to an adsorption/desorption mechanisms of the chitosan microspheres. Some parts of the system can adsorb a large amount of oil, however, due to the flux of oily water, desorption phenomenon occurs, and therefore, a certain amount of oil is removed from the polymer surface.

Although not been reached saturation of the chitosan microsphere with oil, the test was stopped at the volume of 28 L, considering that values above the TOG already accepted by CONAMA limit (29 ppm).

In order to evaluate the efficiency of oil removal from contaminated water using another flow of water, the same procedure was used with the flow of 3 mL/min. At the end of the test 50 liters of oily water was eluted in the column.

As can be seen in the Figure 3b the efficiency was also greater than 90% even in the beginning of the test. It can be observed that from the 17th liter there was an increase in the values of TOG for values above the limit, but from the 21th liter these values decreased and remained within the limit until the end of the test. It can be observed that was eluted almost the double volume of oily water for the same bed volume when the flow was reduced. The lower oily water flow resulted in a significant increase in the volume of treated water, in view of the longest contact time of crude oil with the chitosan microspheres.

Optical microscopy

We carried out optical microscopic analyses of the chitosan microspheres before and after the elution of the

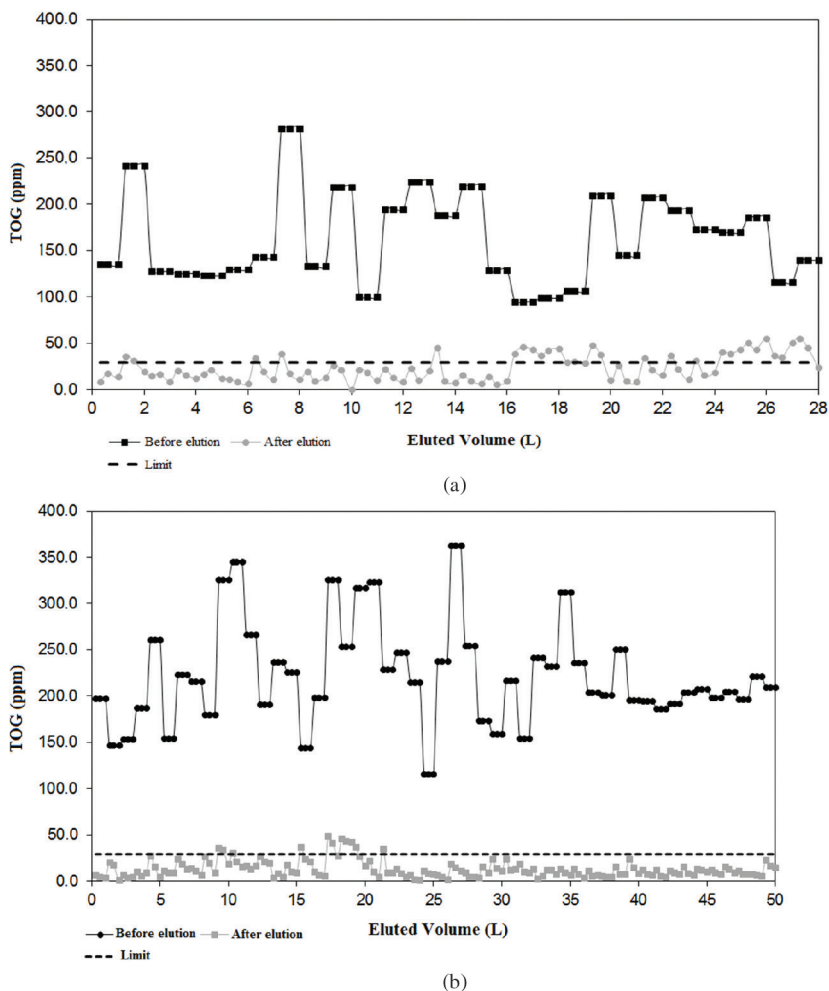


Figure 3. Graph of elution of oily water through columns packed with chitosan microspheres, at flows: (a) 7.0 mL/min; (b) 3.0 mL/min.

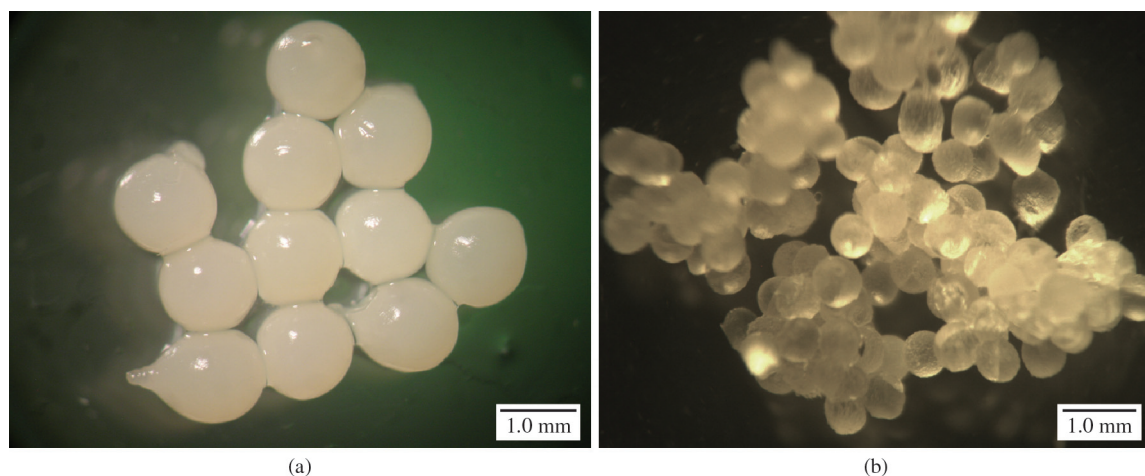


Figure 4. Optical micrographs of the chitosan microspheres before packing (a) wet and (b) dry.

oily water (Figures 4 and 5, respectively). The chitosan microspheres were opaque both before and after drying.

The opacity of these microspheres is related to their porosity. Greater opacity indicates higher porosity^[29]. It was also observed the reduction of the particle size after drying. As can be seen in Figure 4, there was a substantial

reduction in the particle size before (a) and after (b) drying.

The micrographs contained in Figure 5 show the adsorption of the oil by the chitosan microspheres after the test using the flow of 7 mL/min. Samples of microspheres

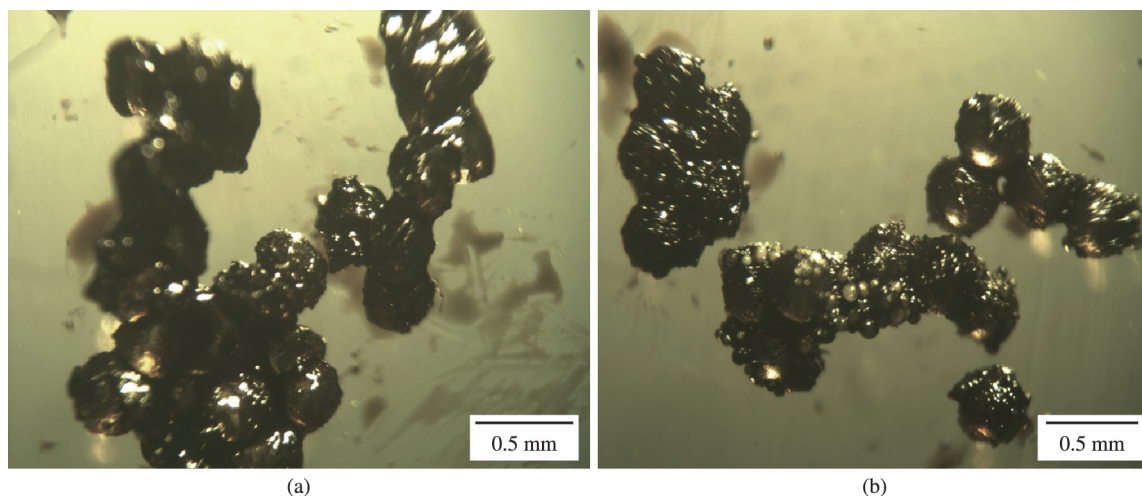


Figure 5. Optical micrographs of the chitosan microspheres after packing (a) bottom and (b) top, with 2.5x magnification.

at the end of the tests were removed from the bottom and top of the column.

They remained spherical after the column test, despite the high percentage porosity value (about 78%), indicating good resistance to the pressure exerted by the pump, even the spheres that were at the top of the column, where the oily water is initially introduced, which could cause a larger deformation on the particle.

Conclusions

The results obtained show that the chitosan microspheres used as natural polymeric resins perform well in removing heavy oil from produced water, with adsorption efficiency greater than 90% in the beginning of the test, ie, over than 180 ppm of these oil was removed from oily water for both flow used. During the test the flow reduction had great influence on efficiency, having the lowest flow a volume of treated water much higher. Considering that the concentration of the incoming water was about 200ppm of oil, and that the outlet was below the limits set by CONAMA, which is 29 ppm, it is material present high capacity for this application. Besides this, the microspheres had good resistance, maintaining their spherical shape despite the pressure applied on them in the elution column.

Acknowledgments

We thank the National Scientific and Technological Research Council (CNPq) for funding.

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Received: 02/16/13

Revised: 08/22/13

Accepted: 09/03/13