

Nanocomposites Based on Ionene–Bentonite Used to Treat Oily Water

Claudia R. E. Mansur, Roberta S. Oliveira, Vanessa Akeda, Yure G. C. Queirós, Luciana S. Spinelli, Elizabete F. Lucas

Federal University of Rio de Janeiro, Institute of Macromolecules, Rio de Janeiro, RJ, Brazil

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ABSTRACT: A large number of processes are used to treat the oily water (oil emulsions in water) produced in the petroleum industry. The treatment strategy depends not only on the strictness of the environmental requirements in the jurisdiction where the water is discharged, but also on the relative treatment cost. The present study reports tests to assess the effectiveness of removing oil from oily water by adsorption in polymer nanocomposites. These composites were prepared from ionenes (cationic polyelectrolytes) and sodium bentonite or organophilic bentonite. They were characterized by infrared spectrometry, thermogravimetry, X-ray fluorescence, and

X-ray diffraction. The oil-removal effectiveness was evaluated by mixing nanocomposites and oily water in a shaker bath (batch test). In the tests conducted only with treated sodium bentonite and organophilic bentonite, the oil removal was $\sim 70\%$, whereas the use of polymer nanocomposites raised the adsorption of oil to $\sim 90\%$. These values depended on the mass of material, concentration of oil in the contaminated water, and the contact time. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 218–226, 2012

Key words: nanocomposites; contaminated water; ionenes

INTRODUCTION

Clay minerals are generally crystalline hydrous aluminum phyllosilicates, in some cases containing other elements such as Mg, Fe, Ca, Na, K, and Li. All types of bentonite contain one or more clay minerals of the smectite group, with montmorillonite as the predominant clay mineral. The clays that contain the highest percentage of montmorillonite are bentonite and Fuller's earth.^{1,2}

Bentonite has the capacity to exchange the cations naturally present on its internal and external surfaces with other cations from aqueous solutions of inorganic and organic salts. This property is mainly responsible for bentonite's great adsorption power, especially for ions in solution. This property can be used to chemically modify a natural bentonite (NB) to obtain a homoionic bentonite, which is a type that enables exchange of cations with a single cation of a selected inorganic salt. This allows obtaining homoionic bentonites of Na, K, Ca, Al, Cr, etc.³

When NB is in contact with aqueous solutions of quaternary ammonium salts, the exchangeable cations of the clay are replaced by organic cations. The compounds obtained are called organophilic bentonites or just organobentonites.⁴

A new class of composite materials has been developed in recent years by combining inorganic metal alkoxides with polymers or organic materials having low molecular weight (frequently functionalized). Nanocomposites are defined as a new class of composites, in which at least one dimension of the dispersed particles have nanometric size.⁵

Polymer–clay composites are divided into three general classes according to the arrangement of their constituents: conventional composites, in which the clay acts as a conventional filler; intercalated nanocomposites, consisting of a regular insertion of the polymer between the clay layers; and delaminated nanocomposites, in which 1-nm thick layers are dispersed in the matrix to form a monolithic structure in microscale.⁶

Various characteristics have been observed for the materials prepared with clays and polymers: various composite species are synthesized by combining a large variety of polymers and host materials²; polymers can be accommodated in the interlamellar region with retention of the structural factors and the lamellae; the interlamellar spaces are adaptable to the size of the polymer accommodated; the species aggregated in the interlamellar spaces are

Correspondence to: C. R. E. Mansur (celias@ima.ufrj.br).

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influenced by the environmental characteristics of the nearby layers; and the properties are controlled by the interactions between layers and polymers along with the properties of the layers and polymers themselves.

Ionenes are 100% cationic polyelectrolytes of the polyamine type, whose quaternary nitrogen atom is located in the principal chain.^{7–9} The term ionene indicates that these polymers can be obtained by ionization of amines.^{10,11}

The various applications of ionenes are based on the direct interaction of their positive charges with the negative charges of the materials to be treated.⁵ The potential or suggested applications include medicine,¹² preservation of flowers,¹³ humidity sensors,¹⁴ animal antihelmintics,¹⁵ and flocculants for wastewater treatment,^{10,11,16,17} among others.

During offshore production of oil in systems that operate with secondary recovery, some water from the injection process often returns with the oil. As a result, large volumes of water have to be discharged in the sea. But this oily water must be treated first. Water treatment systems are generally divided into three broad categories, considering the purity requirements (primary treatment, using gravitational separators, secondary treatment, using flocculants and flotation process and tertiary treatment, by the adsorption process). The use of tertiary separation systems such as adsorption in active carbon is necessary to reach levels at which the oil content of the discharged water is less than 10 mg/L. In addition to removing oil, this kind of treatment is also designed to remove aromatic compounds contained in the production water, which are the most toxic to the environment.^{18–20}

The present study aimed to obtain nanostructured materials with an ionene–bentonite base, derived from commercial sodium bentonites and polymers of the (2- γ -tetramethyl-ionene) type, for use to purify water contaminated with oil.

EXPERIMENTAL

Materials

We used ditertiary diamine, tetramethylethylenediamine (TMEDA), and linear α,ω -dibromoalkane with 4, 6, 10, and 12 carbon atoms in their chains, obtained from Sigma-Aldrich, to previously synthesize the ionenes studied. The molar mass of the polymers were 13,000, 15,000, 12,000, and 5,000 g/mol, respectively.²¹ They were selected because their load density and hydrophobic chain size can be varied easily.

The commercial clays used were Na-35 sodium bentonite, donated by the firm Schumacher Insumos para Indústria, and Viscogel B8-S8, an organophilic bentonite, donated by the company Química Roveri.

The latter product is modified clay with hydrocarbon chains containing 18 carbon atoms. All the samples were used as received. Crude oil with medium API grade from an offshore Brazilian well was used to prepare the synthetic oily water for testing. Hexane P.A., obtained from Vetec Química Fina, was used as the extraction solvent, to help in determining the concentration of oil present in the oily water.

Methods

The ionenes studied were previously synthesized²¹ through a polycondensation reaction between ditertiary diamine (TMEDA) and the four α,ω -dibromoalkanes indicated in the earlier section, according to methods reported in the literature.^{7,10,22} The general method of synthesizing these polymers relies on a Menshutkin reaction.²³

The polyionenes, two types of clay, and the nanocomposites obtained were characterized by Fourier transform infrared spectrometry (FTIR) and thermogravimetry analysis (TGA). The absorption spectra in FTIR were obtained using a Perkin–Elmer model 1720X spectrometer, in the wavelength band between 4000 and 400 cm^{-1} , with 50 scans and resolution of 2 cm^{-1} . All the analyses were conducted at room temperature ($\sim 25^\circ\text{C}$), with the samples in the form of KBr pellets.

All the samples (ionenes, clays, and nanocomposites) were evaluated in a Perkin–Elmer model TGA7 thermogravimetric analyzer, in a temperature range of 30 to 700°C and heating rate of 10°C/min, using nitrogen as the purge gas. The clay and nanocomposite samples were also characterized by X-ray fluorescence and X-ray photoelectronic spectroscopy.

The X-ray fluorescence spectra were obtained by the LiB_4O_7 fusion method in a Rigaku model RIX3100 spectrometer with a rhodium tube. All the analyses were carried out at room temperature. The purpose of this analysis was to determine the cation exchange capacity (CEC) of the clay.

The X-ray photoelectronic spectroscopic analyses were performed in a Rigaku equipment, Philips, Miniflex goniometer model, utilizing $\text{K}\alpha$ radiation from copper ($\lambda = 1.5418 \text{ nm}$), voltage of 40 kV and current of 40 mA. The measurements were taken at small angles (between 2θ and 12θ). The aim was to verify the interlamellar space in the clay before and after chemical modification.

Preparation of the nanocomposites

Different ionene concentrations were used, based on the CEC of the bentonite. The polycation quantities needed to satisfy the CEC were calculated by multiplying the CEC by the polycation's molar mass. Nanocomposites were prepared containing 100% polymer.

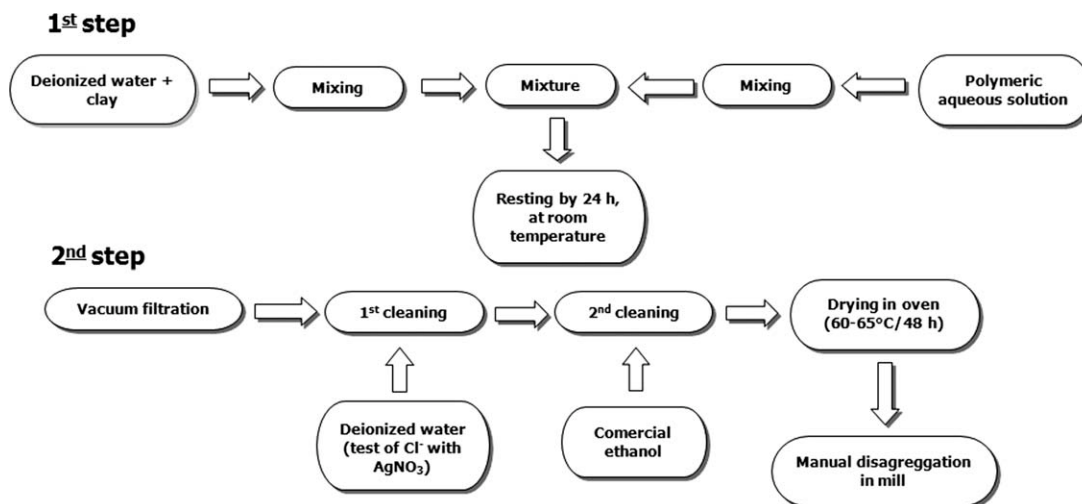


Figure 1 Scheme of nanocomposite preparation.

The bentonite/polyionene nanocomposites were prepared according to the process shown in Figure 1.

The coprecipitation method used to intercalate the ionenes in the clay consisted of adding an aqueous solution of the polymer to a sodium bentonite solution in deionized water under agitation.²

To prepare the Viscogel/polyionene nanocomposites, first organophilic clay was swollen with three different solvents: methanol, ethanol and acetone. Only the TM2,6 and TM2,12 polyionenes were used together with this type of clay, to test the influence of the interplanar distance generated by the two different levels of polyionene incorporation. For this purpose, the mass of these polymers was 1.5–5 g of Viscogel. This ratio was selected based on the mass calculated for formation of the bentonite Na-35 nanocomposites with 100% TM2,12 polyionene (~ 1.7–5.0 g).

Preparation of the synthetic oily water

The purpose of this work was to study the application of the nanocomposites obtained to remove oil from water. Therefore, we prepared synthetic oily waters to simulate those produced by offshore oil wells (salinity, temperature, and composition in function of the oilfield of origin). This preparation consists of two steps: preparing the saltwater and adding the oil to the water.

The method for preparing the saltwater and contaminated water has been described in a previous work.²⁴ Three oil concentrations were used: 50, 100, and 200 ppm.

Evaluation of the oil-absorption performance of the nanocomposites

The performance of the nanocomposites in removing the crude oil from the contaminated water was assessed in function of the quantity of nanocompo-

site and clay, and also the nanocomposite's contact time with the clay (from 15 to 120 min with defined intervals).

In all the tests, the mixture of nanocomposite–clay in the oily water was kept in a Haake model SWB25m thermostatic shaker bath at a controlled agitation speed. Blank tests were also performed using only clay (natural and organophilic) and oily water.

After the defined times, aliquots of the treated water were removed, allowed to settle for 30 min and then subjected to liquid–liquid extraction with hexane to remove the oil present in the water. The extraction was carried out in a test tube in a water-to-solvent ratio of 45 : 100. After the phases separated, an aliquot of the organic phase containing the oil was diluted to 1 : 10 in hexane and then analyzed in a Varian Cary Eclipse spectrofluorimeter to obtain the total oil and grease concentration, by comparison with response curves. These curves were plotted from analyzing the solutions of oil in hexane, with concentrations varying from 5 to 200 ppm.

The analytic conditions of the spectrofluorimeter were defined after previous checks to establish the excitation wavelength of the organic compounds present in the oil: a wavelength of 350 nm and absorption and emission slits of 5 nm; scanning of emission spectrum ranging from 360 to 750 nm, with pure *n*-hexane as the blank (0 ppm) and absorption intensity readings at wavelengths of 402 and 440 nm, for comparison against the results of another study reported in the literature.²⁵

RESULTS AND DISCUSSION

Characterization by infrared spectrometry and thermogravimetry

Figures 2 and 3 show the results of the infrared spectrometry and TGAs, respectively, for the Na-35

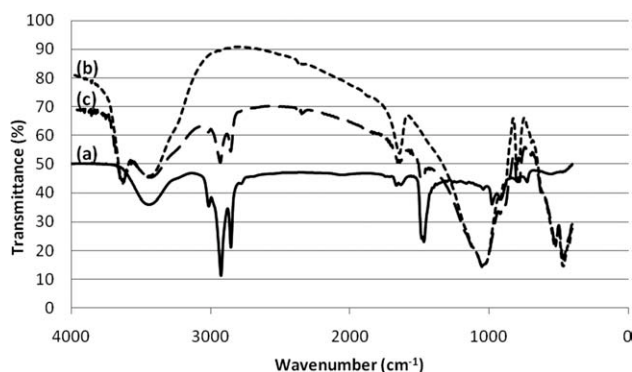


Figure 2 Absorption spectra of FTIR: (a) TM2,12 polyionenes; (b) Na-35 bentonite and (c) Na-35 bentonite/TM2,12 polyionenes.

bentonite, TM2,12 polyionene, and the nanocomposite prepared from them (Na-35 bentonite/TM2,12 ionene). Figure 4 shows the results of the TGAs for the Viscogel B8-S8 and the nanocomposite prepared from it and TM2,12 ionene (Viscogel B8-S8/TM2,12 ionene).

Polyionenes

We named the polyionenes according to the dibromoalkane used to synthesize them. By this scheme, we called the polyionene obtained with the dibromoalkane with a hydrocarbon chain containing four carbon atoms TM2,4, because the reaction was carried out using TMEDA. For the same reason, we designated the other polymers as TM2,6, TM2,10, and TM2,12.

Aliphatic ionenes present characteristic bands when analyzed by infrared spectroscopy,^{24–26} as can be seen in Figure 2 for the TM2,12 ionene: at 3450 cm^{-1} , due to the O–H axial vibration; 2930 cm^{-1} , due to the asymmetric axial deformation of CH_3 and CH_2 (strong bands); 2850 cm^{-1} , due to the symmet-

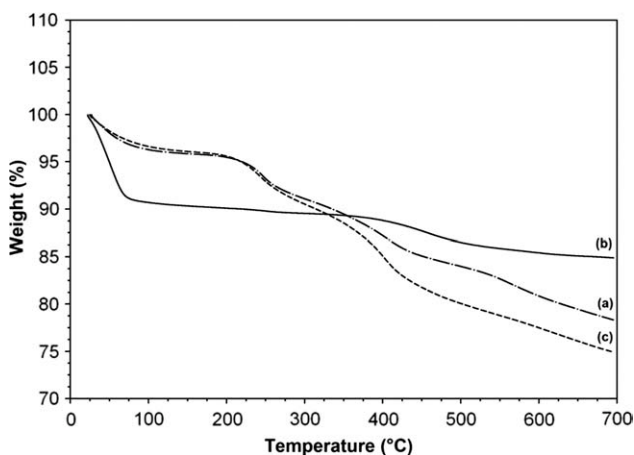


Figure 3 Thermogravimetric analysis of: (a) TM2,12 polyionenes; (b) Na-35 bentonite and (c) Na-35 bentonite/TM2,12 polyionenes.

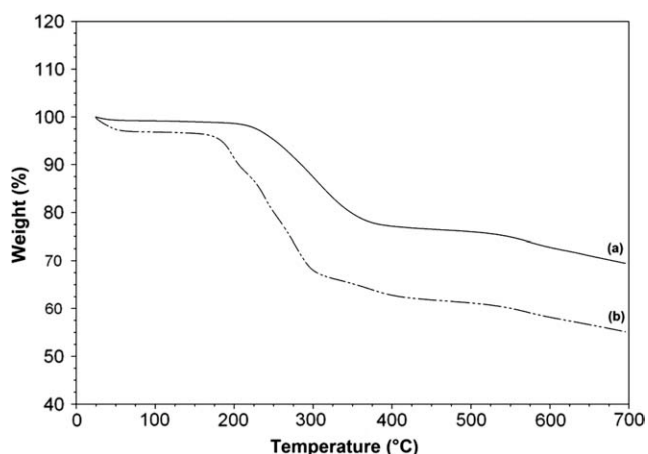


Figure 4 Thermogravimetric analysis of: (a) organophilic clay Viscogel B8-S8 and (b) Viscogel B8-S8/TM2,12 nanocomposite.

ric axial deformation of CH_3 and CH_2 (medium bands); 2070 cm^{-1} , due to the stretching vibration of $\text{N}^+\text{—CH}_2$ (weak band); 1470 cm^{-1} , due to the symmetric angular deformation on the CH_2 plane (strong band); 905–1040 cm^{-1} , due to the stretching vibration of C–C (medium and weak band); and 720 cm^{-1} , due to the asymmetric angular deformation on the CH_2 plane (weak band).

The thermogravimetry results for the polyionenes in all cases showed more than one peak related to the degradation stages. Figure 3 shows the thermogram obtained for sample TM-2,12. The peak related to the first stage, between approximately 30 and 120°C, is due to the loss of water linked to the ionene, because of the hygroscopicity of these polymers. The second stage, between 200 and 400°C, can be attributed to the polymer's degradation. By thermogravimetric/differential thermogravimetric (TG/DTG) curves, the percentage of mass loss and maximum degradation temperature can be observed that TM2,12 had the highest degradation temperature: 240°C.

The greater stability of this ionene is apparently related to its long methylene chain, which upon breaking can generate monomeric units or aliphatic structures with low molar mass. The other polyionenes started degrading at 231, 229, and 219°C, respectively, for TM2,10, TM2,6, and TM2,4.

Na-35 bentonite and bentonite/TM-ionene nanocomposite

Differences can be observed between the infrared spectra of the nanocomposites and of the pure: besides the characteristic bands for the clay (mainly the 3623, 3410, 1614, and 1010 cm^{-1} bands referring to the complex vibrations of the OH group), the spectrum of the Na-35 bentonite/TN-2,12 ionene nanocomposite (Fig. 2) shows bands at 1471 cm^{-1} ,

due to the symmetric angular axial deformation vibration on the CH_2 plane, and at 2852, 2940, and 3010 cm^{-1} , due to the asymmetric axial deformation of CH_3 and CH_2 , confirming the presence of dimethylammonium ions from the polycations in the clay. Similar behavior has been reported in the literature when monoquaternary ammonium salts containing 1, 3, 4, and 12 carbon atoms in their chains are intercalated in a sodium montmorillonite.²⁶ The infrared spectra for the nanocomposites Na-35 bentonite/TM2,4, TM2,6, and TM2,10 ionene are similar to the nanocomposite spectrum shown in Figure 2.

The thermogravimetric analysis (TGA) produced similar thermal degradation curves for the Bt-TM-ionene nanocomposites because these materials prepared with polymers have very similar structures.

Figure 3 shows the thermogravimetric curves for the Na-35 bentonite and the Na-35/TM2,12 nanocomposite, confirming that the clay originally contained 5% organic material in the range from 100 to 600°C . However, according to data in the literature,²⁴ a percentage of this mass loss can also be associated with the decomposition of water molecules linked by hydrogen and the OH groups of the tetrahedral layers.

There was also an initially significant mass loss between 25 and 100°C , of $\approx 10\%$, corresponding to the removal of water from the interlayers coordinated to Na^+ , and interaction of the ionene with the clay in the nanocomposite, evidenced by comparing the total mass losses of the nanocomposites and pure clay.

In general, the total mass losses were $\sim 18\text{--}21\%$, increasing as the length of the α,ω -dibromoalkane chain increased. For the nanocomposites, the mass loss in the first decomposition stage (between 25 and 100°C) was 4–5%, lower than that for pure bentonite. This indicates that the nanocomposites absorbed less water, due to their organophilic properties (already observed by infrared spectroscopy). Similar behavior has been reported in other studies, where hydrophobicity increased in clays treated with monoquaternary ammonium salts evaluated in a sequence of increasing numbers of carbon atoms in the salt chain.²⁷

In the temperature range from 100 to 600°C , the mass loss of the nanocomposites was substantially greater than for the pure bentonite (5%), ranging from 13% for the Na-35/TM2,4 nanocomposite to 17% for the Na-35/TM2,12 nanocomposite. These mass losses are caused by the oxidation and decomposition of the intercalated polycations and the water adsorbed below 220°C , whose contribution declines with increasing spacing of the ionene.^{27,28}

The DTG curves also showed that as the chain of the polymer spacer increased, there was a tendency for the first degradation peak to become less intense, unlike the behavior of the second peak, which gradually became more intense. This behavior probably is associated with the ionene's structure. The second peak

appears to be involved with the successive breaking of the bonds of the methylenes in the spacer's chain.

Viscogel B8-S8 and Viscogel-TM-ionene nanocomposites

We also used the organophilic clay Viscogel B8-S8 to prepare nanocomposites with the synthesized polymers. As mentioned, this clay contains chains with 18 carbon atoms. The spectrum of the organophilic clay shows that besides the characteristic bands of an unmodified clay (Fig. 2), bands can be observed related to the symmetric angular deformation vibration on the CH_2 plane ($\sim 1470\text{ cm}^{-1}$) and to the asymmetric axial deformation of CH_3 and CH_2 (in the region between 2840 and 3000 cm^{-1}). These bands confirm the presence of hydrocarbon chains in this modified clay.

It was not possible from the qualitative infrared spectra to confirm the incorporation of the polyionenes for the Viscogel B8-S8/TM2,12 nanocomposite, because the same bands could be observed related to the CH_2 and CH_3 groups. To do this, it would be necessary to perform a quantitative analysis, considering the increase in the intensity of these characteristic signals.

The thermogravimetric analysis of the Viscogel B8-S8 is shown in Figure 4(a), where a total mass loss of $\sim 30\%$ can be seen. Figure 4(b) shows the thermogravimetric analysis of the Viscogel+TM2,12 nanocomposite, where the degradation stages of the polyionene can be observed. Besides this, the total mass loss increased to 44%, confirming the incorporation of this polymer in the organophilic clay.

Characterization of the clay by X-ray fluorescence

X-ray fluorescence was used to determine the CEC of the sodium bentonite. This is a quick and reliable technique that does not require manual laboratory work. The CEC was determined using stoichiometric calculations, considering the percentage by mass of Na_2O , according to eq. (1).

$$\text{CEC} = \text{meq Na}/100\text{g of clay} \quad (1)$$

where CEC is the cation exchange capacity, and meq Na is the quantity of sodium in milliequivalents.

Table I presents the data from the semiquantitative analysis of the sodium bentonite. Its CEC was 97 meq/100g of clay. This result agrees with other reports in the literature, according to which smectites have CEC values between 80 and 150 meq/100 g of clay.¹

The polymer concentration in aqueous solution added to the clay suspension used to prepare the nanocomposite was obtained by multiplying the CEC of the clay and the molar mass of the polycation.

TABLE I
Results of Semi-Quantitative Analysis of the Sodium Bentonite Obtained by X-Ray Fluorescence (wt %)

Oxide	Na-35 bentonite
Na ₂ O	3
MgO	3
Al ₂ O ₃	18
SiO ₂	60
K ₂ O	1
CaO	2
H ₂ O	8
Fe ₂ O ₃	5

Characterization of the nanocomposites by X-ray diffraction

Among the advantages of X-ray diffraction to characterize crystalline phases in ceramic materials is its simplicity, quickness, and reliable results (each crystalline phase has a particular diffraction profile), as well as the possibility of analyzing materials composed of a mixture of phases.^{30,31}

Because the sodium bentonite (Na-35) used in this work is a commercial product, it was necessary to characterize it by X-ray diffraction to identify which minerals it contains. Figure 5 presents the X-ray diffractogram of the untreated sodium bentonite. The peaks referring to montmorillonite (M) and quartz (Q) are easily identified.³⁰

The intercalation modes of the ionenes in the bentonite's interlamellar spaces were established by the shift to lower values of the angle in $2\theta = 7.1^\circ$ (attributed to montmorillonite).³⁰ The shifts of the 2θ angle to lower values in all the nanocomposites analyzed indicated intercalation of the ionenes.

Because the distances between the quaternary nitrogen atoms of ammonium were constant for all ionenes, according to the $N^+CH_2N^+$ portion, it is the size of the spacer that is related with the cationic percentage of these polymers, in function of the greater or smaller distance they allow between the quaternary ammonium sites. It can be said that the larger spacers contribute to a lower cationic percentage in the polymer. Similar behavior was observed when poly((*N,N,N*-trimethylammonio)ethyl acrylate chloride salt) acrylamide and chloride copolymers, with few chloride units in their chains, were adsorbed in clays,²⁶ forming a large number of "folds" to increase the basal space of the clay. Therefore, in nanocomposites prepared with ionenes having smaller distances between the quaternary ammonium sites, these polycations will be intimately adsorbed on the clay surface, with little chance of being rearranged, that is, showing high adsorption. In contrast, ionenes with spacers containing 12 carbon atoms in their chains have a greater chance of being adsorbed and folded, and thus expanding the basal space of the bentonite.

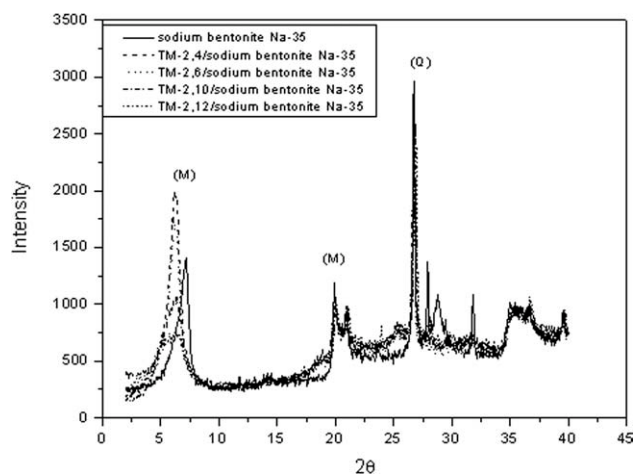


Figure 5 X-ray diffractogram of Na-35 bentonite and nanocomposites based on polyionenes (with 100% of polymer). (M = montmorillonite e Q = quartz).

In the case of the Viscogel B8-S8/TM2,6 and Viscogel B8-S8/TM2,12 nanocomposites [Figs. 6(a,b), respectively], it can be seen that when using different polymer masses there was a more pronounced reduction in the basal spacing of the nanocomposite formed with TM2,6.

Performance of the nanocomposites in absorbing oil in the synthetic oily waters produced with crude oil

Preliminary blank tests were conducted to obtain the nanocomposite mass that would be utilized in the oil removal tests from the contaminated water. For this purpose, the masses were varied between 0.025 and 0.3 g, with different contact times (15, 30, 45, 60, 90, and 120 min).

The results of these tests allowed determining the adsorbent mass (clay) that was least efficient in removing the oil, to enable evaluating the efficiency of using

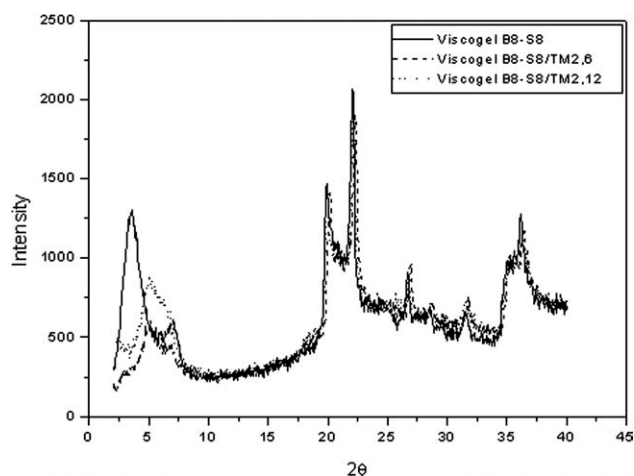


Figure 6 X-ray diffractogram of organophilic clay Viscogel B8-S8 and nanocomposites based on polyionenes.

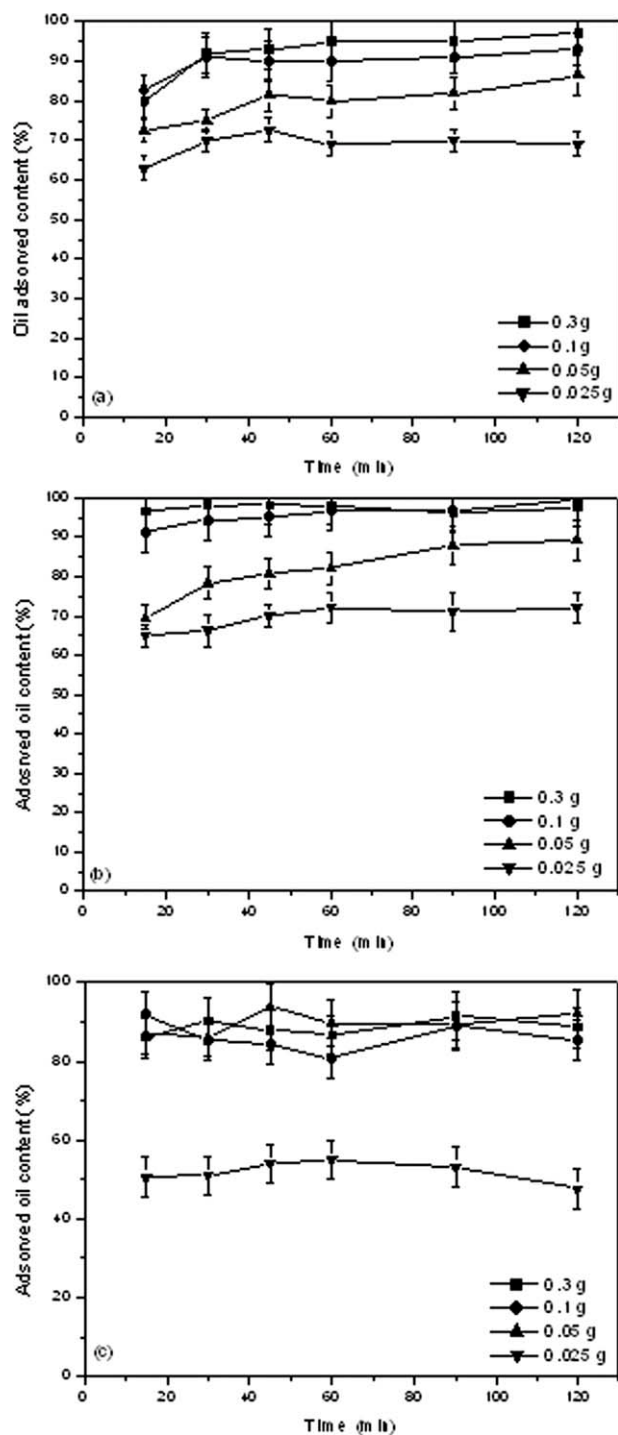


Figure 7 Decontamination of oily waters containing oil concentrations of (a) 50, (b) 100 and (c) 200 ppm by using different masses of Na-35 bentonite.

nanocomposites to remove contaminants from water with systems in which the clay has low efficiency.

Oil absorption tests of Na-35 sodium bentonite

In the oil absorption tests only with the Na-35 sodium bentonite, it showed potential to absorb oil in

all cases, because the solution appeared much cleaner. Figure 7 shows the results obtained in the decontamination of oily waters containing oil concentrations of 50, 100, and 200 ppm, respectively.

As the mass of pure sodium bentonite increased, its oil-removal capacity increased as well. For clay masses of 0.3 and 0.1 g, ~ 100% of the oil was removed, because the oil found in the residual oily water was very low. This high absorption occurred even after short contact times (15 or 30 min). The lowest absorption values in the clay were obtained with a mass of 0.025 g.

These tests served to choose the mass to be utilized in the oil removal tests, namely with nanocomposites prepared with 0.025 g of clay.

Oil-absorption tests with Na-35 bentonite/polyionene nanocomposites

Figure 8 shows the quantities of oil adsorbed in the different oily waters (with oil concentrations of 50, 100, and 200 ppm) by the Na-35 bentonite/TM2,6

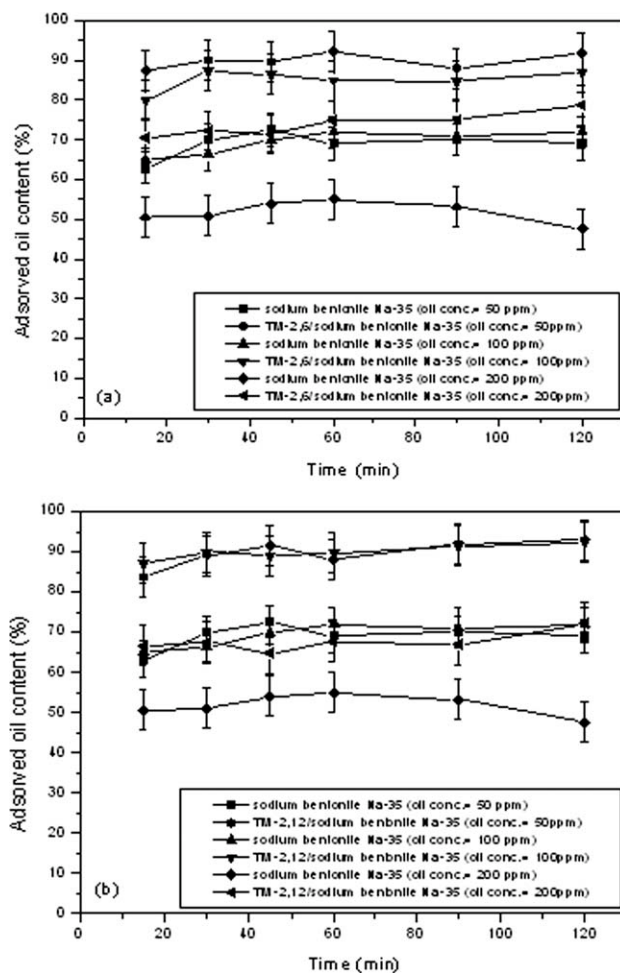


Figure 8 Decontamination of oily waters containing oil concentrations of 50, 100 and 200 ppm by using (a) Na-35 bentonite/TM2,6 and (b) Na-35 bentonite/TM2,12 polyionenes.

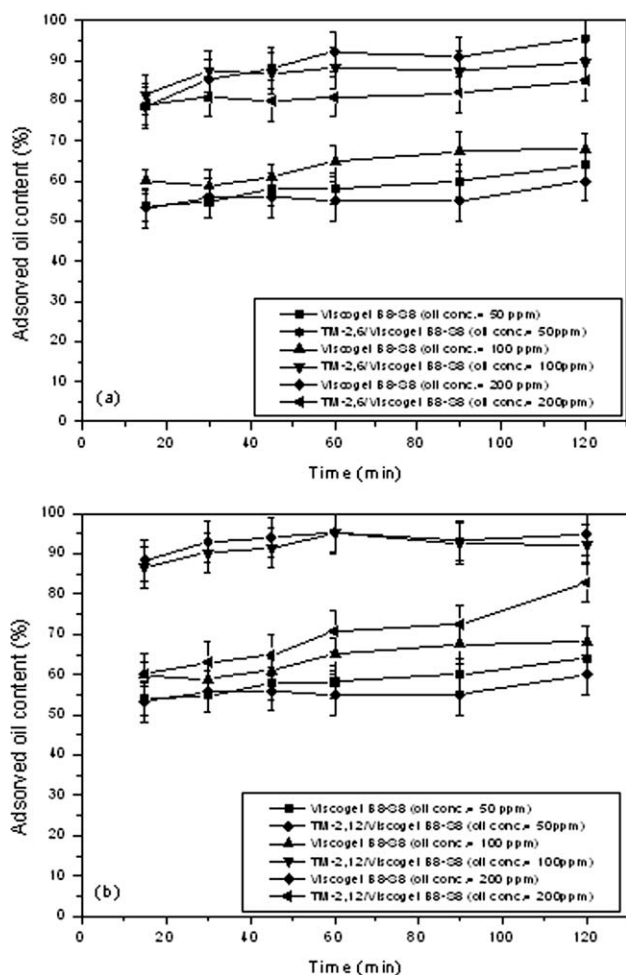


Figure 9 Decontamination of oily waters containing oil concentrations of 50, 100 and 200 ppm by using (a) organophilic clay Viscogel B8-S8/TM2,6 and (b) organophilic clay Viscogel B8-S8/TM2,12 polyionenes.

ionene and Na-35 bentonite/TM2,12 ionene nanocomposites. The nanocomposites were more efficient than the pure bentonite in oily water containing lower oil concentrations, attaining removal rates of 92% soon after the start of the tests (30 min).

In oily water containing 200 ppm of oil, as expected, the greatest efficiency achieved by the nanocomposites was 80% [with the nanocomposite composed of NB + TM2,6; Fig. 8(a)].

Oil absorption tests of the organophilic clay (Viscogel B8-S8)

In the oil absorption tests with the organophilic clay swollen in different solvents, all the systems with mass of 0.3 g were ~ 100% efficient in removing the oil from water with an oil concentration of 100 ppm. The efficiency declined as the mass of organophilic clay declined. For this reason, in evaluating the nanocomposites formed with Viscogel B8-S8 and the

polyionenes, we chose a mass of 0.025 g and ethanol as the solvent to promote its swelling.

Oil absorption tests of the Viscogel B8-S8/polyionene nanocomposites

Figure 9 shows the results obtained with the Viscogel B8-S8/TM2,6 and Viscogel B8-S8/TM2,12 nanocomposites in synthetic water containing oil concentrations of 50, 100, and 200 ppm. In both cases, 100% of the polyionene was incorporated in the organophilic clay.

The Viscogel B8-S8/TM2,6 and Viscogel B8-S8/TM2,12 nanocomposites were more efficient in water containing lower oil concentrations (50 and 100 ppm), that is, the oil removal efficiency of the pure Viscogel B8-S8 was increased to levels over 95%. This efficiency was similar to the result at concentrations of 50 and 100 ppm of the bentonite/polyionene nanocomposites (Fig. 8).

In oily water containing the highest oil concentration tested (200 ppm), the greatest efficiency attained by the nanocomposites was ~ 80%, similar to the efficiency achieved previously by the bentonite/polyionene nanocomposites.

CONCLUSIONS

The efficiency in removing oil from contaminated water by nanocomposites formed from sodium clay was similar to that observed for those formed from organophilic clay. The oil removal efficiency of the systems studied was above 90% when the oil concentration was low. For concentrations of 200 ppm, this efficiency declined to ~ 80%.

The nanocomposites were characterized by complementary techniques: FTIR spectroscopy to reveal the mixture of the polymer with the clay; thermogravimetry to evidence the interaction of the components and X-ray diffraction to confirm the intercalation of the ionenes in the bentonite, which was useful for visualizing the increase of clay basal space mainly due to the way of polycations adsorption; the polycations with the longest chain lengths can be adsorbed in a configuration characterized by the greater number of "folds" and "tails" of the nonadsorbed polymer chain at the clay's surface.

The nanocomposites formed with the polyionenes TM2,6 and TM2,12 were equally efficient in removing the oil, showing that the length of the carbon chain did not cause a significant variation in the oil absorption efficiency in the systems evaluated. However, the evaluation of these systems was specific for a determined mass of clay used, oil concentration in the contaminated water and clay's contact time with the contaminated water.

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