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PERFORMANCE OF ORGANOPHILIC CLAY AS ADSORBENT IN THE OIL/WATER SEPARATION PROCESS

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ABSTRACT

The main objective of this study was to conduct an investigation on the performance of organophilic clay as adsorbent in the oil/water separation process. The originality of this work is its focus on Brazilian clay. The gray organophilic clay was prepared from gray clay and quaternary ammonium salts. The samples were characterized by X-Ray Diffraction, Differential Thermal and Thermogravimetric Analysis, Infrared Spectroscopy, Cation Exchange Capacity, Adsorption Capacity and the Foster Swelling test. The results indicated that the quaternary ammonium salts were intercalated between the layers of clay. A 2^2 factorial design was conducted with three central points in finite bath tests to determine the rate and capacity of oil removal by the organophilic clays. Values as high as 99.3 % of removal efficiency and 32.5 mg/g of removal capacity were reached in the assays, thus indicating that the use of organophilic clay has great potential in the oil/water separation process.

KEYWORDS

clays; organophilic clay; oil/water separation process; adsorption; removal capacity

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1. INTRODUCTION

Water-cut measurement in crude oil is an important and widely practiced routine in all aspects of oil industry operations, crude oil production, processing, transportation, and refining. In particular, water-cut measurement is used to determine production rates, custody transfer, and pipeline oil quality control **(Gamal et al., 2005)**.

Clay particles have been shown to stabilize water-oil emulsions **(Menon and Wasan, 1988)**. An X-ray detector coupled to an electron microscope was used to identify clays at the water-oil interface in water-oil emulsions **(Mikula, 1987)**. Clays at the interface were detected by the presence of clay-derived silicon. Large phytoplankton blooms give rise to high concentrations of organic particulates. Clay particles and organic-clay particulates have both hydrophobic and hydrophilic regions, so that such particles would be located at the water-oil interface and would be expected to stabilize emulsions **(Tsugita et al., 1983)**.

Montmorillonites (MMT) have attracted considerable attention because of their high cation exchange capacity (CEC), swelling capacity, high surface areas, and consequential strong adsorption capacities **(Jacobs et al., 2006; Xi et al., 2007)**. Natural montmorillonite with exchangeable cations can be transformed into hydrophobic organic montmorillonite by replacing the metal ions with organic ones such as quaternary ammonium salts. Such modified materials have larger basal spacing of the layers and lower surface energy, and can be compatible with organic liquids or polymers. The change of surface properties affects the applications of the montmorillonite. There are many applications of modified montmorillonite as sorbent in pollution prevention and environmental remediation **(Zhou et al., 2009)**. In recent years, it has been widely cited on account of its performance-enhancing properties when used as a nanoscale additive in plastics to generate polymer nanocomposites **(Kurose et al., 2007; Jang et al., 2005)**.

Clay minerals can react with different types of organic compounds in particular ways. Kaolin species (kaolinite, nacrite, and dickite) adsorb particular types of neutral organic compounds between the layers. The penetration of organic molecules into the interlayer space of clay minerals is called intercalation. Intercalated guest molecules can be displaced by other suitable molecules.

A broader diversity of reactions characterizes the behavior of 2:1 clay minerals. Water molecules in the interlayer space of smectites and vermiculites can be displaced by many polar organic molecules. Neutral organic ligands can form complexes with the interlayer cations. The interlayer cations can be replaced by various types of organic cations. Alkylammonium ions are widely used in modifying bentonites **(Lagaly, 2006)**. In industrial applications, the main compounds comprise quaternary alkylammonium ions.

In Brazil, smectites can be encountered in relatively small deposits. The most important of them is localized in the State of Paraiba, in the town of Boa Vista. These clays were discovered in the 1960’s, and initial studies demonstrated that they were naturally polycationic and could be transformed into sodium smectites. It was verified that these clays consisted of the clay minerals montmorillonite, illite and kaolinite, and mixed layers of illite-montmorillonite and quartz. It has been discovered that, upon treatment of these polycationic clays with an aqueous solution of Na_2CO_3 at an appropriate concentration, it is possible to obtain sodium bentonites **(Amorim et al., 2004)**.

In view of all this, the objective of this work was to evaluate the efficiency of gray clay. The originality of this work is that the study includes a Brazilian clay, and examines its swelling ability on the separation of oil-water emulsions.

2. EXPERIMENTAL

2.1 Materials

A gray clay, provided by Sud-Chemie (Brazil), was used during the preparation of the organoclays. This gray clay was typically in the sodium monocationic form and was sieved according to the Brazilian ABNT standard Nº 200 (0.074 mm) sieve. The ammonium quaternary salt (cetyltrimethyl ammonium bromide, CTAB), purchased from Vetec, was used as surfactant.

2.2 Preparation of the Samples

The method used involves cation exchange reactions, and was carried out in order to obtain the organoclays. It is based on a conventional method, which was adapted by reducing the preparation time to one day. Originally, the steps comprising the 24-hour settling periods, namely that after clay dispersion in water and that after the addition of 9.8 g of cetyltrimethyl ammonium bromide, are not performed **(Beall and Goss, 2004; Pereira, 2003)**.

2.3 Characterization of the Samples

X-Ray Diffraction (XRD): the powder method was used, whereby the samples were sieved in an ABNT Nº 200 (0.074 mm) sieve and then placed in an aluminum sample door for X-Ray diffraction, using a Shimadzu XRD 6000 equipment. Operational details of the technique have been set as follows: Copper Kα radiation at 40 KV/30 mA, with a goniometer velocity of 2°/min and a step of 0.02° in the range of 2θ scanning from 2º to 45º. The only *d*-spacings of interest in the X-Ry patterns were the basal spacing along the *c* axis.

Infrared Spectroscopy (IR): the organoclays obtained by two different methods were sieved (ABNT Nº 200) and then submitted to a physical treatment as in the KBr method, which consists in mixing 0.007 g of the sample and 0.1 g of KBr, grinding and pressing the solid mixture to 5 ton during 30 s in order to form a pastille that allows the passage of light. The characterization was realized using an infrared spectrophotometer AVATAR TM 360 FT-IR E.S.P., with wavelengths ranging between 4000 to 400 cm^{-1}, increments of 500 cm^{-1} and resolution of 4 cm^{-1}.

Differential Thermal and Thermogravimetric Analysis (DTA / TG): Thermal analysis was performed using TA instruments operating at a ramp of 10 °C/min from room temperature up to 1000 °C.

Cation Exchange Capacity (CEC): The cation exchange capacity (CEC) was determined with the Marconi nitrogen distiller, model MA-036Plus. Initially, 5.0 grams of a sample, weighed on an analytical balance, were transferred to an Erlenmeyer flask containing 200 mL of a 3-M ammonium acetate solution; then the flask with the solution was put on a magnetic stirrer and left under constant agitation for 12 hours. After this period it was centrifuged and collection of only the sample was performed, which was washed with ethanol to remove excess ammonium acetate and centrifuged again. The collected material was transferred to a watch glass and remained at room temperature at 60 °C ± 5 °C for 24 hours for drying. After drying, 1.5 gram of material was weighed on an analytical balance. The material was then manually disaggregated in a mortar and transferred to a Kjeldahl flask, to which 50 mL of distilled water and 3 drops of phenolphthalein were added and engaged in the apparatus. Sodium hydroxide (solution 50 % w/v) was added to the solution in the Kjeldahl flask until it became pink. Afterwards, vapor was injected into the reaction flask, causing a release of ammonia. The loose NH_3 was passed through a distiller, and was then collected in a flask containing 50 mL of 4 % boric acid with mixed indicator (methyl red and 0.50 % bromocresol green in 0.75 % ethanol). The distillation time was about 10 minutes. The boric acid indicator at first showed a red color, then became green when it received NH_3. After distillation, the material was withdrawn from the Erlenmeyer flask and the system proceeded to titration with 0.1-M hydrochloric acid until the color became red. The volume (in mL) used for titration was then recorded. The Cation Exchange Capacity (CEC) is obtained with Equation 1.

$$CEC = \frac{M \times f \times V_{HCl} \times 100}{M} \qquad (1)$$

Where:

CEC – Cation Exchange Capacity;

M – molarity of HCl = 0.1 M;

f – conversion factor of the acid = 1;

V_{HCl} – volume of HCl spent in titration, in mL;

M – mass of sample, in g.

The Foster Swelling Test: This technique is employed to carry out studies on the compatibility of specific organoclays and clays that were obtained after the modification with ammonium quaternary salt with some different organic liquids. The organic solvents for the study of the swelling phenomena were: gasoline (Petrobras), diesel oil (Petrobras), kerosene (Ares) and lubricating oil

(Lubrax MG1). The test consisted in adding 1 g of the powder sample to 50 mL of solvent in a test tube. After 24 hours of rest, the reading of the clay column volume (swelling of the clay without agitation) was registered. Afterwards, the content of the test tub was stirred with a glass stick during 5 minutes and, after a further 24-hour settling period, a new reading of the clay column volume (swelling of the clay with agitation) was taken. The following parameters have been fixed for the interpretation of the test: non-swelling (minor or equal to 2 mL/g of clay), low swelling (between 3 and 5 mL/g of clay), intermediate swelling (between 6 and 8 mL/g of clay) and high swelling (more than 8 mL/g of clay) **(Pereira et al., 2005)**.

Adsorption Capacity: The gasoline, diesel, kerosene and lubricating oil sorption capacity was measured following a method based on the “Standard Methods of Testing Sorbent Performance of Adsorbents” **(ASTM F716-82 and ASTM F 726-99)**. In this method, the adsorbent sample is weighed (minimum 1 g), and the exact value is recorded. The test cell is filled with an initial layer of test liquid. The adsorbent is placed in a basket (a 200-mesh stainless steel basket), which is then lowered into the test cell. The adsorbent should be allowed to float freely within the test cell. After 15 minutes ± 0.33 minute, the basket with the adsorbent is removed manually in a vertical direction and allowed to drain for 15 seconds ± 3 seconds. A tared weighing support is placed under the adsorbent sample/mesh basket set to catch any additional drips and the entire system is weighed. All the tests are conducted in duplicate with a minimum of two runs used for calculations. Based on the data obtained, the adsorbed oil is calculated as the weight ratio of adsorbed oil to dry adsorbent. The adsorption capacity is then obtained with Equation 2. The results of the adsorption capacity are reported in grams of solvent adsorbed per gram of clay.

$$Ad = \left(\frac{P_1 - P_2}{P_2}\right) * 100 \qquad (2)$$

Where:

P_1 – weight of the material after adsorption, in g;
P_2 – weight of dry adsorbent material, in g;
Ad – efficiency of adsorption to adsorbent tested, in %.

2.4 Factorial experimental design

A factorial design was proposed with three factors aiming to analyze the influence of initial oil concentration in aqueous solution (C_0) on the separation of oil-water emulsions. The variables obtained from this study were: the total oil removal percentage (Rem (%)) and removal capacity oil at equilibrium.

The design included four assays at the coordinates points xi =±1 for both factors (corresponding to the factorial part), besides three repeated tests at the central point (xi = 0), corresponding to average values between the variables’ inferior and superior levels, totalizing eleven tests. Repetitions at the central point have the purpose of supplying a value of pure error and stabilizing the variance of forecasted results.

The analysis of variance were originated by the ANOVA utilizando o Software Minitab 15.0 and it was used as a basis for the interpretation of results obtained experimentally.

The values for levels (+) and (–) are shown in Table 1.

Table 1. 2^2 Factorial experimental design.

Assay	C_0	A
1	–	–
2	+	–
3	–	+
4	+	+
5	0	0
6	0	0
7	0	0

Where:

C_0 – initial oil solution (water/oil emulsion) concentration;

A – mechanical agitation.

2.5 Finite bath tests

The experiments were performed simultaneously, where 0.5 g clay was weighed and put in contact with a 50-mL solution containing a water/oil emulsion (LUBRAX MG1) with concentrations of 100, 300 and 500 mg/L. The mixture (oil/water emulsion + clay) was kept under mechanical agitation from 100 to 200 rpm for 6 hours to ensure the balance of the system **(Curbelo, 2002)**. Similarly, the process without agitation was carried out.

Oil-water separation test: The concentration of oil present in the aqueous phase was determined by analysis of absorbance using a UV-visible spectrophotometer. Initially, a calibration curve of absorbance versus concentration was constructed using different known concentrations of oil. These concentrations ranged from 0 to 100 ppm and the solvent used for extraction was chloroform, showing a response (significant peak) at a wavelength of 262 nm for the samples analyzed. The absorbance at this wavelength is commonly used to estimate the concentration of oil in water samples **(Apha, 1985; Henderson et al., 1999)** and also in produced water. Bands of aromatic CH in the media are measured at this wavelength. Based on this, the analyses of absorbance were read at this wavelength. This implementation procedure was designed to standardize how the presence of oil and grease is determined.

Determination of the amount of oil: The total oil removal percentage (Rem (%)) and the removal capacity oil at equilibrium (q_{eq}) will be obtained with Equations 3 and 4, respectively:

$$\%\mathrm{Rem} = \left(\frac{C_0 - C_{eq}}{C_0}\right) \times 100 \tag{3}$$

Where:
%Rem – total oil removal percentage;
C_0 – initial solution (water/oil emulsion) concentration, in ppm;
C_{eq} – final solution (water/oil emulsion) concentration, in mg/L.

It is possible to determine the amount of adsorbed oil, expressed in mg of aqueous solution per gram of adsorbent solid, by means of a relatively simple calculation, as in Equation 4.

$$q_{eq} = \frac{V}{m}(C_0 - C_{eq}) \tag{4}$$

Where:

q_{eq} – removal capacity oil at equilibrium, in mg of oil/g of adsorbent;

C_0 – initial solution (water/oil emulsion) concentration, in mg/L;

C_{eq} – final solution (water/oil emulsion) concentration, in mg/L;

V – volume of adsorbate, in mL;

m – mass of adsorbent, in g.

3. RESULTS AND DISCUSSION

Figure 1 shows the X-Ray patterns of the untreated clay and the gray clay treated with the ammonium quaternary salt (CTAB).

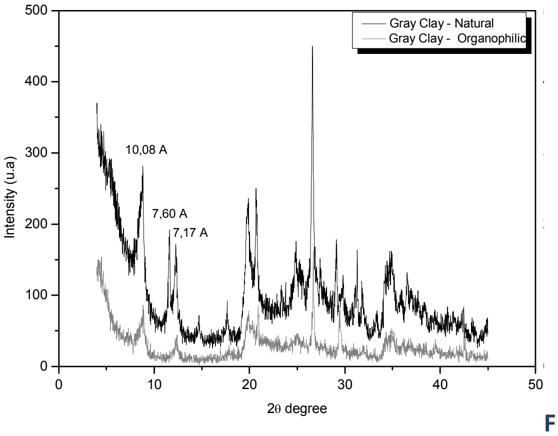

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Figure 1. . X-Ray patterns of the gray clay: untreated and treated with CTAB.

From the XRD patterns shown therein, it has been verified that both untreated and treated clay feature an interlamellar distance (d_{001}) of 10.8 Å.

The basic 2:1 structure with silicon in the tetrahedral sheets and aluminum in the octahedral sheet, without any substitution of atoms, is called pyrophyllite. Since the layers do not expand in water, pyrophyllite has only an external surface area and essentially no internal one. When silicon in the tetrahedral sheet is replaced with aluminum, the resulting structure is called mica. Due to this substitution the mineral is characterized by a negative surface charge, which is balanced by interlayer potassium cations.

However, because the size of potassium ions matches the hexagonal hole created by the Si/Al tetrahedral layer, they are able to accommodate very tightly between the layers. Consequently, the interlayers collapse and the layers are held together by the electrostatic attraction between the negatively charged tetrahedral layer and the potassium cations. Therefore, micas do not swell in water and, like pyrophyllite, have no internal surface area **(Dixon, 1991)**. On the other hand, if, in the original pyrophyllite structure, the trivalent Al-cation in the octahedral layer is partially substituted by the divalent Mg-cation, the structure of montmorillonite is formed, which is the best-known member of a group of clay minerals, called "smectites" or "smectite clays". In this case the overall negative charge is balanced by sodium and calcium ions, which are hydrated in the interlayer **(Manias et al., 2001)**. A particular feature of the resulting structure is that, since these ions do not fit into the tetrahedral layer, as in mica, and the layers are held together by relatively weak forces, water and other polar molecules can enter between the unit layers, causing the lattice to expand **(Chin et al., 2001)**.

In Figure 2, infrared spectra are shown for untreated gray clay and gray clay treated with CTAB. It can be observed that the 3624 cm^{-1} band is resolved in the untreated sample, due to the presence of the hydroxyl structural group in the clay. The interlamellar water molecules in the bentonite structure are resolved in the band at a wavenumber of 3635 cm^{-1}. The wavenumber of 1651 cm^{-1} indicates the presence of adsorbed water. At 1045 cm^{-1} and between 523 and 525 cm^{-1}, vibrations of the Si-O group and the octahedral layers are represented, respectively.

The peaks at 660 cm^{-1} correspond to the vibrations of the Al-O group, while those at 924 cm^{-1} and 523 cm^{-1} correspond to the Si-O-Al group (Pan et al., 2008). The infrared spectrum of the sample treated with CTAB, shown in Figure 2, is very similar. It was verified that the treated clay presented wavenumbers in the range from 2929 to 2852 cm^{-1}, indicating the presence of CH_2 groups. The asymmetric angular deformation of the CH_3 groups occurs at about 1471 cm^{-1}. The presence of CH_2 and CH_3 groups in the infrared spectrum of the treated samples is a good evidence of the intercalation of the ammonium quaternary cation of the surfactant within the interlamellar spaces of the sample.

In Figure 3, for natural gray clay, endothermic peaks are observed occurring between 70 ºC and 80 °C, with the loss of free water. These changes are due to water being intercalated and adsorbed by clay minerals. The presence of an endothermic peak with a maximum at 200 °C has been observed, which has been attributed to dehydration of the water that was coordinated with cations, then causing the formation of the cation basis. A small endothermic peak between 450 ºC and 500 °C was detected because of loss of structural hydroxyl from the structure of clay. This peak is typical of natural clays which are rich in iron. As for gray organophilic clays, an exothermic peak, attributed to the decomposition of salt, is found between 250 ºC and 450 ºC. The curve analysis obtained for gray organoclay exhibits endo-exo peaks in the range of 600 °C to 900 °C, referring to dehydroxylation of the organoclay and second combustion of carbonaceous residue from prior burning **(Sora et al., 2005)**.

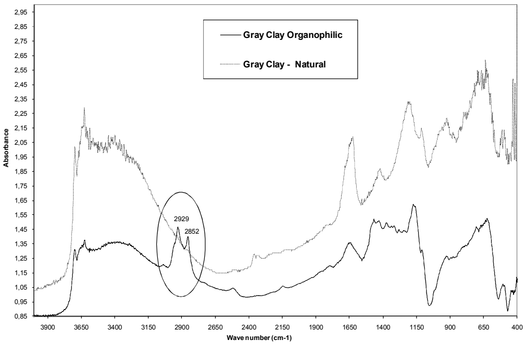

Figure 2. Infrared spectra of the gray clay: untreated and treated with CTAB.

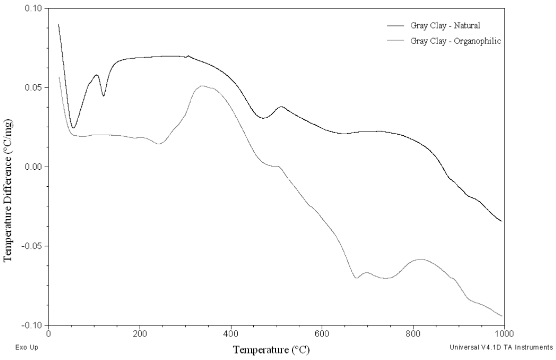

Figure 3. DTA curves of the gray clay: untreated and treated with CTAB.

The thermogravimetric analysis (TG) for the untreated gray clay and gray organoclay is shown in Figure 4.

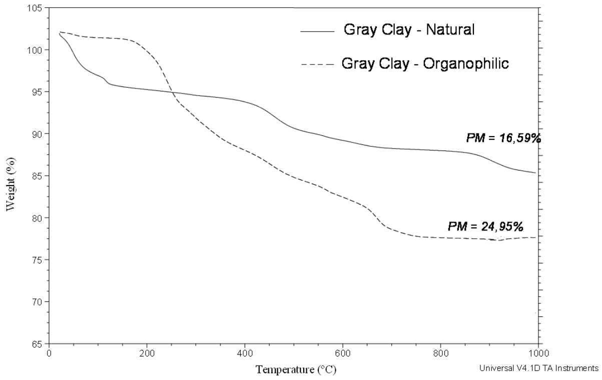

Figure 4. Thermal analysis of the gray clay: untreated and treated with CTAB.

Several mass-loss steps are observed. An initial mass-loss step is observed from room temperature and is attributed to mass loss due to dehydration/dehydroxylation (adsorption water). A second mass-loss step is observed just above 200 ºC and is also attributed to the dehydration of water adsorbed by metal cations such as Na^+ and Ca^{2+}. The inflection over the temperature range 450 ºC to 500 ºC is also attributed to the removal of residual organic substances.

For untreated clay, the total weight loss of adsorption water was 16.59 %; for gray clay treated with CTAB, this value was as high as 24.95 %.

The quantitative Cation Exchange Capacity (CEC) values obtained for untreated gray clay was 0.84 meq/g.

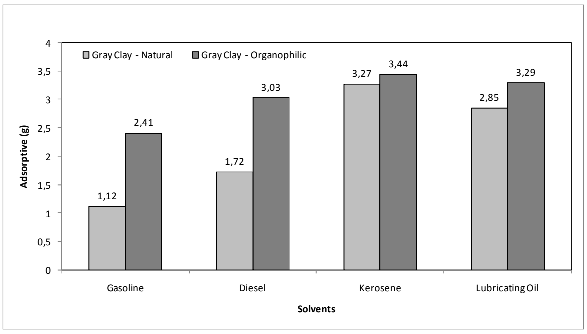

Figure 5. Adsorption capacity of gasoline, diesel, kerosene and lubricating oil.

The experimental results of the adsorption capacity for natural gray clay and gray organophilic clay are shown in Figure 5. From these results, it is possible to suggest that organic samples have better potential for adsorption in all solvents when compared with natural gray clays, with the following order: kerosene > lubricating oil > diesel > gasoline.

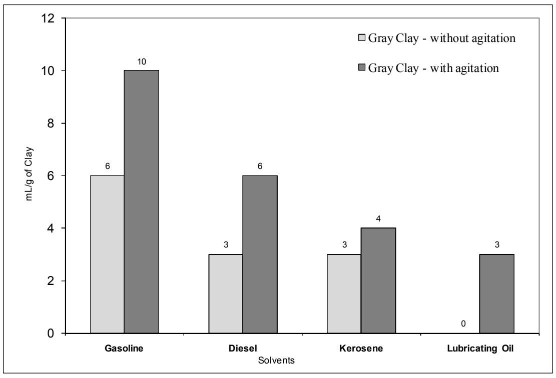

Figure 6. Results of the Foster Swelling Tests performed in different organic solvents, without and with agitation, for gray clay treated with CTAB.

Figure 6 shows the results of the Foster swelling tests of the gray clay treated with CTAB. In these assays, all samples were allowed to interact with different organic solvents.

From the results shown in Figure 6, it was noticed that the treated sample presented a high swelling capacity (with agitation) and intermediate swelling (without agitation) when tested in gasoline. On the other hand, when inserted in diesel oil without agitation, the treated samples presented low swelling capacity, but when the assay was performed under agitation, it yielded a high swelling capacity. In kerosene and lubricant oil, the samples presented low swelling, both without and with agitation.

The results obtained for the percentage of oil removal and the removal capacity are presented in Table 2. This study was carried out by means of a 2^2 factorial planning for the system used to remove oil from synthetic effluents with clays treated with CTAB.

Table 2. 2^2 Factorial experimental design results for gray clay treated with CTAB.

Assay	$C_{0\ calc}$ / (mg/L)	$C_{0\ exp}$ / (mg/L)	A / rpm	Oil / (mg/L)	%Rem	q_{eq} / (mg/g)
1	100	225	0	5.11	97.73	21.99
2	500	327	0	2.41	99.26	32.46
3	100	225	200	9.46	95.80	21.55
4	500	327	200	6.03	98.16	32.10
5	300	209	100	20.36	90.26	18.86
6	300	209	100	20.96	89.97	18.80
7	300	209	100	35.46	83.03	17.35

Where:

C_0 calc – theoretical initial concentration;

C_0 exp – real initial concentration;

A – mechanical agitation;

%Rem – total oil removal percentage;

q_{eq} – removal capacity oil at equilibrium.

The best result was this of assay 2, reaching total oil removal percentage as high as 99.26 %. It was also observed that for the removal capacity oil at equilibrium, i.e. q_{eq} (amount of metal removed per gram of clay), the best result was obtained in assay carried out with higher concentration, the best result being that of assay 2, where 32.46 mg of oil are removed for every gram of gray clay.

In terms of surface chemistry, kaolinite has some degree of isomorphous substitution, but the resulting negative charges are mostly located at the surface and broken edges of the crystals, as kaolinite has no expandable interlayer spaces **(Mohamed and Antia, 1998; Theng, 1974; Yong et al., 1992)**.

Therefore, kaolinite will adsorb cations, including ionic organic molecules, however almost exclusively on its surface. The charge on the clay surface may even induce polarization of some organic molecules. Moreover, silanol groups will be present at the surface of the silicon oxide layer of kaolinite (Mohamed and Antia, 1998; Sposito, 1989). It should be noted that, in bentonite, there is also some charge imbalance at the surface of the crystals as well as on the siloxane surface capable of bonding organic compounds **(Jaynes and Boyd, 1991)**.

Organoclays have a large capacity to bind organic compounds, including petroleum hydrocarbons **(Lagaly, 1984; Theng, 1974)**. Polar hydrocarbons in the oil would compete with hydration water for the solvation sites around adsorbed inorganic cations. This mechanism would cause the retention of oil in the bentonite structure in a relatively ordered fusion **(Egli and Lee, 2002)**.

4. CONCLUSIONS

In this study, the removal of oil was investigated using clay treated with an ammonium quaternary salt (cetyltrimethyl ammonium bromide, CTAB). By analyzing the results obtained in this study, particularly those provided by infrared spectroscopy, it was concluded that the treated, organophilic sample (modified with CTAB) comprised CH_2 and CH_3 groups in its structure, which provides evidence of the efficiency of the organophilization process.

The presence of CTAB molecules in the interlamellar space has been confirmed by DTA. Decomposition of the intercalating agent has occurred in two stages.

The Foster Swelling Test results indicated that the lowesest affinity of CTAB occurred in the treated clay tested in all organic solvents (kerosene, lubricating oil, diesel, gasoline), without and with agitation. Therefore, these clays can be used for the removal of oils and greases from polluted aqueous effluents of the petroleum industry.

Total oil removal percentage as high as 99.26 % could be obtained, when the initial solution (water/oil emulsion) concentration is used on its higher level (500 mg/L) and the degree of agitation is at the lower level (100 rpm). It was also observed that, for the removal capacity oil at equilibrium (q_{eq}), the best results were obtained in tests performed with higher (500 mg/l) concentration, the best result being a total of 32.46 mg of oil removed for every gram of clay.

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