

## Use of organophilic Bofe clay in removing oily contaminants

### Uso de argila Bofe organofílica na remoção de contaminantes oleosos

DOI:10.34117/bjdv7n5-223

Recebimento dos originais: 07/04/2021

Aceitação para publicação: 11/05/2021

#### **Rochelia Silva Souza Cunha**

DOUTORA em Engenharia Química – Universidade Federal de Campina Grande (UFCG)

LABNOV - UFCG

Endereço: Rua João Quirino 845 Ap 102 Catolé, Campina Grande -PB cep. 58410-370

E-mail: rocheliachel@hotmail.com

#### **Joseane Damasceno Mota**

Doutora em Engenharia Química – Universidade Federal de Campina Grande (UFCG),

Endereço: Docente da Faculdade Irecê (FAI), Rua Rio Iguaçu, 397, cep: 44900-000, Bairro Recanto das Árvores, Irecê/BA.

E-mail: joseanemota2006@hotmail.com

#### **Anna Karoline Freires de Sousa**

Mestre em Engenharia Química – Universidade Federal de Campina Grande (UFCG)

Endereço: R. Aprígio Veloso, 882 - Universitário, Campina Grande - PB, 58429-970.

E-mail: kah\_freire@hotmail.com

#### **Meiry Gláucia Freire Rodrigues**

Doutora em Chimie Appliqué – Université de Poitiers – France.

Instituição de atuação atual: LABNOV - UFCG

Endereço: R. Aprígio Veloso, 882 - Universitário, Campina Grande - PB, 58429-970.

E-mail: meirygfr@hotmail.com

## RESUMO

A modificação de argilominerais em organofílica pela incorporação do surfactante é extremamente importante em questões ambientais e industriais porque faz com que a argila atraia contaminantes hidrofóbicos e outros compostos orgânicos apolares. Uma argila Bofe foi utilizada como matéria-prima para a preparação de argila organofílica sintetizada com cloreto de cetiltrimetilamônio. As propriedades de sorção desta organofílica foram avaliadas para remover o óleo. A organofílica foi preparada por método direto e caracterizada por difração de raios-X, adsorção-dessorção de N<sub>2</sub>, capacidade de troca catiônica, espectroscopia na região do infravermelho, teste de expansão (capacidade de adsorção e inchamento de Foster). Foram realizadas medições para avaliar o desempenho das reações de troca iônica e grau de afinidade com derivados de petróleo. O aumento significativo em d<sub>(001)</sub> de CTAC-BC mostra a incorporação efetiva de CTAC nas camadas de argila. Os resultados de DRX e infravermelho indicaram que o CTAC foi intercalado entre as camadas de argila. Com base no sistema batelada, fica evidente que o CTAC-BC tem potencial para remover 99,35 % da concentração inicial de gasolina e 98,54 % da concentração inicial de óleo diesel. Os dados experimentais

obtidos com um conjunto de técnicas (difração de raios X e espectroscopia de infravermelho) evidenciam que o CTAC-BC apresenta excelente afinidade com a gasolina e o diesel. O alto percentual de remoção de contaminantes oleosos justifica o uso da argila organofílica no sistema de remoção de óleo/água.

**Palavras-chave:** Organofilização, surfactante CTAC, capacidade de sorção e remoção, Gasolina, Diesel, óleo emulsionado.

## ABSTRACT

The modification of clay minerals in organoclays by incorporating the surfactant is extremely important in environmental and industrial matters because it causes the clay to attract hydrophobic contaminants and other non-polar organic compounds. Objective: A Bofe clay was used as a starting material for the preparation of organoclay synthesized with cetyl trimethyl ammonium chloride. The sorption properties of this organoclay was evaluated to remove oil. Organoclay was prepared by direct method and was characterized by X-ray diffraction, N<sub>2</sub> adsorption-desorption, cation exchange capacity, infrared spectroscopy, expansion test (adsorption capacity and Foster swelling) measurements were performed in order to evaluate the performance of the ion exchange reactions and degree of affinity with oil products. The significant increase in  $d_{(001)}$  of CTAC-BC shows the effective incorporation of CTAC in the interlayer of the clay layers. XRD and infrared results indicated that CTAC was interleaved between the layers of clay. Based on batch system, it is evident that the CTAC-BC has the potential of removing 99.35 % of the initial concentration of gasoline and 98.54 % of the initial concentration of diesel oil. The experimental data obtained a set of techniques (X-ray diffraction and infrared spectroscopy) evidence that CTAC-BC show a excellent affinity to gasoline and diesel. The high percentage of removal of oily contaminates justifies the use of the organoclay in the oil/water removal system.

**Keywords:** Organophilization, surfactant CTAC, sorption and removal capacity, Gasoline, Diesel, emulsified oil.

## 1 INTRODUCTION

One of the serious problems in recent years is water pollution due to industrial development, especially in developing countries. Although there are ecological movements that advocate the preservation of fauna, flora and natural resources, even today, measures are needed to reduce the environmental impact, as well as establish new patterns of consumption and even develop technologies to recover the impact areas [1, 2].

The chemical compounds, aromatic hydrocarbons and volatile flammables such as petroleum products

effluents into waterways directly affects the environment and consequently human healthy [3-5]. There are concerns about the adverse effects caused to the health of humans

and animals, causing damage to kidneys, liver abnormalities and digestive tract, as well as skin irritation [4, 6-7].

According to the National Council for the Environment (Conama), the maximum permissible concentrations of oil in the oil industry is specified in an arithmetic mean of 29 mg/ L, by month, with a daily maximum value of 42 mg/L produced water. It is assumed that the production of this effluent is around 250 million barrels per day, compared to the production of 80 million barrels of oil per day, that is, for each barrel of oil produced, three barrels of human water contaminated by oil are generated [7].

Therefore, the removal of these petroleum products from water and wastewater is essential. Treatment methods such as filtration in porous media such as sand, activated carbon and biological treatment (activated sludge, trickling filters) or physical treatments, such as centrifugal separation and settling tanks are being used. But some of these technologies have a high cost and are more restricted to be used in the chemical industry [8-10].

Adsorption process is one of the best treatment options for removing these pollutants from aqueous solutions, depending on the material used, it is possible to regenerate the adsorbent [11-13]. Among the adsorbents used clays have attracted great interest from researchers due to its wide availability in world reserves, they are extremely affordable [14] and high area surface [15] which promotes for the adsorption process.

However, natural clays which possess hydrophilic nature is ineffective for removal of organic. To overcome this problem, the surface of clay should be modified with the inclusion of organic molecules between the layers cationic surfactants structural modification which enables the interlayer, the expansion occurring between planes  $d_{(001)}$ , thus making them, organoclays [16].

Many studies have been widely conducted for the removal of oily compounds from petroleum refineries from modified clays in aqueous solutions with cationic surfactants agents [17- 24]

Recently, many studies [19-20, 24-29] investigated the increasing sorption capacity of organic contaminants, specifically oily compounds from petrochemical industry from modified clays. They reported that this increase can be improved by replacing the exchangeable cations with surfactants.

Organoclays are abundantly investigated for a important variety of environmental applications because of their unique adsorption capacity. In particular, hydrophobic organoclays become effective adsorbents to remove organic pollutants.

But based on our knowledge, there is no data available for the removal of pollutants, specifically (gasoline and diesel), using modified clay. In this study, bofe clay was modified by the cetyltrimethylammonium chloride (CTAC) surfactant as a cationic surfactant and used to remove gasoline and diesel oil emulsified in aqueous solutions in a series of batch experiments. The effect of the initial concentration and the agitation, the removal of the effluent were determined by analysis of variance.

## **2 MATERIALS AND METHODS**

### **2.1 MATERIALS**

Bofe clay (BC), obtained from the Bentonit Northeast Union (BUN), Campina Grande, Paraíba, Brazil was selected as the mineral raw material. It was sieved according to the Brazilian ABNT standard No 200 (0.074 mm) sieve. Quaternary ammonium salt used was cetyl trimethyl ammonium chloride (Genamin-CTAC) purchased from Clariant.

### **2.2 PREPARATION OF ORGANOPHILIC CLAY**

The organophilic clay synthesis was performed by a procedure involving the cation exchange reaction based on the "direct method" [22, 30]. Initially, a clay dispersion (4 wt%) was prepared in water and processed with a solution of sodium carbonate, with stirring (600 rpm for 20 minutes) at 95 °C. After sedimentation of the sample was then dispersed into the surfactant solutions and stirred for 30 min. The organoclay sample, separated by filtration and rinsed with water and dried at  $60 \pm 5^\circ\text{C}$  for 24 h ground in an agate mortar, and then sieved by the 200-mesh sieve. The organophilic clay was denoted CTAC-BC.

### **2.3 CHARACTERIZATION**

X-ray powder diffraction (XRD)

X-ray diffraction measurements were performed using a diffractometer Shimadzu XRD 6000m, Kyoto, Japan) with Copper  $K\alpha$  radiation ( $\text{CuK}\alpha=1.5418$ ). The diffractograms were performed between  $2^\circ$  to  $50^\circ$  with angular and time step of  $0.02^\circ$ .

### Textural characterization by physical adsorption of nitrogen

Surface area and porosity were determined by physical adsorption of nitrogen (N<sub>2</sub>) at -196 °C performed on a ASAP 2020 - Surface Area and Porosity Analyzer (Micromeritics Norcross, USA) using the BET technique. Infrared spectroscopy (IR): measurements in the range 400–4000 cm<sup>-1</sup> were performed using a Nicolet Avatar infrared spectrophotometer AVATAR TM 360 FT-IR E.S.P. (Thermo Electron Corporation, USA).

### Adsorption Capacity

Gasoline, diesel, kerosene and lubricating oil adsorption capacities were measured following a method based on the “Standard Methods of Testing Sorbent Performance of Adsorbents (ASTM F716-82 and ASTM F 726-99) [31].” All the tests are conducted in triplicate with a minimum of two runs used for calculations.

### Foster’s Swelling Test

Technique used to test the compatibility of organophilic clay and natural clay with different organic solvents [32, 33]. This method is based on the “Standard Test Method for Swell Index of Clay Mineral Component of Geosynthetic Clay Liners” (ASTM D 5890-95). Cation Exchange Capacity (CEC): was measured using the nitrogen distiller, Marconi model MA-036Plus. Cation Exchange Capacity (CEC) is obtained with Equation 1.

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

where CEC is the Cation Exchange Capacity, M corresponds to the molar concentration of HCl = 0.1 (M), f is a conversion factor of the acid = 1, V<sub>HCl</sub> is the volume of HCl used for titration, expressed in mL, M mass of sample, in g.

## 2.4 FACTORIAL EXPERIMENTAL DESIGN

A factorial design of two levels with three replicates at the center point was designed. The purpose of this study was to evaluate the trend towards maximizing the efficiency of the process [34]. Two independent variables were designed: the initial concentration of oil-water emulsion (C<sub>0</sub>), estimated in the range of 100 to 500 mg/L and the agitation (A) kept within the range from 100 to 300 rpm. Values are coded as the levels (+) and (–), as shown in Table 1.

**Table 1. 2<sup>2</sup> Factorial Experimental Design**

Variables	Levels
Initial concentration (mg/L)	(-1) = 100 ( 0 ) = 300 (+1) = 500
Agitation (rpm)	(-1) = 100 ( 0 ) = 200 (+1) = 300

## 2.5 BATCH EXPERIMENTS

The properties of lubricant oil are given in Table 2.

**Table 2. Properties of lubricant oil selected.**

Characteristics	Method	Specification
Appearance@ 30 °C	Visual	Clear liquid
Density@ 29.5 °C, g/mL	IS 1115-86 P: 32	0.8833
Kinematic viscosity	IS 1115-86 P: 25	168

**Density:** The density of the sample was determined with a digital Anton Paar densitometer, model 30px.

**Viscosity:** Viscosity measurements were carried out with lubricant oil by using the Brookfield DV-II Pro(rotational) viscometer.

In order to prepare the oil-water emulsion, the required amount (0.05, 0.15 and 0.25 g) of gasoline or diesel oil (commercial) in 500 ml of distilled water and were shaken on a high speed stirrer (17000 rpm) for 20 min, sufficient rotation to form stable emulsions.

The tests were carried out simultaneously. 0.5 g organoclay was weighed and dispersed in 50 mL solution containing gasoline-water solution or diesel-water solution with concentrations of 100, 300 and 500 mg/L. The set (emulsion oil-water/clay) was kept under agitation ranging from 100 to 300 rpm for 6 h at 25 °C to ensure the system equilibrium [19, 22, 26].

## 2.7 ANALYSIS OF OIL

Chloroform method was used to analyse the oil concentration of the samples [26]. The concentration of oil present in the aqueous phase was determined by analysis of absorbance using spectrophotometer (UV – visible/UV 1800 Shimadzu). A calibration curve of absorbance versus concentration using different concentrations of effluent

ranged from 0 to 100 mg/L, was built with a coefficient of determination ( $R^2$ ) equal to 0.9684 for gasoline and 0.9994 for diesel. Chloroform was used and 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 [35, 36] and also in water produced. The samples were again shaken on an shaking table for 5 min at 100 rpm. Two phases were formed: denser phase or extracted solution (oil solubilized in chloroform) and soft phase with the remaining water. Extracted solution absorbance was measured at 262 nm. Absorbance value was converted to concentration via calibration curve.

## 2.8 DETERMINATION OF THE AMOUNT OF OIL

The total oil removal percentage (%Rem) and the capacity of oil removal at equilibrium ( $q_{eq}$ , in mg of oil/g of adsorbent) were obtained with Equations 2 and 3, respectively:

$$\% \text{Rem} = \left( \frac{C_0 - C_{eq}}{C_0} \right) \cdot 100 \quad (2)$$

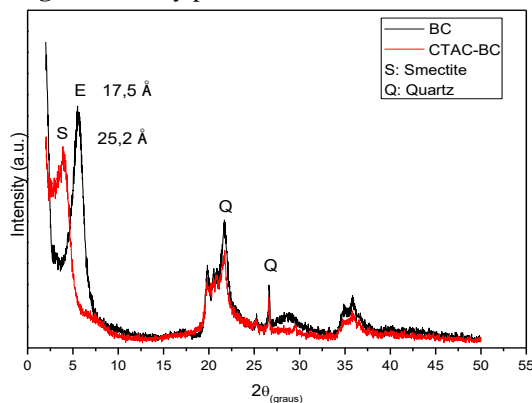
$$q_{eq} = \frac{V}{m} (C_0 - C_{eq}) \quad (3)$$

where,  $C_0$  is the initial concentration of oil in the emulsion, in mg/L,  $C_{eq}$  is the final concentration of oil in the emulsion, in mg/L,  $V$  is the volume of adsorbate, in mL, and  $m$  is the mass of adsorbent, in g, % Rem is the percentage of total removal of oily wastewater,  $q_{eq}$  is the removal capacity of the effluent at equilibrium.

## 3 RESULTS AND DISCUSSION

Figure 1 presents the X-ray patterns of BC and CTAC-BC. Qualitatively clay mineral smectite Bofe presents as it is also observed the presence of quartz. Results agrees with those found in the literature [24, 37].

**Figure 1.** X-ray patterns of BC and CTAC-BC.



It can be seen that after treatment the BC with the cetyltrimethyl ammonium chloride (CTAC), changes in the interlayer space was compared with that of BC. This change can be attributed to the difference in interlayer space. 001 diffraction pattern of the organoclay shift to lower angular value underlining the expansion of the interlayer space at 25.2 Å for CTAC-BC. It is also observed other peaks that are not related to smectite mineral like quartz that has as an impurity [38-41].

This significant increase in  $d_{(001)}$  of CTAC-BC (7.7 Å) evidence the effective incorporation of CTAC in the interlayer of the BC layers. This expansion of the clay layer was also found in the literature regardless of the salt used [19, 42].

In the analysis of the other peaks present one can observe the presence of the same peaks presented in the clay without treatment to the presence of quartz, which indicates that the incorporation of the quaternary ammonium salt did not alteration the chemical structure of the clay, the ion exchange took place only between the exchangeable cations of the clay layers smectitic the cations of the surfactant CTAC.

Textural properties of BC are summarized in Table 3. It can be see the BC showed a specific surface area of 107 m<sup>2</sup>/g, a value close to the one obtained by author [37] for the red clay, 103 m<sup>2</sup>/g. These values are typical of smectite clays and desired for microporous materials, used in adsorption processes. The specific surface area of the present clay is relatively high compared to other clay (68 m<sup>2</sup>/g) [43]. Bofe clay, also showed mesopores volumes exceed the volume of micropores.

**Table 3. Textural properties of BC.**

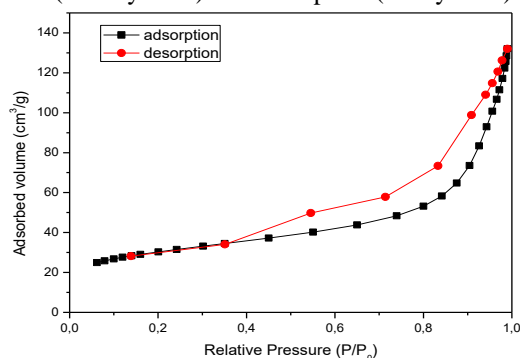
Sample	$S_{BET}$ (m <sup>2</sup> /g)	$V_{tot}$ (cm <sup>3</sup> /g) <sup>a</sup>	$V_{micro}$ (cm <sup>3</sup> /g) <sup>b</sup>	$V_{meso}$ (cm <sup>3</sup> /g) <sup>c</sup>	$d_p$ (nm)
BC	107	0.1951	0.0120	0.1831	7.25

$V_{total}$ : total pores volume  $V_{micro}$ : micropores volume;  $V_{meso}$ : mesopores volume

<sup>a</sup> P/P<sub>0</sub>; <sup>b</sup> Method t-plot; <sup>c</sup>  $V_{meso} = V_{total} - V_{micro}$

According to the classification of the International Union of Pure and Applied Chemistry (IUPAC) [42], BC showed isotherms with profile similar to type II (Fig. 2). This isotherm is characteristic of the formation of multiple layers of adsorbed molecules on the solid surface. This type of sigmoidal isotherm is often found on solid non-porous or with larger pores than micropores, which explains the low values of micropore volume [42].

**Figure 2.** Nitrogen adsorption (dark symbol) and desorption (red symbol) isotherms at  $-196^{\circ}\text{C}$  of BC.



In this comparative study it was analyze the CEC differences for each clay (Table 4). BC presented CEC value 71 meq/100 g of clay, BSN-03 clay [24] show a CEC value of 77 meq/100 g of clay and gray clay [44] presents a CEC about 84 meq/100g of clay, similar to the capacity of the clay from this work. The author [45] reports that these high values indicate the clay has a low amount of impurities or a high isomorphous substitutions level, so the value of the cationic exchange capacity are in agreement with the expected range for smectite clays.

**Table 4. Comparison of the values CEC of different clays.**

Sample	CEC (meq/100 g of clay)	References
BC	71	This work
BSN-03	77	[24]
Gray clay	84	[44]
clay	80-150	[45]

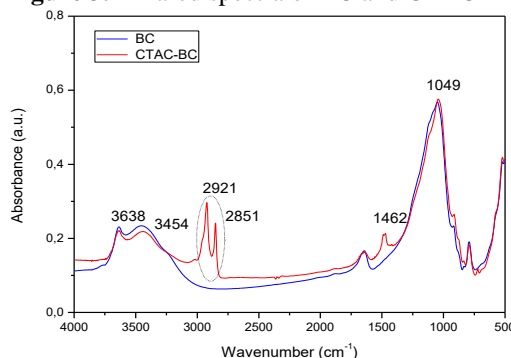
Infrared spectra of BC and CTAC-BC are presented in Fig. 3. The spectrum of BC shows bands in the region of  $3640\text{--}3400\text{ cm}^{-1}$  that are attributed to O–H stretching of free and adsorbed water [46]. The hydrophilic surface of swelling clay minerals can be altered to hydrophobic by exchange of the naturally occurring inorganic cations with various alkyl-organocations [47]. IR technique can be used to study the interactions between clay

minerals and organic molecules [48]. Bands are observed for the samples BC and CTCAC-BC in the region between 1100 - 1045  $\text{cm}^{-1}$  characteristic of Si-O-Si and about 915 and 523  $\text{cm}^{-1}$  assigned to the octahedral layers of aluminosilicate Al-O-Si [30]. It is also possible to detect vibrations of the Si-O group (1045  $\text{cm}^{-1}$ ) and octahedral layers (between 523 and 525  $\text{cm}^{-1}$ ) for both samples. The organoclay also show the characteristic peaks of clay minerals, although of low intensity, which indicates that the natural clay was properly modified [49].

Organophilic clay (CTAC-BC) also shown at 2923  $\text{cm}^{-1}$  a band corresponding to asymmetric stretching vibrations of the  $\text{CH}_2$  group. A characteristic peak at 2850  $\text{cm}^{-1}$  corresponding to a group  $\text{CH}_2$  symmetric stretch and 1470  $\text{cm}^{-1}$ . The asymmetric angular deformation of the  $\text{CH}_3$  groups occurs at about 1459  $\text{cm}^{-1}$ . The presence of  $\text{CH}_2$  and  $\text{CH}_3$  groups in the infrared spectrum is an evidence of the intercalation of the quaternary ammonium cations within the interlamellar spaces of the sample [19, 30, 50].

As the bands that appear after the next process organophilization the region of 2950-2800  $\text{cm}^{-1}$  are characteristic of the stretching of the links of methane ( $\text{CH}_2$ ), and the bands near 2900  $\text{cm}^{-1}$  for the asymmetric stretching, and the bands close to 2800  $\text{cm}^{-1}$  to the symmetric [51]. The bands near 1480  $\text{cm}^{-1}$  is related to the bending  $\text{CH}_3$ , indicating the presence of the surfactant in the clay [52]. The bands present in the region around 1045  $\text{cm}^{-1}$  are characteristic of the Si-O-Si region and next to 530  $\text{cm}^{-1}$  are attributed to the characteristics of octahedral layers of aluminosilicate Si-O-Al [50].

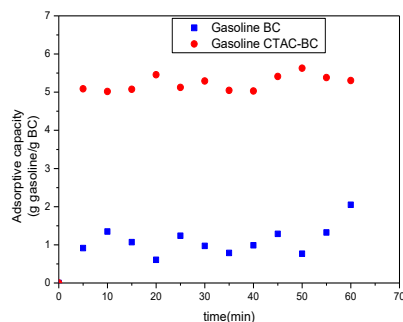
**Figure 3.** Infrared spectra of BC and CTAC-BC.



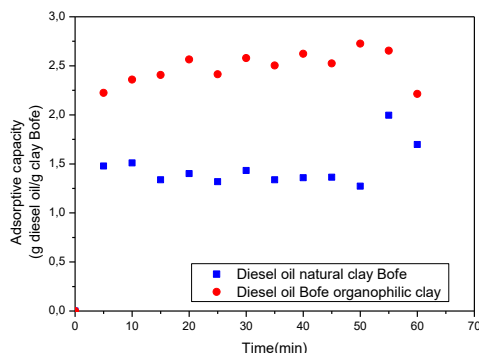
Sorption experiments were performed in order to assess the potential for sorption of BC and CTAC-BC in organic solvents, such as, gasoline and diesel.

Figure 4 shows the sorptive capacity (qeq), as a function of time, of the gasoline for BC and CTAC-BC and Figure 5 shows the sorptive capacity (qeq), as a function of time, of the diesel for BC and modified CTAC-BC.

**Figure 4.** Sorption capacity of gasoline using the BC and CTAC-BC. Experimental conditions running time of 60 min and temperature 25 °C



**Figure 5.** Sorption capacity of diesel using BC and CTAC-BC. Experimental conditions running time of 60 min and temperature 25 °C.



CTAC-BC have better sorption capacity in solvents (gasoline or diesel) when compared with BC.

In the specific case of the CTAC-BC sorption capacity was in the following order: gasoline > diesel. The best result is obtained with the organic solvent gasoline, which evidence that a better interaction with the solvent organoclay gasoline. This interaction may be explained in part due to the chemical structure of gasoline [53], and also due to the viscosity of each solvent, in view of gasoline is less viscous as viscosities results are: diesel - 8 CP (600rpm) e 3,5 CP (300rpm) and gasoline - 2 CP (600rpm) e 1 CP (300rpm).

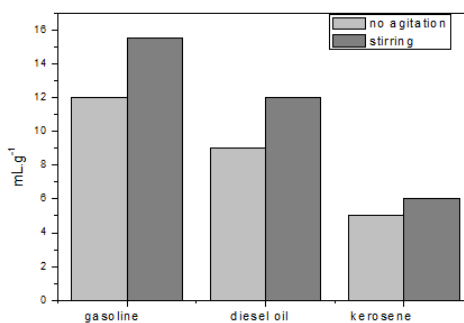
For comparison (Figure 4) it is observed that the total amount of gasoline sorbed by the CTAC-BC was greater than when the BC was used. An average of 5.23 g of gasoline

was sorbed per gram of CTAC-BC, BC, while the adsorption capacity during the contact time showed an average sorption capacity of only 1.11 g per gram of gasoline clay.

Fig. 5, the best performance is observed in the CTAC-BC, where after 20 minutes of contact, 2.48 g of diesel fuel were sorbed per gram of CTAC-BC, BC has sorbed more rapidly during the first 10 minutes, however the maximum adsorption capacity was 1.46 g of diesel oil per gram of BC. These results are in agreement with the results of Foster swelling, and corroborate the results found in the literature [18, 19, 24]. Results show that in which the process of organophilization promotes the potential of the clay modified with organic salts in the removal of organic compounds and is therefore an alternative to sorption processes of organic contaminants.

The affinity of CTAC-BC with gasoline or diesel was verified with the Foster Swelling Tests. The results are exhibited in Fig. 6.

**Figure 6.** Results of the Foster swelling tests performed in gasoline, diesel and kerosene, without and with agitation, for CTAC-BC.



In these tests, the samples were put in contact with organic compounds (gasoline, diesel and kerosene). According to the results shown in Fig. 6, the CTAC-BC exhibited a high swelling capacity (with and without agitation) for gasoline and diesel [19, 26, 30, 54].

### 3.1 BATCH EXPERIMENTS

The potential of CTAC-BC in oil removal was evaluated in a batch system, according to a factorial design 2<sup>2</sup> shown in Table 5, wherein: C<sub>0-exp</sub> is the actual initial concentration, A: agitation used in the system, C: final concentration after the process; % Rem: percentage of total removal of oily wastewater, q<sub>eq</sub> refer to removal capacity of the effluent at equilibrium (gasoline mg/g CTAC-BC).

**Table 5. Results of the 2<sup>2</sup> Factorial experimental design for CTAC-BC. Temperature = 25 °C, time = 6 h.**

Entry	C <sub>0-exp</sub> (mg/L)	A (rpm)	Gasoline emulsion (mg/L)	% Rem	q <sub>eq</sub> (mg/g)
1	104	100	8.80	91.54	9.52
2	104	300	3.47	96.67	10.05
3	502	100	3.70	99.26	49.83
4	502	300	3.26	99.35	49.87
5	302	200	3.32	98.90	29.87
6	302	200	3.20	98.94	29.88
7	302	200	3.70	98.78	29.83

Statistical analysis showed a significant effect of C<sub>0</sub> and agitation on the removal capacity of gasoline. It can be observed that the removal capacity of about 90 % is easily obtained, under the conditions adopted in the experiments (Table 5).

The regression models (Eqs. (4) and (5)) show that the system is dependent on the concentration C<sub>0</sub> and agitation, which positively contributes to the removal station. As to the effect of curvature is also considered, as it has significance, resulting in coefficients (R<sup>2</sup><sub>máx</sub>) equal to 99.97 %, Rem% to 100 %, and q<sub>eq</sub>, respectively.

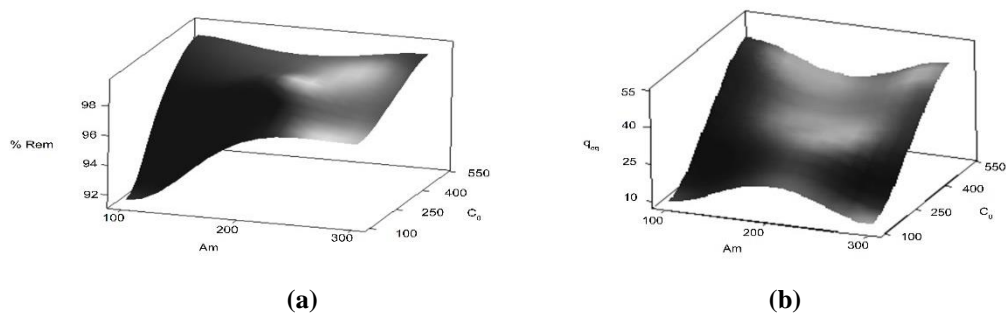
$$\% \text{ Rem} = 83.70 + 0.058C_0 + 0.032Am - 5.42 \times 10^{-5}C_0^2 - 6.30 \times 10^{-5}C_0 \times Am \quad (4)$$

$$q_{eq} (mg.g^{-1}) = -0.884 + 0.101C_0 + 0.003Am - 6.12C_0 \times Am \quad (5)$$

Equations 4 and 5 are represented as response surfaces for the percentage of total gasoline removal (Fig. 7a) and the removal capacity of the gasoline oil at equilibrium (Fig. 7b). It was observed that in both cases there is a significant effect on the concentration and agitation the response variables.

**Figure 7.** Response Surface plot for the (a) percentage total of gasoline removal and (b) the removal capacity of the gasoline oil at equilibrium with CTAC-BC. Experimental conditions: Temperature = 25 °C, time = 6 h.

Table 6 presents the experimental results obtained in the removal of diesel emulsified using the CTAC-BC.



**Table 6.** Results of the  $2^2$  Factorial experimental design for CTAC-BC. Temperature = 25 °C, time = 6 h.

Entry	$C_{0-exp}$ (mg/L)	A (rpm)	Diesel emulsion (mg/L)	% Rem	$q_{eq}$ (mg/g)
1	112	100	14.07	87.44	9.79
2	112	300	9.87	91.18	10.21
3	514	100	7.49	98.54	50.65
4	514	300	12.23	97.62	50.18
5	316	200	11.10	96.49	30.49
6	316	200	6.73	97.87	30.93
7	316	200	7.11	97.75	30.89

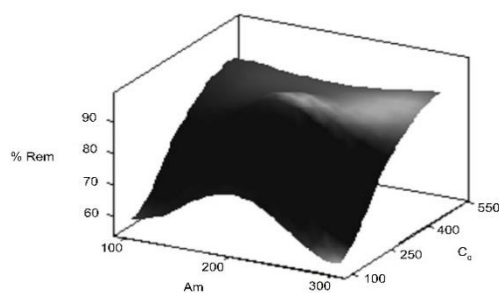
Results shown that the CTAB-BC has a maximum efficiency of removing 98.54 % of the initial concentration of diesel, equivalent to 50.65 mg of diesel per gram of CTAC-BC. Statistical analysis showed a significant effect of the initial concentration  $C_0$  of the removal percentage and the equilibrium removal capacity ( $q_{eq}$ ). On the other hand the agitation does not affect the behavior of the removal process of diesel oil. As can be seen, the regression models (equations 6 and 7) predict well the experimental data, which show that the system is strongly dependent on the concentration  $C_0$ , contributing decisively to the removal of diesel oil emulsified in water.

The quadratic model proposed is considered, the model fit is significantly improved, resulting in coefficients ( $R^2_{max}$ ) equal to 97.55 % to 99.74 %, and Rem% to  $q_{eq}$ , respectively. The models are represented as response surfaces for the percentage of total diesel removal (Fig. 8a) and the removal capacity of the diesel oil at equilibrium (Fig. 8b).

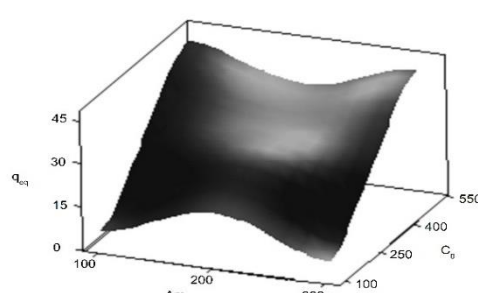
$$\%Rem = 27.18 + 0.376C_0 - 5.05 \times 10^{-4}C_0^2 \quad (6)$$

$$q_{eq}(mg.g^{-1}) = -3.91 + 0.099C_0 \quad (7)$$

of the diesel oil at equilibrium with CTAC-BC. Experimental conditions: Temperature = 25°C, time = 6 h.



(a)



(b)

#### 4 CONCLUSION

Organophilic clay showed potential to be sorbents. The incorporation of the CTAC surfactant by XRD and IR was shown. X-ray diffraction was verified significant changes between plans interlayer after treatment with CTAC.

The effects of process parameters such as initial concentration and agitation were studied. The predictions of the multiple linear regression models developed based on the  $2^2$  factorial design were excellent in the experimental range evaluated. Results demonstrated that the initial concentration had important effects on the removal capacity at equilibrium  $q_{eq}$ .

Based on batch system, it is evident that the CTAC-BC has the potential of removing 99.35 % of the initial concentration of gasoline and 98.54 % of the initial concentration of diesel oil, which justifies its use in the removal system oil/water emulsion. Finally, the results confirmed that the use of organoclays appears to hold great promise in the sorption of gasoline, diesel and kerosene in the processing of organic waste.

#### LIST OF ABBREVIATIONS

ABNT	Brazilian Association of Technical Standards
ASTM	Standard Methods of Testing Sorbent Performance of Adsorbents
BC	Bofe clay
BUN	Bentonit Northeast Union
CEC	Cation Exchange Capacity
CTAC	Cetyltrimethylammonium chloride
CTAC-BC	Bofe clay with cetyltrimethylammonium chloride
$C_{eq}$	final concentration of oil in the emulsion
$C_0$	initial concentration of oil in the emulsion
IR	Infrared spectrophotometer
$q_{eq}$	removal capacity of the effluent at equilibrium
$R^2$	correlation coefficient
$S_{BET}$	total surface area
UV-Vis	spectrophotometer UV-visible
$V_{total}$	total pore volume
$V_{micro}$	micropores volume
$V_{meso}$	mesoporous volume
XRD	X-ray powder diffraction
%Rem	percentage of total removal of oily wastewater

#### ACKNOWLEDGEMENTS

The authors gratefully acknowledge Petrobras, CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) and CNPq (Conselho Nacional de Pesquisa e Desenvolvimento) for the financial support.

## REFERENCES

- [1] Walker DB, Baumgartner, DJ, Gerba CP, Fitzsimmons K. Surface Water Pollution. In: Environmental and Pollution Science. Third Edition. Academic Press, 2019.
- [2] Qadri R, Faiq MA. Freshwater Pollution: Effects on Aquatic Life and Human Health. (eds) Fresh Water Pollution Dynamics and Remediation. Springer, Singapore, 2020.
- [3] Jindrova E, Chocova M, Demnerova K, Brenner V. Bacterial aerobic degradation of benzene, toluene, ethylbenzene and xylene. *Folia Microbiol* 2002; 47: 83–93.
- [4] Aivalioti M, Pothoulaki D, Papoulias P, Gidarakos E. Removal of BTEX, MTBE and TAME from aqueous solutions by adsorption onto raw and thermally treated lignite. *J Hazard Mater* 2012; 207–208: 136–146.
- [5] Malhat F, Loutfy N, El Menyawi MAI, Ahmed MT. Review of Contamination by Polycyclic Aromatic Hydrocarbons (PAHs) in Egyptian Aquatic Environment, Polycyclic Aromatic compounds, 2019.
- [6] Price JM, Johnson WR, Marshall CF, Ji ZG, Rainey GB. Overview of the oil Spill risk analysis model for environmental impact assessment. *Spill Sci Technol Bull* 2003; 8: 529–533.
- [7] Fakhru'l-Razi A, Pendashteh A, Abdullah LC, Biak DRA, Madaeni SS, Abidin ZZ. Review of technologies for oil and gas produced water treatment. *J Hazard Mater* 2009; 170: 530-551.
- [8] Nordvik AB. Oil and Water Separation in Marine Oil Spill Clean-up Operations. *Spill Sci Technol Bull* 1996; 3: 107-122.
- [9] Owens N, Lee DW. The use of micro bubble flotation technology in secondary & tertiary produced water treatment - A technical comparison with other separation technologies. 5th Produced Water Workshop Aberdeen, Scotland, 2007.
- [10] Bader MSH. Seawater versus produced water in oil-fields water injection operations. *Desalination* 2007; 208: 159-168.
- [11] Zhu R, Zhu J, Ge F, Yuan P. Regeneration of spent organoclays after the sorption of organic pollutants: A review. *J Environ Manage* 2009; 90: 3212–3216.
- [12] Aktas O, Cecen F. Bioregeneration of activated carbon: a review. *Int Biodeterior Biodegrad* 2007; 59: 257–272.
- [13] Bouraada M, Lafjah M, Ouali MS, Menorval LC. Basic dye Removal from aqueous solution by dodecyl sulfate and dodecyl benzene sulfonate intercalated hydrotalcite. *J Hazard Mater* 2008; 153: 911–918.
- [14] Zhou Y, Jin XY, Lin H, Chen ZL. Synthesis, characterization and potential application of organobentonite in removing 2,4-DCP from industrial wastewater. *Chem Eng J* 2011; 166: 176-183.
- [15] Souza Santos P. *Ciência e Tecnologia de Argilas*. 2th Edn. São Paulo: Edgard Blücher, 1992.
- [16] Yuri P, Ayoko GA, Kristof J. A thermoanalytical assessment of an organoclay. *J Therm Anal Calorim* 2011; 104: 1-6.
- [17] Alther G. Using organoclays to enhance carbon filtration. *Waste Manage* 2002; 22: 507-513.

- [18] Gonzaga AC, Sousa BV, Santana LNL, Neves GA, Rodrigues MGF. Study of different methods in the preparation of organoclays from the bentonite with application in the petroleum industry. *Brazilian Journal of Petroleum and Gas* 2007; 1: 16-25.
- [19] Rodrigues SCG, Queiroz MB, Pereira KRO, Rodrigues MGF, Valenzuela-Diaz, F.R. Comparative Study of Organophilic Clays to be Used in the Gas & Petrol Industry. *Mater Sci Forum* 2010; 660: 1037-1042.
- [20] Alther G. Cleanig wastewater: Removing oil from water with organoclays. *Filtr Sep* 2008; 45: 22-24.
- [21] Queiroz MB, Rodrigues SCG, Laborde HM, Rodrigues MGF. Swelling of Brazilian Organoclays in Some Solvents with Application in the Petroleum Industry. *Mater Sci Forum* 2010; 660-661: 1031-1036.
- [22] Mota MF, Silva JA, Queiroz MB, Laborde HM, Rodrigues MGF. Organophilic clay for oil/water separation process by finite bath tests. *Brazilian Journal of Petroleum and Gas* 2011; 5: 097-107.
- [23] Mota MF, Rodrigues MGF, Machado F. Influence of Exchanged Surfactant on the Structure and Adsorption Properties of Brazilian Green Mud Clay. *Mater Sci Forum* 2012; 727-728: 473-1478.
- [24] Oliveira GC, Mota MF, Silva MM, Rodrigues MGF, Laborde HM. Performance of natural sodium Clay treated with ammonium salt in the separation of emulsified oil in water. *Brazilian Journal of Petroleum and Gas* 2012; 6: 171-183.
- [25] Park Y, Ayoko GA, Frost RL. Application of organoclays for the adsorption of recalcitrant organic molecules from aqueous media. *J Colloid Interface Sci* 2011; 354: 292-305.
- [26] Mota MF, Rodrigues MGF, Machado F. Oil-Water Separation Process with Organoclays: A Comparative Analysis. *Appl Clay Sci* 2014; 99: 237-245.
- [27] Silva EL, Patrício ACL, Oliveira GC, Rodrigues MGF. Evaluation of a Sodic Organoclay as Adsorbent for Removing Oil/Water in a Synthetic Wastewater. *Mater Sci Forum* 2014; 798-799: 127-132.
- [28] Mota MF, Patrício ACL, Silva MM, Rodrigues MGF. Preparation and Characterization of Clay Chocolate "A" Organoclay Using Stearyltrimethyl Ammonium Chloride as a Surfactant. *Mater Sci Forum* 2015; 805: 667-671.
- [29] Lima WS, Rodrigues MGF, Mota MF, Patrício ACL, Silva MM. Study of Chocolate Clay (Boa Vista, Paraíba) Organophilization Using the Mixture of Quaternary Ammonium Salts through Direct Method. *Mater Sci Forum* 2015; 805: 672-677.
- [30] Pereira KRO, Hanna RA, Vianna MMGR, Pinto CA, Rodrigues MGF, Valenzuela-Diaz FR. Brazilian organoclays as nanostructured sorbents of petroleum-derived hydrocarbons. *Mater Res* 2005; 8: 77-80.
- [31] ASTM. Standard Methods of Testing Sorbent Performance of Adsorbents – Designation: ASTM F716 –82 (Reapproved 1993); ASTM F726 –99; ASTM D5860-65, ASTM D7503-10.
- [32] Foster MD. The importance of exchangeable magnesium and cation-exchange capacity in the study of montmorillonitic clays. *Am Mineral* 1951; 36: 717-730.

- [33] Foster MD. Geochemical studies of clay minerals. 2. Relation between ionic substitution and swelling in montmorillonites. *Am Mineral* 1953; 38: 994–1006.
- [34] Montgomery DC, Runger GC. *Applied Statistics and Probability for Engineers*, 3rd Ed. John Wiley & Sons, Inc., New York, 2003.
- [35] Clescerl LS, Greenberg AE, Eaton AD. *Standard Methods for Examination of Water & Wastewater*, 20th ed. American Public Health Association, Baltimore, 1999.
- [36] Henderson SB, Grigson SJW, Johnson P, Roddie BD. Potential Impact of Production Chemicals on the Toxicity of Produced Water Discharges from North Sea Oil Platforms *Mar Pollut Bull* 1999; 38: 1141-1151.
- [37] Rodrigues MGF. Physical and catalytic characterization of smectites from Boa-Vista, Paraíba, Brazil. *Cerâmica* 2003; 49: 146-150.
- [38] Choy JH, Kwak SY, Han YS, Kim BW. New organo-montmorillonite complexes with hydrophobic and hydrophilic functions. *Mater Lett* 1997; 33: 143-147.
- [39] Shem YH. Preparations of organobentonite using nonionic surfactants. *Chemosphere* 2001; 44: 989-995.
- [40] Wang CC, Juan GLC, Lee CK, Hsu TC, Lee JF, Chao HP. Effects of Exchanged Surfactant Cations on the Pore Structure and Adsorption Characteristics of Montmorillonite. *J Colloid Interface Sci* 2004; 280: 27-35.
- [41] Xi Y, Mallavarapu M, Naidu R. Preparation, characterization of surfactants modified Clay minerals and nitrate adsorption. *Appl Clay Sci* 2010; 48: 92-96.
- [42] Bergaya F, Theng BKG, Lagaly G. *Handbook of Clay Science*. Elsevier, 2006.
- [43] Moraes DS, Angélica RS, Costa CEF, Rocha Filho GN, Zamian JR. Mineralogy and chemistry of a new bentonite occurrence in the eastern Amazon region, northern Brazil. *Appl Clay Sci* 2010; 48: 475–480.
- [44] Vasconcelos PNM, Lima WS, Silva MLP, Brito ALF, Laborde HM, Rodrigues MGF. Adsorption of Zinc from Aqueous Solutions Using Modified Brazilian Gray Clay. *Am J Anal Chem* 2013; 4: 510-519.
- [45] Grim RE. Clay Mineralogy: The clay mineral composition of soils and clays is providing an understanding of their properties. *Science* 1962; 135: 890-898.
- [46] Wang C, Jiang X, Zhou L, Guangqiang X, Chen Z, Duan M, Jiang X. The preparation of organo-bentonite by a new gemini and its monomer surfactants and the application in MO removal: A comparative study. *Chem Eng J* 2013; 219: 469-477.
- [47] Sawhney BL. CMS Workshop Lectures, v.8, Organic Pollutants in the Environment, The Clay Minerals Society, Boulder, CO, USA, 1996.
- [48] Yariv S, in: Yariv, SH. Cross (Eds.), *Organo-Clay Complexes and Interactions*, Complexes and Interactions, Marcel Dekker, New York, 2001.
- [49] El Messabeb-Ouali A, Benna-Zayani M, Kbir-Ariguib N, Trabelsi-Ayadi M. Physicochemical characterization of organophilic clay. *Phys Procedia* 2009; 2: 1031–1037.
- [50] Kozak M, Domka L. Adsorption of the quaternary ammonium salts on montmorillonite. *J Phys Chem Solids* **2004**; 65: 441-445.

- [51] Nguyen VN, Nguyen TDC, Dao TP, Thuan HT, Bang DN, Ahn DH. Synthesis of organoclays and their application for the adsorption of phenolic compounds from aqueous solution. *J Ind Eng Chem* 2013; 19: 640-644.
- [52] Zhou Q, Xi Y, He H, Frost R. Application of near infrared spectroscopy for the determination of adsorbed p-nitrophenol on HDTMA organoclays-implications for the removal of organic pollutants from water. *Spectrochim Acta Part A* 2008; 69: 835–841.
- [53] Gamal ME, Mohamed AMO, Zekri AY. Effect of asphaltene, carbonate, and clay mineral contents on water cut determination in water-oil emulsions. *J Pet Sci Eng* 2005; 46: 209 – 224.
- [54] Valenzuela-Diaz FR. Preparation of organophilic clays from a Brazilian smectitic