Evaluation of Sorptive Capacity of Natural Clay, Pillared Clay, and Alga-modified Clay to Contain Oil Spills in Soil

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Abstract

This paper describes the characterization of natural Patagonian clay (ARC), composed mainly of montmorillonite and illite, and two modifications: one with alga *Codium fragile* (ARC-ALG) and other iron-pillared (ARC-PIL), as oil sorbents. The textural characterization of samples was performed by nitrogen adsorption isotherms at 77K, obtaining 36, 2 and 105 m^2/g of BET surface area, respectively. The pore size distribution was calculated from isotherms data by the method of density functional (NLDFT). Oil sorption capacities were determined and expressed in g oil/g sorbent by tests in batch, sorption isotherms were obtained in a concentration range of 50 to 300 mg/L of oil in organic solvent. The quantification of remnant concentrations in solution was performed by UV-Vis spectrophotometric techniques. The results of sorption capacity are consistent with the BET surface area for ARC and ARC-PIL, but are not in agreement with ARC-ALG, since it has the lowest BET surface area and the highest sorption capacity; this would be mainly due to the organic nature of this material. This information together with the analysis of the respective isotherms, gives the possibility of making inferences about of the action mechanisms for the selection of new sorbents in treating soils spills.

1. Introduction

Oil spills are common in Patagonia because of the intense oil activity that takes place in this region. They are usually caused by accidents and produce environmental damages in the ecosystems. Due to the proximity of high density human population, when these spills occur, human health and environmental quality are put at risk (Frost et al., 2007). The main causes are attributable to difficulties in pumping systems, transport pipelines, storage tanks, plant management and

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transportation. These spill sources can produce leakage of varying magnitude. There are different methods to control and mitigate the effects caused by oil spills. The use of sorbents is appropriate both in the final stages of cleaning as in the removal of hydrocarbon thin films from inaccessible places (Nudelman & Ríos, 2003; Fingas, 2012). The hydrocarbons sorption in soils is a process which affects transport, degradation and biological activity on the environment; hence the importance of considering the phenomenon when evaluating the various remediation techniques and disposal of these pollutants (Ríos et al., 1998).

The different types of synthetic and/or natural sorbents are generally made of materials with high sorption capacity and good retention over time. Smectite type clays are used as sorbents primarily because of their high surface area and sorption capacity. This demonstrates that the high percentage of clay in soils promotes the sorption of petroleum hydrocarbons (Nudelman et al., 2000). The phyllosilicate clay mineral montmorillonite, commercially known as bentonite, is specifically widely used as a sorbent due to its layered structure and high surface area (800 m^2/g)(Zadaka-Amir et al., 2003).

Clay minerals are the most important inorganic components of soil and they are widely used in environmental applications owing to their excellent adsorption properties (Lee et al., 2004). Moreover, the replacement of inorganic exchange cations in clay minerals by organic cation species or neutral species can increase the sorption capacity of the material (Ismadji et al, 2015). The modification of clays by pillaring process has attracted increasing attention since the 1970s, particularly from industry, due to their microporous nature and catalytic potential (Bhattacharyya & Gupta, 2008). Pillared clays have efficient sorptive properties, which could be a good choice in environmental applications. However, the adsorption of hydrocarbons by pillared clay minerals is not yet well understood and reported (Ouellet-Plamondon et al., 2012).

The behavior of different seaweeds as heavy metal biosorbents has been studied with particular interest (Bulgariu et al., 2015). Due to their low cost and renewable nature, they can be used for treatment of effluent in large scale (Vijayaraghavan & Balasubramanian, 2015). Nevertheless, their use as dry biomass in soil spills has not been studied in the same way. Sorption of crude oil in water by dry biomass of *Salvinia sp.* has been described, and resulted a better oil sorbent than Peat Sorb (for crude oil, 4.8 against 2.7 g of oil sorbed per g of biomass) (Hubert et al., 2000). Sorption of diesel and lubricating oil in water was studied on dead algal cultures, *Spirulina sp.* and *Scenedesmus abundans* was to determine the rate and extent of sorption of diesel and lubricating oil on dead algal cultures of *Spirulina sp.* and *Scenedesmus abundans*. Based on both Langmuir and Sips model, diesel sorption capacity on both algae cultures were in the range of 12.5–14.0 g/g. The impact of pH, background ionic strength and temperature on biosorption of oil was also determined (Mishra & Mukherji, 2012). The potential of using the abundant and varied marine algae found on the Atlantic coast of southern Argentina in order to treat oil spills on land is an attractive alternative, especially for their availability at low cost. Furthermore, considering the potential benefits of the addition of nutrients to arid soils such as Patagonia ones (Lichtfouse, 2010).

The aim of this research was to evaluate the hydrocarbon sorption capacity by natural and modified materials found in Patagonian environment, such as clays, alga-clays and pillared clays which could be used in the cleaning of oil spills on land.

2. Materials and Methods

2.1 Sorbate

Crude oil was from San Jorge Gulf Basin. Lacustrine shales of the Pozo D-129 Formation, are the source rocks of the oil bearing sandstones of the middle to late Cretaceous. It was characterized by chromatography column on silica gel to separate the aliphatic, aromatic and polar fractions, previous asphaltene precipitation with n-pentane. The methodology was adapted from the 3600 method C Cleanup EPA. Solvents as hexane, benzene, chloroform-methanol mixture, free of impurities grade HPLC (EPA, 1996) were used. Protocols for obtaining and preservation of the sample were used in previous studies (Nudelman et al., 2008).

2.2 Sorbents

The natural clay (ARC) selected for this study was extracted near Comodoro Rivadavia, Chubut Province, Argentina. The samples were dried at room temperature, ground and sieved (size ≤ 2 μm). Algae samples (ALG) were collected from Comodoro Rivadavia coast, in the intertidal, manually and at low tide. Next, they were dried and grounded with mortar, and sieved (size ≤ 2 μm). The algae identification was made from seaweed during collection in field, for which the relevant geographic area where the collected material comes from was previously consulted in specific literature (Boraso, 2013).

The obtaining procedure of clay-algae (ARC-ALG) consisted on drying samples of about 40 mg ALG powder and 100 mg of ARC, in separate porcelain crucibles, at 80°C for 20 minutes, and mixed them. ARC-ALG paste was formed with the addition of few drops of deionized water. Then, the paste was dried at 80°C for 20 minutes, this wetting and drying process was repeated 3 to 5 times to achieve a better immobilization. After that, the material was sieved to discard the possible presence of free ALG that has not been immobilized on ARC. This procedure is similar to the one used for the production of algae immobilized on silica gel and is included in the methodologies of sustainable chemistry (Neide et al., 2003).

To prepare pillared clay (ARC-PIL) synthesis procedure proposed by Yamanaka et al. (1984) was followed. About 40 g of $Fe(NO_3)_3.9H_2O$ (Fluka 97% purity) were dissolved in ethanol (Merck, 99.8%) at room temperature. The solution was placed in an ice bath and was added, in small portions, a suitable volume of acetic anhydride (Alkemir, 97%) because the reaction is exothermic. The resulting precipitate was decanted in an ice bath and dried at 60°C, pillaring agent solutions were prepared from this. Iron was incorporated by slow dripping of pillaring agent solution on clay slurry in water at 35°C with constant vigorous stirring. After that, it was left to stir for three hours at room temperature. The excess was then removed by filtration and washed with distilled water. Finally, the sample was dried at 60°C and calcinated at 10°/ min to 350°C and 500°C one hour in air (Oliveira et al., 2003).

2. 3 Textural characterization

Textural properties of sorbents were obtained from low pressure nitrogen adsorption-desorption isotherms at 77K. N_2 sorption analyses were performed using a Micrometrics ASAP 2010 surface

area analyzer. Each adsorbent was previously degassed at 323K for 12 hours. Specific surface area was calculated by using the BET equation (BET area, SBET), the pore size distribution and the micropore volumes (Vμp) by a Non-Local Density Functional Theory approach, NLDFT.

2.4 Sorption capacity

Sorption capacity C, which expresses the mass of sorbed oil per gram of dry sorbent material was calculated using equation (1). This parameter is used as an indicator of efficiency for sorption of oil spilled in soils under field conditions.

$$C = \frac{(m_t - m_s)}{m_s} \tag{1}$$

where C is the hydrocarbon sorption capacity (g / g sorbent), m_t is the mass of sorbent and sorbed hydrocarbon (g) and m_s is the mass of dry sorbent (g).
The sorption capacity (C) of different sorbents was evaluated using the modified ASTM F-726-12 norm, which basically consist of a standard gravimetric method.

2.5 Sorption isotherms

To study the sorption process, liquid phase batch tests were performed to obtain sorption isotherms. The tests were conducted by placing approximately 1 g dry sorbent and 100 mL of sorbate solution into vials with periodic stirring at room temperature (23 ± 2 °C). Sorbate solutions were prepared from the stock solution by dilution (at least five-fold dilutions) and characterized by UV-Vis spectroscopy. The bottles were sealed with plastic film and covered with aluminum foil to prevent exposure to air and photooxidation, targets were prepared with each of the sorbents and solvent without sorbate. Seven days were left in contact with periodic shaking, time required to reach the equilibrium condition. After, sorbent and solution were separated, the supernatant solution was centrifuged. The remaining sorbate concentration was determined by UV-Vis spectroscopy, calibrated with solutions of known concentration. The described techniques correspond to those used by our research group in previous works. (Nudelman et al, 2008).

Experimental data have been represented by applying the BET multilayer model that allowed the best fit of the experimental data, provided that oil is considered as a single solute, as suggested in previous studies by our group (Ríos & Nudelman, 2005). It should be mentioned that the representation of the experimental data with the same model, obeys to the need to compare the constants obtained. Equation (2) describes the BET isotherm,

$$Q_e = K_1 K_2 \frac{\sum_i^m i C_e^i}{(1 + k_1 \sum_i^m C_e^i)} \tag{2}$$

where Q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium, K_1 is a constant related to the heat of sorption (mg/L), K_2 is a constant related to the amount of sorbate sorbed in a monolayer (mg/kg), i is the number of layer, m is the total number of layers and C_e (mg/L) is the liquid-phase concentration of adsorbate at equilibrium.

This equation is strictly valid for a single type of molecule and not a mixture, but it is applied, in this study, a mixture of hydrocarbons. In addition, the finite number m of layers should be dependent on K_2. Equation (3) represents the dependence:

$$m = \frac{Q_e}{K_2} \tag{3}$$

K_1 and K_2, represent constant values and therefore take into account the interactions between the components in the liquid phase and global interactions of each with the mineral matrix.

3. Results and Discussion

3.1 Oil characterization

The oil comes from the Basin of San Jorge Gulf in central Patagonia located between parallels 43° and 47° south latitude. It comprises the southern part of the province of Chubut, the northern part of the province of Santa Cruz and much of Argentina's continental shelf in San Jorge Gulf. Elemental analysis of petroleum reveals little about its composition, so as objectives of this work, composition based on their fractions is more useful, mainly because one of the factors that determines the efficiency of remediation techniques used, is the composition in terms of its fractions (Diphare & Muzenda, 2014). The method used to determine the composition was column chromatography, also known as SARA, the oil used in this study presents 45.16% of aliphatic fraction, 32.73% of aromatic fraction, 3.58% of polar fraction and 18.51% of asphaltene fraction.

3.2 Characterization of the algae

The algae used corresponded to *Codium fragile*, these macroalgae are rooted in the lower levels of the intertidal coast of our region. They are hardy plants, moss green, up to 30 centimeters high. Its branches are cylindrical, dichotomously branching, with rámulas to the tenth order. Fig. 1 presents a photo of *Codium fragile.*

Fig. 1. *Codium fragile* collected off the coast of Comodoro Rivadavia.

It is important to mention that *Codium Stackhouse* (*Codiaceae, Siphonales*) is significant because of its abundance, and the most widespread species is *Codium fragile*, which grows in the lower levels of the rocky coast from Buenos Aires to Ushuaia (Zaixso & Boraso of Zaixso, 2015). According to Villaseñor-Parada & Neill (2011) distribution reaches Falkland Islands and Antarctica.

3.3 Textural characterization

As mentioned above, the textural characterization of samples was performed by nitrogen adsorption-desorption isotherms at 77K. Values of the specific surface obtained by the BET method are shown in Table 1.

Table 1 Sorption capacity and BET specific surface area for ARC-ALG, ARC-PIL and ARC

Sorbents	Sorption capacity (g/g)	BET surface area (m^2/g)
ARC- ALG	2.58 ± 0.70	2
ARC-PIL	1.86 ± 0.15	105
ARC	1.61 ± 0.86	36

The BET surface area for ARC-ALG was 2 m^2/g. For comparison purposes could be mentioned that sorbents prepared with algae *Gelidium sesquipedale* and algal waste from the agar extraction industry (mainly composed by 35% algae *Gelidium* without agar and 65% of diatomaceous earth) have BET surface values of 0.23±0.01 and 1.37±0.02 m^2/g, respectively (Vilar et al., 2007).
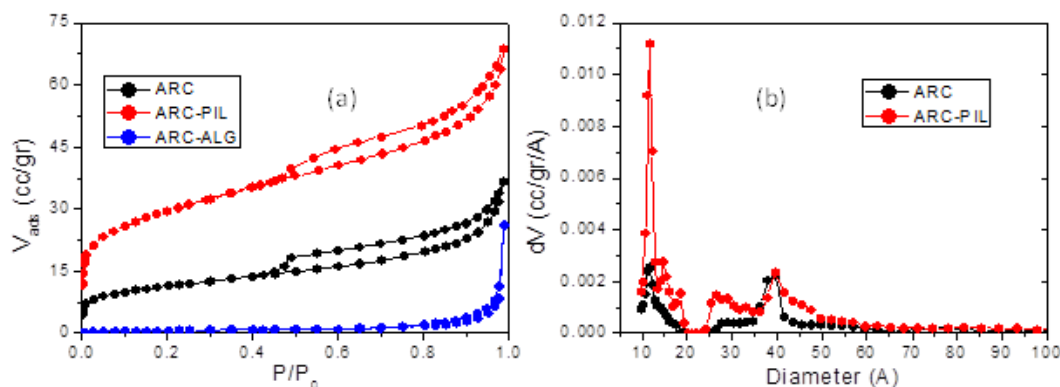
Fig. 2. (a) Nitrogen adsorption–desorption Isotherms. (b) Pore size distribution (NLDFT).

Fig. 2 (a) shows a graph of nitrogen adsorption-desorption isotherm. All isotherms corresponded to type IV according to the classification BDDT (Brunauer et al., 1938) characteristic of mesoporous solids with a hysteresis loop type H3 (De Boer, 1958), associated with slit shaped pores, consistent with the laminar structure of clays. From the isotherms it can be seen that the pillared clay has greatly increased its adsorption capacity, mainly due to increased porosity in the micro-mesoporous region. The increase in both surface area and total pore volume is an important fact to confirm the success of the pillaring agent (Banković et al., 2012). In this work, the pillaring process

was confirmed by the significant increase in the area (105 m^2/g) by a factor of approximately 2.9. Other authors have reported: 36.8 m^2/g (Hou et al., 2010) and 108 m^2/g (Caudo et al., 2007). From the isotherms the pore size distribution was obtained by the method of density functional (NLDFT) (Jagiello & Olivier, 2009). The results are shown in **Fig. 2** (b).

3.4 Sorption capacity

The sorption capacity measures the direct interaction between the hydrocarbon and the surface of the sorbent without any competition for the active sites with the solvent. The sorption capacities are shown in Table 1. The ARC-ALG sorbent showed the best capacity (2.58 g/g) for the sorption of crude oil in dry soils, while ARC-PIL and ARC had lower capacities (1.86 and 1.61 g/g, respectively). This suggested that organic nature of the algae materials promotes the sorption of nonpolar oil components, which are the majority.

3.5 Sorption isotherms

The batch tests allowed obtaining sorption isotherms in a concentration range of 50 to 300 mg/L of oil in organic solvent. The resulting isotherms from all testing experimental batch have been able to represent this model, by allowing the best fit of the experimental data. Parameters of the BET model for the tested sorbent are compared in Table 2.

Table 2 Parameters BET model for oil sorption- ARC-ALG, ARC and ARC-PIL

Sorbate	Sorbents	K_1	K_2	Number of	Total sorbed	Error	R^2
		L mg^{-1}	mg kg^{-1}	layer	mg kg^{-1}	%	
Crude	ARC-ALG	9 10^{-3}	104	19	1976	1.5	0.974
oil	ARC	3 10^{-2}	1000	2	2000	5.6	0.948
	ARC-PIL	1 10^{-2}	1428	2	2856	2.9	0.973

For ARC-PIL the value of K_2 (1428 mg/kg) and the total sorbed (2856 mg/kg) were the highest, indicating that the pillaring increased the basal spacing, providing better accessibility of molecules to the active sites present within the clay structure, achieving greater interaction with chemical components of oil, consistent with literature data (Bergaya et al., 2006; Yang et al, 2013). For ARC-ALG the value of K_1 (9 10^{-3} L/mg) and K_2 (104 mg/kg) were the lowest and the number of layers was the biggest (19). The notion of layers in this cases is figurative due to the mechanism of the sorption process may be absorption into organic matter (algae), but the use of this model allows to compare the experiments.

The fact that the greatest sorption capacity in dry soil was for ARC-ALG and the greatest sorption capacity in solvent was for ARC-PIL, suggests differences in the accessibility of the active sites of the sorbents. In the first case, the crude oil absorption in organic matter (ARC-ALG) could be the most efficiently mode of interaction, compared with inorganic clays components in ARC and ARC-PIL. In the second case, the organic solvent was mainly absorbed in ARC-PIL, while in inorganic sorbents, the mobility of the polar and smaller molecules was the mainly reason of sorption.

4. Conclusions

In this paper, we have investigated the sorption of oil in the ARC, ARC-ALG and ARC-PIL sorbents, characterizing both sorbate and sorbent. By applying the multilayer model, it has been able to predict more accurately the experimental data of oil in the three sorbents tested with a mean absolute deviation of 1.5 to 5.6%, being a potentially useful and powerful tool, leading to improve the applications of sorption in soil treatment.

Moreover, it has been shown that the clays are capable of sorbing petroleum hydrocarbons in nonpolar solvents, which occurs in the early stages of a spill, reducing dispersion and movement of the oil. Thus, inexpensive sorbents, such as clays and clays modified algae, could be added as temporary retention barriers, avoiding costly methods in areas where oil exploration is done.

Since the cleaning can be performed by a wide range of sorbents, is important to understand the most basic features governing sorption process for that the application be more beneficial. We have chosen typical materials of the region as clays, algae and modifications of these natural sorbents. Good sorption capacity, mainly for the modified material ARC-ALG was obtained. This result opens a promissory field for our future investigations. More research would be needed in order to intensify the study of the mechanisms involved in sorption to obtain better results in the application of the sorbents studied.

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Conflict of Interest

None.

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