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Assessing raw materials as potential adsorbents to remove acidic compounds from Brazilian crude oils by ESI (-) FT-ICR MS

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Abstract: The presence of acidic compounds as naphthenic acids in crude oil causes several problems for the petroleum industry, including corrosion in both upstream and downstream production processes. Based on this scenario, the main objective of this work was to investigate the removal of the acidic compound from two Brazilian heavy oils by adsorption processes using six potential adsorbents: powdered shale, activated carbon, bentonite, silica gel, powdered sandstone and powdered wood. These raw materials were previously characterized by conventional and surface analysis techniques, which show that they offer a good surface area and thermal stability. To evaluate the removal efficiency at the molecular level, the crude oil samples and the filtered oils were analyzed by negative electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry [ESI (-) FTICR MS]. The O₂ class, which is related to the relatively high acidity of the samples, was the most abundant in both crude oil samples, moreover, this class was more retained by adsorbents. Silica gel, activated carbon and bentonite were the best adsorbents of acidic compounds from the tested oils, in agreement with their markedly higher surface area and porous volume. Additionally, a chromatographic analysis was performed and showed no changes in the oil profile.

Key words: petroleum, adsorbent, polar compounds, naphthenic acid, ESI (-) FT-ICR MS, petroleomics.

INTRODUCTION

The mixture of many hydrocarbon compounds, nonhydrocarbon compounds containing heteroatoms, and metallic compounds (mainly nickel and vanadium) makes the petroleum matrix quite complex. Although the general petroleum composition is known, it may present different concentrations among classes of compounds as well as distinct physical and chemical properties depending on their generative characteristics, which is related to their source rock (organic-matter type, depositional environment and level of maturity), and also depending on potential alteration process in the reservoir, such as biodegradation and water washing (Nunez et al. 1996, Yaghi & Al-Bemani 2002, Wenger et al. 2002). For instance, the naphthenic acids (NA), the topic of this work, can be originated from the source rock, biosynthesized by microorganisms, or be originated by the biodegradation of the hydrocarbons in the reservoir (Watson et al. 2002).

Due to the diversified concentration of the different classes in petroleum, it is possible to find oils with various API gravities (American
Petroleum Institute gravity scale) around the world, ranging from extra light (API> 40) oils, such as those found in many fields in central Saudi Arabia (Ali et al. 2002), to asphalt oil, API<15, such as that from Bachaquero in Venezuela, with an API gravity of 12.3 (Davudov & Moghanloo 2017). However, most of the explored oil fields currently register the production of heavy and extra heavy oils (Georgie & Smith 2012, Ghannam et al. 2012, Bahadori et al. 2015, Temizel et al. 2018), and according to data from the International Energy Agency (IEA), almost 50% of the world’s recoverable oil resources are heavy oil, with an API gravity less than 20 (Ghannam et al. 2012).

Brazil has a diversified petroleum production from onshore and offshore fields and produces asphaltic oil, such as Hárpia (Sergipe e Alagoas Basin) and Fazenda Alegre (Espírito Santo Basin), with an API gravity of 13.3, to super-light oil, such as Condensado de Merluza (Santos Basin), with an API gravity of 57.7 (ANP 2019). These differences represent a heterogeneous quality in the produced oil. However, Brazilian resources are among the most acidic in the world, similar to other sources in South America (Gruber et al. 2012). This diversification in petroleum composition directly impacts all refinery processes, and therefore, compositional information is vital for advances in effective petrochemical processing (Rodgers et al. 2002).

The inconvenience of heteroatom species in crude oil is due to environmental reasons, contamination and poisoning effects during refining processes (Ramirez-Corredores 2017), and problems during the production processes, in reason of their high viscosity, low hydrogen-to-carbon ratios, and high total acidity, which also cause a negative impact on the commercial value of the oil and its derivatives (Ghannam et al. 2012, Gruber et al. 2012). For example, species containing nitrogen are known to cause catalyst deactivation through coke formation on the catalyst surface (Rodgers et al. 2002, Pinto et al. 2017). For its part, acidic compounds, known as naphthenic acids, may cause serious damage to refineries, leading the corrosion of equipment, pipings, transfer lines, and distillation towers also the formation of environmental pollutants (Slavcheva et al. 1999, Clement & Fedorak 2005, Zhang et al. 2012).

Therefore, the petroleum industry has been investing in practices to remove polar compounds, especially NA and nitrogen compounds, usually with unsatisfactory results and/or high operating costs (Huang et al. 2006, Wu et al. 2019). One of the used technologies, liquid-liquid extraction (LLE) is capable of extracting NA but it requires large quantities of alkaline or ammonia solutions, several kilograms of samples and liters of solvent (Seifert et al. 1969, Seifert & Teeter 1970). The efficiency of this technique may be compromised due to the formation of emulsions (Clement & Fedorak 2005). Nonaqueous ion-exchange based methods also have been used to isolate acidic fractions from petroleum for many years, but they often involve complex multistep separations and use relatively large-scale ion-exchange chromatographic columns and large volumes of solvents (Green et al. 1984, Tomczyk et al. 2001). Solid phase extraction is another method used for removing acidic fractions; however, it also requires several steps to isolate the NAs (Jones et al. 2001). Hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) are common methods used worldwide in oil refineries for the removal of nitrogen compounds in crude oil. However, these processes require elevated temperatures, high pressures and high hydrogen consumption (Pinto et al. 2017). All these procedures present reagents or operational limitations.

Adsorption techniques have been suggested as promising options for the removal of analytes.
present at low concentrations, such as NA, in oil samples (Gaikar & Maiti 1996), and they have proven to be economical and efficient for removing organic pollutants, heavy metals and dyes from polluted waters (Karnib et al. 2014). Accordingly, the adsorption process has the potential to remove the polar compounds from crude oil. It has a low cost and is a nondestructive process (Ding et al. 2009, Wu et al. 2019), and not involve a complex operation.

Several techniques, such as $^{13}$C and $^1$H nuclear magnetic resonance ($^{13}$C NMR and $^1$H NMR) and high-performance liquid chromatography coupled to mass spectrometry (HPLC-MS/MS), are used to identify these acids compounds, but recent applications of the FT-ICR MS technique have shown great results. This technique allows the molecular analysis of crude oil without any previous stages of separation or derivatization, being able to distinguish several different polar compound classes (e.g., neutral nitrogen and carboxylic acids), and can identify thousands of distinct masses since it offers the highest available broadband mass resolution, mass resolving power and mass accuracy, which allows the assignment of a unique elemental composition (C$_{h}$H$_{n}$N$_{o}$O$_{s}$$_{s}$) to each peak in a mass spectrum (Hughey et al. 2004, Headley et al. 2007, 2009, Chen et al. 2012, Geng et al. 2012). FT-ICR MS, when used with electrospray ionization in the negative ion mode, ESI (-), allows the detection and monitoring of acidic polar compounds that are quick to deprotonate, such as carboxylic acids, alcohols and pyrroles (Quian et al. 2001, Oldenburg et al. 2014). The extensive range of modern techniques for the characterization and structural identification of polar compounds, mainly involving mass spectrometry, has been summarized in numerous reviews published over the last decade (Grewer et al. 2010, Headley et al. 2013, Brown & Ulrich 2015).

In this context, this study aims to evaluate the efficacy of six potential adsorbents (powder shale, activated carbon, bentonite (commercial clay), silica gel, sandstone and wood powder) to remove acidic polar compounds, especially naphthenic acids, from Brazilian heavy crude oils. To qualitatively evaluate the compound removal efficiency at the molecular level, the abundance of heteroatom compounds was monitored by FT-ICR MS using negative ion mode electrospray ionization.

**Acronyms**

ESI (-) FT-ICR MS - Negative Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
NA - naphthenic acids
API - American Petroleum Institute
IEA - International Energy Agency
LLE - liquid-liquid extraction
HDN - hydrodenitrogenation
HDS - hydrodesulfurization
$^{13}$C NMR / $^1$H NMR - Carbon Nuclear Magnetic Resonance and Hydrogen Nuclear Magnetic Resonance
HPLC-MS/MS – High Performance Liquid Chromatography-tandem Mass Spectrometry
TOC - total organic carbon
KOH - potassium hydroxide
SH - shale
AC - activated carbon
BENT - bentonite
SG - silica gel
SAND - sandstone
WP - wood powder
XRF - X-Ray Fluorescence
XRD - X-Ray Diffractometry
TGA - Thermogravimetric Analysis
BET - Brunauer, Emmet and Teller protocol
SEM - Scanning Electron Microscopy
C13 / C20 - crude oil samples
F1 - saturate fraction
F2 - aromatic fraction
F3 - polar fraction
NSO - nitrogen, sulfur, oxygen
HPLC - High Performance Liquid Chromatography
GC/MS - Gas Chromatography/Mass Spectrometry
SIM - selected ion monitoring
TAN - total acid number
DBE - double bond equivalent
Pr - pristane
Ph - phytane

MATERIALS AND METHODS

Adsorbents: pretreatment and characterization

Six raw materials were tested in this study: (i) powdered shale; (ii) activated carbon, synthesized from bovine bone; (iii) commercial bentonite (unidentified supplier); (iv) commercial silica gel 60, for column chromatography (Macherey-Nagel); (v) powder sandstone; and (vi) wood powder. The powdered shale (i) was obtained from shale rock with low total organic carbon (TOC < 0.02%) collected from the Irati Formation, and the powder sandstone (v) was obtained from sandstone rock collected from the Botucatu Formation, both from the sedimentary Paraná Basin, Brazil. The activated carbon was donated and its carbon content is between 9% and 11% of the overall weight.

Chemical modification

The adsorbents wood powder, sandstone and silica gel received a previous chemical treatment to obtain an alkaline surface that improves their removal potential of naphthenic acids. This treatment was performed by using KOH (potassium hydroxide) in isopropyl alcohol solution (1.1 mol/L), both purchased from Merck. For a volume of 16 mL of KOH solution was added to 8 g of each adsorbent. This mixture was stirred until form a uniform suspension and then, the solvent was evaporated under vacuum.

The modified and other materials (shale, bentonite, activated carbon) were dried for 12 h at 120 °C, and they had their grain size distribution controlled by dry sieving (230 mesh) and finally, they were stored in sealed flasks to avoid humidity. Subsequently, the material was characterized and applied in the adsorption experiments and received the following acronyms: SH (shale), AC (activated carbon), BENT (bentonite), SG (silica gel), SAND (sandstone) and WP (wood powder).

X-ray fluorescence (XRF)

The elemental composition (metal oxides) of the studied adsorbents was determined by X-ray fluorescence (XRF) with S2 Ranger XRF equipment (Bruker), operating with a rhodium X-ray source of 30 kW and using 5 g of each adsorbent put into a sample cup and covered by polypropylene film.

X-ray diffractometry (XRD)

The identification of mineral composition was determined using the D2-PHASER equipment (Bruker). The measurements were performed operating in continuous scan mode, with Cu-Kα radiation 1.5418 Å and a nickel filter with a voltage of 30 kV and 10 mA current. The 2θ values were varied from 5 ° to 80 ° at a rate of 0.02 °/min.

Thermogravimetric analysis (TGA)

About 10 mg of each sample was heated in Platina pans from 25 °C to 700 °C at 20 °C/min in a Q500 TGA instrument (TA), using nitrogen as carrier gas at 60 mL/min. The temperature used for the adsorbents pretreatments was determined based on these results. And the
software coupled determined the mass loss curve and its derivative.

**Textural characterization**

These analyses included the measure of the specific area, the volume and the average size of the adsorbent pores, by the BJH method. These parameters were determined by nitrogen adsorption-desorption (at 77 K) using an ASAP 2010 Micromeritics apparatus. The dry samples were degassed under vacuum condition (50 mtorr) at 300 °C for 1 h. Then the specific area was obtained by using the Brunauer, Emmet and Teller (BET) protocol.

**Scanning electron microscopy (SEM)**

The surface morphology of the adsorbents before and after the adsorption process was characterized by a JSM-6510LV microscope (Thermo Scientific). The Au-coated samples were examined under secondary electron mode with an accelerating voltage of 25 kV.

**Oils characterization**

The crude oil samples used in this study, named C13 and C20, are from turbidite reservoirs of the Campos Basin and were provided by Petrobras. The API and TAN values are shown in Table I. These values were relevant for choosing these oil samples once these characteristics, previously evaluated by Martins L.L. (unpublished data) and Martins et al. (2017), pointed to heavy and acid oils, which justify the application of the tested adsorbents in our study.

To investigate the saturates (F1 fraction), aromatics (F2 fraction) and NSO fractions (F3 fraction), the classic liquid chromatographic separation (ASTM D2007 2011) was performed. Silica gel activated at 120 °C for 12 h in an oven was slurry packed into a glass column (210 mm x 15 mm i.d.) with hexane. Around 40 mg of oil sample was deposited on the top of the column, and the saturated hydrocarbons were eluted with 40 mL of n-hexane. The aromatic compounds were collected by elution with 40 mL of n-hexane/methylene chloride (80:20 v/v), and the NSO fraction was eluted with 40 mL of methylene chloride/methanol (90:10 v/v). The solvents were evaporated under vacuum and the quantification of the fraction was performed using the gravimetric method.

**Adsorption experiments**

Each adsorbent was packed inside a glass column (210 mm x 15 mm i.d.) using methylene chloride from Sigma Aldrich. Two crude oils, C13 and C20, were tested, and for each adsorption test nearly 1 g of crude oil was deposited on the top of the column. The filtered fraction, named of filtered oil, was eluted with 10 mL of methylene chloride and collected in a beaker, previously weighted. The amount of total adsorbed oil, which may contain polar and non-polar compounds, was obtained by gravimetric method, from the ratio between the crude oil concentration in the

| Properties            | Crude oils |
|-----------------------|------------|
|                       | C13        | C20        |
| API gravity           | 26         | 23         |
| TAN (mg of KOH/g)\(^a\) | 1.20       | 0.82       |

Note: \(^a\)Total Acid Number (ASTM D-664).
solvent (mg/mL) before (initial concentration) and after adsorption (final concentration, e.g., filtered oil), as calculated by Equation 1.

\[
\%\text{Removal} = \left( \frac{C_i - C_f}{C_i} \right) \times 100
\]  

\(C_i\) = oil concentration in solution before addition of the adsorbent;
\(C_f\) = oil concentration in solution after adsorption.

The filtered oils obtained in the adsorption tests were also fractionated according to the procedure of classic liquid chromatographic separation performed for crude oils, to compare any changes in the saturated, aromatic and NSO fractions.

**ESI (−) FT-ICR MS analyses**

To assess the efficiency of acidic polar compound removal, especially NA, by the adsorbents and to monitor the changes of heteroatom class distribution in the crude oil and filtered oils, a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) was employed using electrospray ionization (ESI) in negative-ion mode.

The analyses were performed according to Martins et al. (2017), and solvents were of high-performance liquid chromatography (HPLC) grade; they were purchased from Sigma-Aldrich. Two milligrams of the sample (crude and filtered oil) were dissolved in 1 mL of toluene and then diluted with 1 mL of methanol containing 0.2% ammonium hydroxide. Direct infusion ESI (−) MS in the negative-ion mode was performed, and samples were analyzed by a 7.2 T LTQ FT Ultra mass spectrometer (Thermo Scientific, Bremen, Germany) with a resolving power of 400 000 in the 200–1000 Da mass range. A 5 \(\mu\)L min\(^{-1}\) syringe flow was used, with a spray voltage of 3.1 kV, and a 100 scans spectrum was acquired for each sample. For each spectrum, automated processing was performed to assign formulas to ion peaks with a signal-to-noise ratio of >3, using a custom algorithm the PetroMS software (Corilo et al. 2010), developed especially for petroleum data processing. This software was designed for the formula attribution and recalibration of a known homologous series (O2 class, in this case) from the measured \(m/z\) values of polar crude oil compounds. Allowed elements were \(^{12}\text{C}, ^{13}\text{C}, ^{1}\text{H}, ^{16}\text{O}, ^{14}\text{N}, \text{and } ^{32}\text{S}\). The maximum allowed formula error was 1 ppm.

**GC-MS analyses**

To investigate possible modifications in the saturated compounds due to the adsorption experiments, the F1 fractions from the crude and filtered oils were analyzed by gas chromatography/mass spectrometry (GC-MS). The samples were analyzed using an Agilent 7890A gas chromatograph equipped with DB-5 MS (30 m × 0.25 mm × 0.25 \(\mu\)m film thickness) coupled to an Agilent 5975C-MSD mass spectrometer. The MS was operated in the electron ionization mode with ionization energy of 70 eV and a source temperature of 230 °C. The injector and transfer line temperatures were 290 and 300 °C, respectively. The injection was performed in the splitless mode, with a volume of injection of 1 \(\mu\)L. Data were collected in selected ion monitoring (SIM) for \(m/z\) 85 and full scan (50-550 Da) modes. The compounds were identified based on literature, reference chromatographic profile and the mass spectra.

**RESULTS AND DISCUSSION**

**Adsorbents characterization**

The chemical compositions of all adsorbents obtained by XRF analysis, including the composition of silica gel, sandstone and wood powder before (unmodified) and after (modified) the treatment with KOH, is shown in Table II. The amount of \(\text{SiO}_2\) ranged from 1.23%
in the modified wood powder to 98.36% in the unmodified silica gel. Before modification, silica gel, sandstone and wood powder showed amounts of Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) ranging from 0.86% to 24.00% and 0.03% to 1.49%, respectively, along with small amounts of K\(_2\)O. However, after modification, the same adsorbents showed smaller Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) values and increasing K\(_2\)O. These results allow pointing out that there was an increase in the mass percentage of K (K\(_2\)O) due to chemical modification using KOH. The other adsorbents presented results according to the literature, in which the shale and bentonite showed percentages of SiO\(_2\) >50%: 54.15% and 68.89%, respectively. These results are consistent since the shale and bentonite are clay silicates (Teixeira-Neto & Teixeira-Neto 2009). Activated carbon from waste bovine bone is an adsorbent that has a porous structure of hydroxyapatite [(Ca\(_{10}\)(PO\(_4\))\(_6\)(OH)\(_2\)] (Choy & McKay 2005), in addition to calcium sulfate. So, the large percentage of CaO (58.56%) is acceptable due to the origin of the material.

To identify the minerals present in the samples of adsorbent, the mineral composition was performed exclusively for crystalline materials, i.e, bentonite, shale and sandstone before and after chemical modification, according to Figure 1. XRD analyses show that sandstones consist primarily of three minerals: quartz [SiO\(_2\)] (74%), albite [NaAlSi\(_3\)O\(_8\)] (9%) and kaolinite [(Al\(_4\)(Si\(_2\)O\(_5\))(OH)\(_4\)] (17%), similar to other works (Wu & Caetano-Chang 1992, Gesicki A.L.D., unpublished data). The shale sample presented six minerals: quartz (10%), albite (11%), calcite [CaCO\(_3\)] (3.4%), talc [Mg\(_{3}\)Si\(_4\)O\(_{10}\)(OH)\(_2\)] (51%), chlorite [(Mg\(_{4}\)Fe\(_2\)Li\(_{1}\)Al\(_{2}\)Si\(_3\)O\(_{10\frac{1}{2}}\)(OH)\(_2\)] (10.2%) and biotite [(K(Mg\(_{2}\)Fe\(_{3}\))(OH)\(_2\)Al\(_{2}\)Si\(_3\)O\(_{10\frac{1}{2}}\)] (15.1%). The main minerals, talc and albite, are also reported by Santos W.H. (unpublished data). Most of

### Table II. Chemical characterization of adsorbents obtained by X-ray fluorescence (XRF).

| Chemical Composition (wt%) | Adsorbents |  |  |  |  |  |
|----------------------------|------------|---|---|---|---|---|
|                            | SH  | AC  | BENT | SG  | SAND | WP |
|                            |  |  |  | unmod. | unmod. | mod. | unmod. | mod. | unmod. | mod. |
| SiO\(_2\)                  | 54.15 | 2.57 | 68.89 | 98.36 | 88.64 | 77.82 | 63.59 | 13.73 | 1.23 |
| MgO                       | 19.33 | 0.00 | 2.93 | 0.36 | 0.39 | 1.21 | 0.00 | 11.40 | 1.39 |
| Al\(_2\)O\(_3\)             | 5.61 | 1.08 | 13.07 | 0.96 | 0.86 | 14.70 | 5.37 | 24.00 | 3.75 |
| Fe\(_2\)O\(_3\)              | 13.73 | 1.14 | 11.21 | 0.03 | 0.02 | 1.49 | 1.29 | 0.92 | 0.25 |
| Na\(_2\)O                  | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 35.55 | 0.00 |
| TiO\(_2\)                  | 0.718 | 0.276 | 1.09 | 0.05 | 0.00 | 0.52 | 0.31 | 0.53 | 0.00 |
| Cr\(_2\)O\(_3\)              | 0.027 | 0.000 | 0.05 | 0.00 | 0.00 | 0.01 | 0.00 | 0.03 | 0.00 |
| NiO                       | 0.012 | 0.000 | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.03 | 0.00 |
| CaO                       | 3.47 | 58.56 | 1.42 | 0.16 | 0.16 | 0.28 | 0.00 | 1.96 | 0.00 |
| MnO                       | 0.35 | 0.02 | 0.05 | 0.00 | 0.00 | 0.03 | 0.00 | 0.05 | 0.00 |
| V\(_2\)O\(_5\)               | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| SO\(_3\)                  | 0.13 | 0.27 | 0.17 | 0.00 | 0.19 | 0.00 | 0.00 | 5.47 | 1.11 |
| K\(_2\)O                  | 1.87 | 0.32 | 0.50 | 0.00 | 9.66 | 3.69 | 29.20 | 1.54 | 91.22 |
| ZnO                       | 0.03 | 0.03 | 0.01 | 0.00 | 0.00 | 0.03 | 0.00 | 0.07 | 0.00 |

Note: SH=shale; AC= activated carbon; BENT=bentonite; SG=silica gel; SAND= sandstone; WP= wood powder; 1 unmodified (before modification); 2 modified (after modification).
the minerals found in the shale sample were also observed in previous studies of the Irati formation (Dos Anjos & Guimarães 2008). Finally, bentonite presented the montmorillonite as predominant mineral \([\text{Al}_2\text{Ca}_{0.5}\text{O}_{12}\text{Si}_4]\) (50%) and gypsum \([\text{CaH}_4\text{O}_6\text{S}]\) (34%), followed by quartz (2.2%) and albite (14%). These results are similar to those obtained by Carrera et al. (2008) and Gan et al. (2019). The mineral composition of the adsorbents corroborates to the results obtained by XRF since the main oxides correspond to the obtained minerals. The X-ray diffractograms are presented in Supplementary Material (Figure S1).

A decrease in the adsorbent samples mass, ranging from 1.2 to 10.6%, was observed by the TGA analysis until approximately 150 °C, which can be related to the loss of surface adsorbed water (Bayrak 2006, Silva et al. 2013). Since water can probably compete with the acid compounds for the adsorption sites, this temperature was used for the thermal pretreatment of the adsorbent before the adsorption experiments. The data from this analysis are presented in Figure S2.

The results of the textural characterization indicated different results of surface area, pores volume and pore average diameter for the tested adsorbents (Figure 2), in which the activated carbon, bentonite and silica gel presented the larger surface area (47.49 to 652.45 m\(^2\)/g) and pores volume (0.11 to 0.69 cm\(^3\)/g) than other adsorbents. The isotherms to the experimental data are shown in Figure S3, each profile was classified as a type V isotherm (Sing et al. 1985). Type V isotherms are mostly given by mesoporous solids although also can be observed in microporous solids, and their adsorption behavior is determined by relatively weak adsorbent–adsorbate interactions (Nalwa 2001, Thommes et al. 2005, Verbraeken & Brandani 2019). The average pore diameter (\(4V/A\) by BET) given in Figure 2 are within the mesoporous range (20Å<\(D_p<500\)Å). Thus, structural characterization suggests that the adsorbents tested can be able...
to retain polar compounds such as asphaltene, which the average size of its micelles in solution is 23-25 nm (Groenzin & Mullins 1999, Priyanto et al. 2001, Buch et al. 2003, Rajagopal & Silva 2004).

Since the crude oil samples used in this study are very complex mixtures, it was impossible to essay the adsorption process to compare with BET isotherms, nevertheless a similar study observed a good representation between BET isotherm and the adsorption behavior of the investigated system (Silva et al. 2013).

In order to complement the adsorbents characterization, the SEM analyses were performed and showed the surface morphology before adsorption experiments, according to Figure S4. It was possible to identify the different shapes and grain sizes of adsorbents, for example, the edges of the silica gel grains (Figure S4a) and the fibrous structure (cellulose, hemicellulose and lignin) of the wood powder (Figure S4b) (Tarley & Arruda 2003, Carvalho et al. 2009), in addition to the grain size difference, such as activated carbon, bentonite, sandstone and shale (Figure S4c-f). It should be emphasized that there was no change in the morphological structure of the adsorbents after contact with oil, as shown in Figure S5.

**Adsorption of NSO compounds**

**Adsorption efficiency**

The total removal percentages of compounds (polar and non-polar) from the crude oil, obtained by Equation 1, are shown in Table III. It is important to emphasize that in addition to silica gel, which is a very widespread material, all other tested materials presented an adsorption
percentage above 20%, especially activated carbon and wood powder. Activated carbon and silica gel presented higher removal percentage, removing 33% and 40% of compounds from the crude oil C13 and 39% and 37% from the crude oil C20, respectively. The wood powder presented the third-highest removal percentage, removing 28% and 33% of compounds from the crude oils C13 and C20, respectively. Also, the shale, bentonite and sandstone adsorbents presented similar adsorption for these compounds, ranging from 23 to 28% from oil C13 and 20 to 24% from oil C20. After modification with KOH, silica gel and wood powder increase the density of the basic sites. Thus, it is suggested that the removal may have occurred by an interaction between the alkaline sites and the polar compounds of petroleum, especially acidic species, typically present in heavy and acidic oils. This intermolecular interaction can occur via hydrogen-bonding (Do Nascimento et al. 2014). In activated carbon there are interactions that can affect the area of exclusion due to its porous structure, which can control the access by adsorbate to the pores of the available adsorption area, so it is a function of molecule size and pore size distribution (Yi et al. 2016). Therefore, in two cases, there is physical adsorption or physisorption.

**O₂ class compounds by ESI (-) FT-ICR MS**

To investigate the types of adsorbed compounds on materials, further investigation was required. Due to the great potential of ESI (-) FT-ICR MS analysis, which study compounds at a molecular level with high precision and mass accuracy, it was possible to identify several heteroatomic classes.

The Figure 3a-b showed variations in the relative abundance of the heteroatom classes N, NO, NO₂, NO₃, O, O₂, O₂S, O₃, O₃S, O₄, O₄S, O₄S, O₄S, and S for the crude oils C13 and C20 and their filtered oils. These heteroatom classes encompass acidic polar compounds, such as alcohols (phenols and aromatic alcohols, O class), pyrroles (N class) and carboxylic acids (O₂ class) (Quian et al. 2001, Kim et al. 2005, Rodgers et al. 2005, Martins et al. 2017). Additionally, the O₂/N ratio was determined by the relative abundance of the O₂ class divided by the relative abundances of the N class, similar to Klein et al. (2003). This ratio is also shown in Figure 3.

Oxygenated compounds (contain oxygen) represent over 70% of the total compounds identified in the C13 and C20 crude oils (Figure 3a and 3b, respectively), with the O₂ class as the most abundant for both crude oils, with 50 and 40%, respectively. This class is likely related to carboxylic acids, which are intermediates formed during petroleum metabolism by microbial degradation (Meredith et al. 2000, Hughey et al. 2007, Vaz et al. 2013). Indeed, biodegradation is the main process believed to form acidic compounds, such as naphthenic acids (O₂ compounds).

### Table III. Compounds removal percentage from oil samples C13 and C20 by adsorbents, obtained by gravimetric method.

| Oil Samples | (%) Removal |
|-------------|-------------|
|             | SH | AC | BENT | SG | SAND | WP |
| C13         | 23 | 33 | 26   | 40 | 28   | 28 |
| C20         | 24 | 39 | 20   | 37 | 23   | 33 |

Note: SH = shale; AC = activated carbon; BENT = bentonite; SG = silica gel; SAND = sandstone; WP = wood powder.
According to Figure 3, in general, oxygenated compounds with two or more oxygen (NO₂, O₂, O₃, O₂S, O₄S, O₅S), potentially related to carboxylic acids, were likely adsorbed on all evaluated adsorbents, with emphasis on NO₂ class compounds, since a relative abundance decreasing is observed, while there was an increase of the relative abundance of the N, NO and O classes. The O₂ class notably decreased for both oil samples, especially for the oil C13 treated with activated carbon and silica gel (decreasing 90%) and bentonite (decreasing 60%) and for the oil C20 treated with shale, bentonite, and activated carbon (decreasing 90%) and silica gel (decreasing 95%). However, the sandstone and wood powder showed a poor reduction of...
the O₂ class compounds, compatible with their very low surface area (4.25 and 1.12, respectively). On the other hand, the relative abundance of the nitrogenous classes (N and NO) increased because of oxygenated compounds adsorption, especially the O₂ class. These results suggest preferential adsorption of O₂ compounds, especially of other compounds that contain two or more oxygen atoms, presenting a reduction in the relative abundance, as seen in Figure 3. These compounds likely contain the carboxylic functional group (a characteristic of organic acids), which accentuates the acidic and polar character of these compounds in comparison to other classes that do not contain oxygen or contain only one oxygen.

High O₂/N ratios, as seen in Figure 3, can indicate a higher abundance of carboxylic acids, which are known to contribute to corrosion issues during the refining process (Klein et al. 2003). Between the crude oils, the O₂/N ratio was higher for C13, as expected, since this oil had a higher relative abundance of the O₂ class, in addition to having a higher TAN (1.2 mg of KOH/g of oil, Table I). Concerning the filtered oils, samples treated with wood powder and sandstone presented a high O₂/N ratio, as these adsorbents adsorbed few carboxylic acid compounds and therefore had a high relative abundance. On the other hand, silica gel and activated carbon showed a low O₂/N ratio, since these adsorbents retained a larger amount of O₂ than N compounds.

The DBE (double bond equivalent) abundance distribution of the O₂ class of the crude oils C13 and C20 and its fractions treated adsorbents (filtered oil) were also compared and are shown in Figure 4, in which compounds with a maximum abundance, at DBE = 3–6 are observed for both crude oils. The same DBE range was also found by Barros et al. (2017) in their study about the degradation of acid crude oil. The results show that relative abundance of filtered oils is lower than crude oil abundance, it is indicating which the NA compounds were adsorbed along with all DBE range, for C13 and C20 samples, although there is a highlight for some adsorbents. In Figure 4a, a significant reduction of the O₂ compound class is observed for samples treated with bentonite, activated carbon and silica gel. In these last two, the NA compounds are partially or completely removed from the crude oil C13, along with all DBE range. Conversely, oils treated with sandstone, shale and wood powder indicate an abundance of the O₂ class species is practically the same as for the crude oil. Now about crude oil C20 (Figure 4b) it is found similar behavior, can be also a significant reduction of the O₂ compound class is observed for samples treated with bentonite, activated carbon, silica gel and shale, in which NA compounds are partially or completely removed from the crude oil C20, for all DBE range. Note that silica gel and activated carbon were able to remove compounds independently of the DBE value for all oil samples. Thus, they are the materials with the best adsorption capacity for O₂ class polar compounds.

The distribution of the detected species can be presented as color plots of DBE versus carbon number, which allows comparing compositional relative abundance changes within a heteroatom class (Ray et al. 2014). Figures 5 and 6 illustrate the DBE versus carbon number plot for the O₂ class of the crude oils C13 and C20, respectively, and their filtered oils. All samples presented a distribution of DBEs ranging from 1 to 17 and the carbon number ranging from C15 to C65. In the crude oils a maximum abundance of C33 can be observed. Our results are in concordance with those reported in the literature (Colati et al. 2013, Yang et al. 2019).

The color plots show distinct trends as a function of the adsorption capacity of the
adsorbents. For crude oil C13 samples treated with bentonite, activated charcoal and silica gel (Figure 5), there was a decrease in the relative abundance of all O₂ compounds, while samples treated with shale, sandstone and wood powder did not show a significant decrease in these compounds. Note that compounds with carbon numbers of 25-35 presented a large relative intensity and were the most adsorbed. However, compounds with a carbon number of 50-65, with a small relative intensity, also presented significant adsorption.

Concerning the crude oil C20 and its fractions, presented in Figure 6, a similar behavior was observed, however in this case higher compound adsorption occurred, probably due to crude oil C20 has a lower intensity of O₂ class compounds (40%) than the other oil. The samples treated with shale, activated carbon, bentonite and silica gel (panels of Figure 6) showed a decrease in the relative abundance of O₂ compounds with a wide range of carbon numbers, 15-60. However, sandstone and wood powder did not show significant adsorption.

Figure 4. DBE distribution of the O₂ class compounds for the (a) crude oil C13 and filtered oils; (b) crude oil C20 and filtered oils. Note: SH= shale, AC= activated carbon; BENT= bentonite, SG= silica gel; SAND= sandstone; WP= wood powder.
Figure 5. Isoabundance contoured plots of DBE versus carbon number for the O₂ class of crude oil C13 and filtered oils.
These results corroborate the silica gel and activated carbon as most efficient to remove O\textsubscript{2} compounds than the other adsorbents, in agreement with their textural characteristics and with their higher removal percentage (Table III).

**Geochemical analyses**

To investigate possible alteration in the chemical composition of the crude oils after the removal of the acidic polar compounds, the crude oils and filtered oils samples were fractionated and quantification of the saturate, aromatic and NSO fractions were performed using the gravimetric method. Oils treated with silica gel and activated carbon were selected to compare for crude oils since they had shown better absorption capacity. These results are presented in Figure 7. The proportions of saturated and aromatic fractions increased while the NSO fractions decreased when comparing the fraction quantification before and after the adsorption test, which agrees with the adsorption of the acid polar compounds included in the NSO fraction. The NSO fraction contains acidic and corrosive compounds in crude oil (Ghannam et al. 2012), being detrimental in the petroleum industry. The decrease of this fraction can represent an expense reduction and an optimization of crude oil refining. The lower proportion of the NSO fraction in filtered oils confirms the adsorption capacity of polar compounds by adsorbents silica gel and activated carbon.

Figure S6 shows the representative mass chromatograms for \textit{m/z} 85 of the C13 and C20 crude oils and filtered oils treated with silica gel and activated carbon, respectively. In all samples, a similar distribution of \textit{n}-alkanes, pristane (Pr) and phytane (Ph) were observed, with a homologous series from the \textit{n}-C13 to \textit{n}-C32 hydrocarbons. No changes in the chromatographic profile of the oils were observed after the adsorption test when compared with the crude oil profile. This is another positive outcome that shows that the adsorbents application in this work were able to remove polar compounds without affecting the saturated fraction since the saturated hydrocarbons are the most important and most valuable fraction for the petroleum industry. These compounds can also provide parameters that indicate the thermal maturation and hydrocarbon potential of source rock and can contain critical biomarkers that have been used to determine the origins and formation of petroleum fluids (Marzi et al. 1993, Bissada et al. 2016). From this fraction, several derivatives consumed worldwide are obtained. Thus, the relative decrease in NSO fraction and consequently the relative increase in saturated hydrocarbons is a positive factor for the oil industry.

**CONCLUSIONS**

Unlike other studies that use commercial solutions or petroleum fractions, this work showed the use of adsorption technique as a cost-effective method to remove acidic compounds from crude oil and obtained adsorption percentages higher than 20%. Activated carbon obtained adsorption rate of naphthenic acid compounds (O\textsubscript{2} classes) as good as a silica gel, presenting excellent adsorbing properties. Wood powder, a waste material, was not effective at NA removing but was promising to remove NO\textsubscript{2} class compounds, so it may be useful in future applications.

The analysis by ESI (-) FTICR-MS showed the efficiency of the proposed process for the removal of oxygenated compounds, providing chemical information on a molecular level. It was also possible to identify types of compounds and
Figure 6. Isoabundance contoured plots of DBE versus carbon number for the O₂ class of crude oil C20 and filtered oils.
the heteroatomic classes from petroleum and thus assist to understand the acidic compounds adsorption process.

Another positive outcome is that the NSO fraction removal by adsorbents was performed without changes in the \( n \)-alkane profile.

In summary, materials yielded promising results in the removal of acidic polar compounds in crude oil fractions and could be suggested for application in the industrial process.

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**Figure 7.** F1 (saturate), F2 (aromatic) and F3 (NSO) fractions obtained by classic liquid chromatographic separation. Note: TR= total recovery.
REFERENCES

ALI MF, AL-KHADHRAWI MR, PERZANOWSKI H & HALPERN HI. 2002. Central Saudi Arabian crude oils: a geochemical investigation. Pet Sci Technol 20: 633-654.

ANP. 2019. Available at: <http://www.anp.gov.br>, accessed in January 2019.

ASTM D2007-11. 2011. Standard Test Method for Characteristic Groups in Rubber Extinguishers and Processing Oils and Other Petroleum-Derived Oils by the Clay-Gel Absorption Chromatographic Method, ASTM International, West Conshohocken, PA.

BAYRAK Y. 2006. Application of Langmuir isotherm to saturated fatty acid adsorption. Microporous Mesoporous Mater 87: 203-206.

BISSADA KK, TAN J, SZYMEZYK E, DARNELL M & MEI M. 2016. Group-type characterization of crude oil and bitumen - part II: Efficient separation and quantification of normalparaffins iso-paraffins and naphthenes (PIN). Fuel 173: 217-221.

BROWN LD & ULRICH AC. 2015. Oil sands naphthenic acids: a review of properties, measurement, and treatment. Chemosphere 127: 276-290.

BUCH L, GROENZIN H, BUENROSTRO-GONZALEZ E, ANDERSEN SI, LIRA-GALEANA C & MULLINS OC. 2003. Molecular size of asphaltene fractions obtained from residuum hydro-treatment. Fuel 82: 1075-1084.

CARRERA AMM, VARAJÃO A & GONÇALVES MA. 2008. Caracterização mineralógica das argilas da península de Santa Elena, Equador. REM, Rev Esc Minas 61: 97-105.

CARVALHO W, CANILHA L, FERRAZ A & MILAGRES AMF. 2009. Uma visão sobre a estrutura, composição e biodegradação da madeira. Quim Nova 30: 809-814.

CHEN X, SHEN B, SUN J, WANG C, SHAN H, YANG C & LI C. 2012. Characterization and comparison of nitrogen compounds in hydro-treated and untreated shale oil by electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Energy Fuels 26: 1707-1714.

CHU X, HAN X, HUANG Q & DENG Y. 2019. Assessing and modifying China bentonites for aflatoxin adsorption. Appl Clay Sci 168: 348-354.

CLEMENT SJ & FEDORAK PM. 2005. A review of the occurrence, analyses, toxicity, and biodegradation of naphthenic acids. Chemosphere 60: 585-600.

COLATI KAP, DALMASCHIO GP, DE CASTRO EVR, GOMES AO, VAZ BG & ROMÃO W. 2013. Monitoring the liquid-liquid extraction of naphthenic acids in Brazilian crude oil using electrospray ionization FT-ICR mass spectrometry (ESI FT-ICR MS). Fuel 108: 647-655.

CORILLO YE, VAZ BG, SIMAS RC, NASCIMENTO HDL, KLITZKE CF, PEREIRA RCL, BASTOS WL, SANTOS NETO EV, RODGERS RP & EBERLIN MN. 2010. Petroleomics by EASI (+) FT-ICR MS. Anal Chem 82: 3990-3996.

DAVUDOV D & MOGHANLOO RG. 2017. A systematic comparison of various upgrading techniques for heavy oil. J Pet Sci Eng 156: 623-632.

DING L, RAHIMI P, HAWKINS R, BHATT S & SHI Y. 2009. Naphthenic acid removal from heavy oils on alkaline earth-metal oxides and ZnO catalysts. Appl Catal A 371: 121-130.

DOS ANJOS CW & GUIMARÃES EM. 2008. Metamorfismo de contato nas rochas da Formação Irati (Permiano), norte da Bacia do Paraná. Rev Bras Geoci 38: 629-641.

DO NASCIMENTO RF, DE LIMA ACA, VIDAL CB, MELO DQ & RAULINO GSC. 2014. Adsorção: aspectos teóricos e aplicações ambientais, 1ª ed., Fortaleza: Imprensa Universitária, 256 p.

GAIKAR VG & MAITI D. 1996. Adsorptive recovery of naphthenic acids using ion-exchange resins. React Funct Polym 31: 155-164.

GEORGIE WJ & SMITH PC. 2012. The challenges in processing heavy oil. In: SPE Oil Conference, 12-14 June, Calgary, Alberta, Canada. Proceedings of the SPE, SPE 157894. Available at: https://doi.org/10.2118/157894-MS.

GHANAM MT, HASAN SW, ABU-JDAYIL B & ESMAIL N. 2012. Rheological properties of heavy & light crude oil mixtures for improving flowability. J Pet Sci Eng 81:122-128.

GREEN JB, HOFF RJ, WOODWARD PW & STEVENS LL. 1984. Separation of liquid fossil fuels into acid, base and
neutral concentrates. An improved nonaqueous ion exchange method. Fuel 63: 1290-1301.

GREWER DM, YOUNG RF, WHITTAL RM & FEDORAK PM. 2010. Naphthenic acids and other acid-extractables in water samples from Alberta: what is being measured? Sci Total Environ 408: 5997-6010.

GROENZIN H & MULLINS OC. 1999. Asphaltene molecular size and structure. J Phys Chem A 103: 11237-11245.

GRUBER LDA, DAMASCENO FD, CARAMÃO EB & JACQUES RA. 2012. Ácidos naftênicos no petróleo. Quim Nova 35: 1423-1433.

HEADLEY JV, PERU KM & BARROW MP. 2009. Mass spectrometric characterization of naphthenic acids in environmental samples: a review. Mass Spectrom Rev 28: 121-134.

HEADLEY JV, PERU KM, MOHAMED MH, FRANK RA, MARTIN JW & HAZEWINKEL RRO. 2013. Chemical fingerprinting of naphthenic acids and oil sands process waters: a review of analytical methods for environmental samples. J Environ Sci Health A 48: 1145-1163.

HUANG MF, ZHAO SL, LI P & HUISINGH D. 2006. Removal of naphthenic acid by microwave. J Cleaner Prod 14: 736-739.

HUGHEY CA, GALASSO SA & ZUMBERGE JE. 2007. Detailed compositional comparison of acidic NSO compounds in biodegraded reservoir and surface crude oils by negative ion electrospray Fourier transform ion cyclotron resonance mass spectrometry. Fuel 86: 758-768.

HUGHEY CA, RODGERS RP, MARSHALL AG, WALTERS CC, QIAN K & MANKIEWICZ P. 2004. Acidic and neutral polar NSO compounds in Smackover oils of different thermal maturity revealed by electrospray high field Fourier transform ion cyclotron resonance mass spectrometry. Org Geochem 35: 863-880.

JONES DM, WATSON JS, MEREDITH W, CHEN M & BENNETT B. 2001. Determination of naphthenic acids in crude oils using nonaqueous ion exchange solid-phase extraction. Anal Chem 73: 703-707.

KARBAN B, KABBANIB A, HOLAIL H & OLAMA Z. 2014. Heavy metals removal using activated carbon, silica and silica activated carbon composite. Energy Procedia 50: 113-120.

KIM S, STANFORD LA, RODGERS RP, MARSHALL AG, WALTERS CC, QIAN K, WENGER LM & MANKIEWICZ P. 2005. Microbial alteration of the acidic and neutral polar NSO compounds revealed by Fourier transform ion cyclotron resonance mass spectrometry. Org Geochem 36: 1117-1134.

KLEIN GC, RODGERS RP, TEIXEIRA MAG, TEIXEIRA AMRF & MARSHALL AG. 2003. Petroleomics: electrospray ionization FT-ICR mass analysis of NSO compounds for correlation between total acid number, corrosivity, and elemental composition. Fuel Chemistry Division Preprints 48: 14-15.

MARTINS LL, PUDENZI MA, DA CRUZ GF, NASCIMENTO HDL & EBERLIN MN. 2017. Assessing biodegradation of Brazilian crude oils via characteristic profiles of O₁ and O₂ compound classes: petroleomics by negative ion mode electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. Energy Fuels 31:6649-6657.

MARZI R, TORKELSON BE & OLSON RK. 1993. A revised carbon preference index. Org Geochem 20: 1303-1306.

MEREDITH W, KELLAND SJ & JONES DM. 2000. Influence of biodegradation on crude oil acidity and carboxylic acid composition. Org Geochem 31: 1059-1073.

NALWA HS. 2001. Handbook of surfaces and interfaces of materials. Volume 5 California, USA. Academic Press p. 280. Available at: https://doi.org/10.1016/b978-012513910-6/50003-7.

NUNEZ G, BRICENO M, MATA C, RIVAS H & JOSEPH D. 1996. Flow characteristics of concentrated emulsions of very viscous oil in water. J Rheol 40: 405-423.

OLDENBURG TBP, BROWN M, BENNETT B & LARTER SR. 2014. The impact of thermal level on the composition of crude oils, assessed using ultra-high resolution mass spectrometry. Org Geochem 75: 151-168.

PINTO FE, SILVA CFPM, TOSE LV, FIGUEIREDO MAG, SOUZA WC, VAZ BG & ROMÃO W. 2017. Evaluation of adsorbent materials for the removal of nitrogen compounds in vacuum gas oil by positive and negative electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. Energy Fuels 31: 3454-3464.

PRIYANTO S, MANSOORI GA & SUWONO A. 2001. Measurement of property relationships of nanostructure micelles and coacervates of asphaltene in a pure solvent. Chem Eng Sci 56: 6933–6939.

QUIAN K, ROBBINS WK, HUGHEY CA, COOPER HJ, RODGERS RP & MARSHALL AG. 2001. Resolution and identification of elemental composition for more than 300 crude acids in heavy petroleum by negative-ion microelectrospray high-field Fourier transform ion cyclotron resonance mass spectrometry. Energy Fuels 15: 1505-1511.

RAJAGOPAL K & SILVA SMC. 2004. An experimental study of asphaltene particle sizes in nheptane-toluene mixtures by light scattering. Braz J Chem Eng 21: 601-609.
REMIVAL OF ACIDIC COMPOUNDS FROM CRUDE OILS

RAMIREZ-CORREDORES MM. 2017. The Science and Technology of Unconventional Oils: finding refining opportunities, 1st ed., San Diego: Academic Press, 776 p.

RAY PZ, CHEN H, PODGORSKI DC, MCKENNA AM & TARR MA. 2014. Sunlight creates oxygenated species in water-soluble fractions of Deepwater horizon oil. J Hazard Mater 280: 636-643.

RODGERS RP, HUGHEY CA, HENDRICKSON CL & MARSHALL AG. 2002. Advanced characterization of petroleum crude and products by high field Fourier transform ion cyclotron resonance mass spectrometry. Fuel Chemistry Division Preprints 47: 636-698.

RODGERS RP, SCHAUB TM & MARSHALL AG. 2005. Petroleomics: MS returns to its roots. Anal Chem 77: 20 A-27 A.

SEIFERT WK, TEETER RM, HOWELLS G & CANTOW MJR. 1969. Analysis of crude oil carboxylic acidic after conversion to their corresponding hydrocarbons. Anal Chem 41: 1638-1647.

SEIFERT WK & TEETER RM. 1970. Identification of polycyclic aromatic and heterocyclic crude oil carboxylic acids. Anal Chem 42: 750-758.

SILVA JP, COSTA ALH, CHIARO SSX, DELGADO BEPC, DE FIGUEIREDO MAG & SENNA LF. 2013. Carboxylic acid removal from model petroleum fractions by a commercial clay adsorbent. Fuel Process Technol 112: 57-63.

SLAVCHEVA E, SHONE B & TURNBULL A. 1999. Review of naphthenic acid corrosion in oil refining. Br Corros J 34: 125-131.

TARLEY CRT & ARRUDA MAZ. 2003. Adsorventes naturais: potencialidades e aplicações da esponja natural (Luffa cylindrica) na remoção de chumbo em efluentes de laboratório. Revista Analítica 4: 25-31.

TEIXEIRA-NETO E & TEIXEIRA-NETO AA. 2009. Modificação química de argilas: desafios científicos e tecnológicos para obtenção de novos produtos com maior valor agregado. Quim Nova 32: 809-817.

TEMIZEL C, CANBAZ CH, TRAN M, ABDELFATAH E, JIA B, PUTRA D, IRANI M & ALKOUSH A. 2018. A Comprehensive Review Heavy Oil Reservoirs, Latest Techniques, Discoveries, Technologies and Applications in the Oil and Gas Industry In: SPE International Heavy Oil Conference and Exhibition, 10-12 December, Kuwait City, Kuwait, Proceedings of the SPE, SPE193646-MS. Available at: https://doi.org/10.2118/193646-MS.

TOMCZYK NA, WINANS RE, SHINN JH & ROBINSON RC. 2001. On the nature and origin of acidic species in petroleum. 1. Detailed acid type distribution in a California crude oil. Energy Fuels 15: 1498-1504.

THOMMES M, KANEKO K, NEIMARK AV, OLIVIER JP, RODRIGUEZ-REINOSO F, ROUQUEROL J & SING KSW. 2015. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure Appl Chem 87: 1-9.

VAZ BG, SILVA RC, KLITZKE CF, SIMAS RC, LOPES NASCIMENTO HD, PEREIRA RCL, GARCIA DF, EBERLIN MN & AZEVEDO DA. 2013. Assessing biodegradation in the llanos orientales crude oils by electrospay ionization ultrahigh resolution and accuracy Fourier transform mass spectrometry and chemometric analysis. Energy Fuels 27: 1277-1284.

VERBRAEKEN MC & BRANDANI S. 2019. A priori predictions of type I and type V isotherms by the rigid adsorbent lattice fluid. Adsorption. https://doi.org/10.1007/s10450-019-00174-7.

WATSON JS, JONES DM, SWANNELL RPJ & VAN DUIN ACT. 2002. Formation of carboxylic acids during aerobic biodegradation of crude oil and evidence of microbial oxidation of hopanes. Org Geochem 33: 1153-1169.

WENGER LM, DAVIS CL & ISAKSEN GH. 2002. Multiple controls on petroleum biodegradation and impact on oil quality. SPE Reservoir Eval Eng 5: 375-383.

WU FT & CAETANO-CHANG MR. 1992. Estudo mineralógico dos arenitos das formações Piramboia e Botucatu no centro-leste do estado de São Paulo. Rev. Instituto Geológico Est S Paulo 13: 58-68.

YAGHI BM & AL-BEMANI A. 2002. Heavy crude oil viscosity reduction for pipeline transportation. J Energy Sources 24: 93-102.

YANG C, ZHANG G, SERHAN M, KOIVU G, YANG Z, HOLLEBONE B, LAMBERT P & BROWN CE. 2019. Characterization of naphthenic acids in crude oils and refined petroleum products. Fuel 255: 115849.

YI Z, YAO J, ZHU M, CHEN H, WANG F & LIU X. 2016. Kinetics, equilibrium, and thermodynamics investigation on the adsorption of lead (II) by coalsbased activated carbon. Springer Plus 5: 1-12.
SUPPLEMENTARY MATERIAL

Figure S1. X-ray diffractograms of crystalline materials (bentonite, shale and sandstone).
Figure S2. TGA thermograms of tested adsorbents.
Figure S3. BET isotherms for adsorbents: (a) shale, (b) activated carbon, (c) bentonite, (d) silica gel, (e) sandstone, (f) wood powder.
Figure S4. SEM images of adsorbents before the adsorption experiments: (a) silica gel, (b) wood powder, (c) activated carbon, (d) bentonite, (e) sandstone and (f) shale.
Figure S5. SEM images of adsorbents with oil: (a) silica gel, (b) wood powder, (c) activated carbon, (d) bentonite, (e) sandstone and (f) shale.
Figure S6. Mass chromatograms (RIC for the m/z 85 ion) of crude oils and filtered oils from C13 and C20 samples.

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