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Naphthenic acids recovery from petroleum using ionic silica based hybrid material as stationary phase in solid phase extraction (SPE) process

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Abstract Naphthenic acids cause corrosion in the equipment used in the petroleum processing. Considering difficulties in the identification of the compounds present in the petroleum sample, it is necessary to study new methodologies to identify or remove the acid compounds from complex matrix. Solid phase extraction (SPE) with ionic phases has been used for this purpose, because it promotes greater selectivity, lower consumption of solvents and small amount of the stationary phase. The proposed study is the recovery of acid compounds using SPE method. An ionic silica based hybrid material containing the pyridinium group was developed and used as stationary phase (*SiPy*). Linear and monocyclic acids were used as standard mixture in the SPE for calculation of recovery. Further tests were performed with Brazilian petroleum. The *SiPy* stationary phase showed satisfactory results for the recovery and identification of the acidic compounds presented in the standard mixture as well as in the resin fraction from petroleum.

Keywords Solid phase extraction · Naphthenic acids · Petroleum · Sol–gel

1 Introduction

The petroleum is constituted basically of organic chemical compounds with hydrogen and carbon and other minority compounds, such as nitrogen, sulfur, oxygen and some metals. The average percentage in weight of each chemical element present in the petroleum is 11–14 % of hydrogen, 83–87 % of carbon, 0.06–8 % of sulfur, 0.11–1.7 % of nitrogen, 0.1–2 % of oxygen and up to 0.3 % of metals (Thomas et al. 2004). Even in small amount the, oxygenated compounds found in the petroleum are a problem in the refine process, mainly carboxylic acids known in the industry as naphthenic acids. These compounds are corrosion agents in petroleum refining equipment (Wu et al. 2004). The naphthenic corrosion occurs in the refine equipment in which the temperature is between 220 and 400 °C. At temperatures higher than 400 °C the naphthenic acids break down, forming a protective coating in the refinery equipment (Clemente and Fedorak 2005). The naphthenic corrosion depends on the presence and nature of a determined acid group, of size and structure of the naphthenic acid (Damasceno et al. 2014; Gruber et al. 2012). Considering that, the corrosion in the refinery equipment is caused by specific naphthenic acids, which are present in low concentration in the crude oil, some analytical procedures related to these acids have been developed (Purcell et al. 2007; Nielsen et al. 2008).

The liquid–liquid extraction (LLE) and SPE using Amberlyst 25 were applied by Borgund et al. (2007) to extract acid compounds from petroleum. According to these authors, when the SPE technique was applied, the

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amount of acids extracted was three times greater than those obtained by LLE. Indeed, the SPE is a technique that has been used to concentrate and separate naphthenic acids from petroleum. One can verify that the SPE methodology using the ionic exchangers has been already reported. Some commercial ionic exchange resins were applied as stationary phase in the SPE process for this purpose. Jones et al. (2001) used a quaternary amine (strong anion exchanger - SAX) to isolate the aliphatic and naphthenic acids from the crude oil samples. According to these authors this methodology is effective in the separation of acid compounds from light and heavy oils. Campos et al. (2006) performed the isolation of acids fraction through the SPE technique with an ionic exchange resin (Amberlyst 27). By using this stationary phase, it was possible to obtain a pure acid fraction, which allows the analysis and identification of the acid compounds present in the petroleum. More recently, de Conto et al. (2012) developed a new stationary phase, Dab-Al_2O_3, i.e. alumina modified with an ionic quaternary ammonium group to be applied in the acid compound removal from Brazilian petroleum, using SPE methodology. The authors tested the Dab-Al_2O_3 using, firstly, a standard mixture composed by acid compounds and afterwards with a petroleum fraction. The efficiency of the Dab-Al_2O_3 in the acid compounds removal was compared with the two commercial anionic exchanges (SAX and NH_2). It was observed that the Dab-Al_2O_3 shows greater extraction of acid compounds from petroleum matrix than that of the two commercial stationary phases.

Therefore, the proposal of this work is to develop a silica based hybrid material containing ionic pyridinium group, to be applied as stationary phase, aiming to optimize and improve the acid naphthenic removal from petroleum matrix using the SPE technique.

2 Experimental

2.1 Synthesis of the ionic silica based hybrid material

The synthesis of hybrid material was adapted from de Menezes et al. (2012). The synthesis was prepared by the sol–gel method. Tetraethylorthosilicate (TEOS) and 3-chloropropyltrimethoxysilane (CPTMS) were used as precursor reagents, both from Aldrich. It was used 90 % (molar) of TEOS (50 mL) and 10 % (molar) of CPTMS (4.5 mL). The HF (Merck) was used as catalyst. Firstly, the TEOS was pre-hydrolyzed by adding 80 mL of ethanol and 8.0 mL of distilled water, with constant stirring for 2 h, at room temperature. Subsequently, it was added CPTMS. The mixture was stirred for 40 min, at room temperature, followed by temperature increasing to 40 °C for gelation. Afterward, the material was dried in vacuum at 110 °C. The second step consists in the grafting reaction of pyridine using 6.5 g of the hybrid material obtained in the first step. The material was immersed in 70 mL of pyridine in toluene solution (2.5 mol L^{-1}) and heated, at reflux temperature, for 24 h. The solid was separated, washed with toluene, ethanol, ethyl ether, and heated at 50 °C under vacuum. The resulting ionic silica based hybrid material, which contains the pyridinium group, was designated as *SiPy*. This material was packaged in the SPE cartridge.

2.2 Characterization of *SiPy*

The carbon and nitrogen elemental analyses on *SiPy* material, previously treated at 180 °C for 1 h, was carried out in a Perkin-Elmer analyzer, model 2400. The analysis was made in duplicate. To determine the amount of exchangeable chloride ions, 100 mg of the solid was immersed in 30 mL of 0.1 mol L^{-1} HNO_3 solution and the displaced chloride ions in the solution phase were titrated with standard $AgNO_3$ solution, using potentiometric method. The determination was carried out in duplicate.

The *SiPy* material was submitted to transmission FTIR analysis using an IR cell that allows obtaining spectra of sample after heat treatment in vacuum, without air exposition. The IR cell was described elsewhere in detail (Pavan et al. 2002). Self-supporting disk of the *SiPy* material, with a diameter of 2.5 cm, weighing ca. 100 mg was prepared. The disk was heated at 200 °C, under vacuum (10^{-2} Torr) for 1 h. The spectrum of the *SiPy* was obtained at room temperature, using a Varian 640 FT-IR Spectrometer, with a resolution of 4 cm^{-1} and 150 cumulative scans.

The thermogravimetric analysis (TGA) of the *SiPy* was performed under nitrogen flow on a TA Instrument system model TGA Q5000, with a heating rate of 20 °C min^{-1}, from room temperature up to 700 °C.

The N_2 adsorption/desorption isotherm of *SiPy* was determined at the boiling point of liquid nitrogen, using Micromeritics 3020 Krypton equipment. The *SiPy* was previously degassed at 120 °C under vacuum for 10 h. The specific surface area was determined by the BET (Brunauer, Emmett and Teller) multipoint technique and the pore size distribution was estimated using the BJH (Barret, Joyner and Halenda) method (Gregg and Sing 1982).

2.3 Standard mixture and petroleum fraction samples

The general formula for carboxylic acids is $C_nH_{2n}+_ZO_2$, where Z is zero or negative, related to hydrogen deficiency and formation of a ring. An acyclic compound has Z equal to zero, a compound with a single ring has $Z = -2$, a compound with two rings has $Z = -4$ and so on (Clemente and Fedorak 2005). Four acyclic acids ($Z = 0$) with carbon

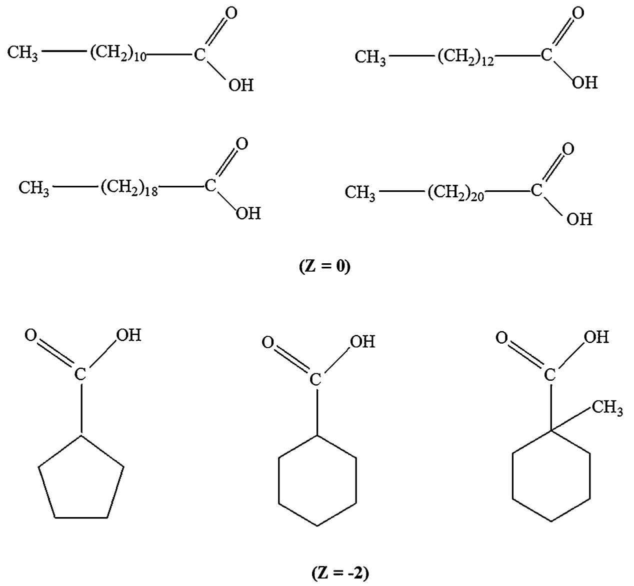

Fig. 1 Naphthenic acyclic (Z = 0) and single ring cyclic (Z = −2) acids of standard mixture

chain C_{12}, C_{14}, C_{20}, C_{22} and three single ring cyclic acids (Z = −2) C_6, C_7, C_8, were employed and their chemical structure are represented in Fig. 1. The standard mixture of acids was prepared at concentrations of 10 mg L^{-1} in dichloromethane for acyclic and cyclic acids. The acid mixture was placed on top of the SPE cartridge and aspirated in a low vacuum, conform described in item 2.4. The procedure was performed in triplicate.

The petroleum sample used in the SPE process was called B1 (24.6 °API and total acid number 0.5 mg KOH/g). Firstly, the petroleum was fractionated in saturates, aromatics, resins, and asphaltenes (SARA fractionation method). SARA fractionation was adapted according to the procedure described in a previous study (Kharrat et al. 2007). The resin fraction (RF) was separated, in order to verify the efficiency of removal acid compounds from petroleum by the *SiPy* stationary phase. The RF was fortified with standard acids to verify the matrix effect. The acids were identified by comparison with the reference ions presented by Clemente and Fedorak (2004).

2.4 SPE procedure

The SPE procedure was described in a previous work (de Conto et al. 2012), using the *SiPy* stationary phase. The SPE cartridge, with 500 mg stationary phase, was conditioned with 5 mL of hexane. Then, 10 mL of the standard sample was eluted through the column and the interferences were removed by elution with 10 mL of hexane. The recovery of the acid fraction was carried out by the elution with 20 mL of ethyl ether, containing 10 % (v/v) of formic acid. Afterwards, 10 mL of methanol were allowed to flow through the cartridge for recovery of polar compounds that could still be adsorbed on the stationary phase. Subsequently, the acidic fraction was dried under N_2 flow and dissolved in 1 mL of dichloromethane (DCM) for later analysis.

2.5 Chromatographic analysis

The acidic fraction was derivatized before the chromatographic analysis with *N*-tert-butyldimethylsilyl-*N*-methyltrifluoro aceta-mide (MTBDSTFA) (de Conto et al. 2012). The samples were dissolved in 900 μL of DCM and 100 μL of ethyl laurate solution 500 mg L^{-1} (internal standard). The chromatographic analyses were performed on a Shimadzu model QP– 2010 Plus gas chromatograph coupled to a mass spectrometry detector (GC/MS). The capillary column used was OV-5 (methyl silicone 5 % phenyl groups) with a 0.25-mm internal diameter, 0.25-mm thickness film of the stationary phase, and 30 m length. The chromatographic conditions were injection mode splitless, injector and interface temperature of 280 and 300 °C, respectively, and the injected volume was 1 μL. The mobile phase was helium gas with flow rate of 1 mL min^{-1}. The temperature program was started at 85 °C for 1 min, heated at 2 °C min^{-1} up to 280 °C, and left at this temperature for 10 min.

3 Results and discussion

3.1 SiPy characterization

The *SiPy* material was obtained in two steps. Firstly, a silica xerogel containing chloropropyl group was synthesized. The second one consists in the reaction of pyridine with these chloropropyl groups leading to a silica based hybrid material that contains the pyridinium ionic group, covalently bonded to the silica surface. A schematic representation of the *SiPy* structure is shown in the Fig. 2.

The *SiPy* material was submitted to carbon and nitrogen elemental analyses and the obtained values were 1.14 and 0.94 mmol of pyridinium group per gram of *SiPy*, respectively. It was also determined the amount of exchangeable chloride ions by potentiometric analysis using ion-selective electrode. The obtained value was 0.95 mmol of chloride ion per gram of *SiPy*. The presence of chloride ion is an indication that pyridine reacted with chloropropyl group, confirming that the silica based hybrid material, containing the pyridinium group, was successfully obtained (Gushikem et al. 2008). Additionally, the obtained values for the amount of pyridinium group, estimated by using these

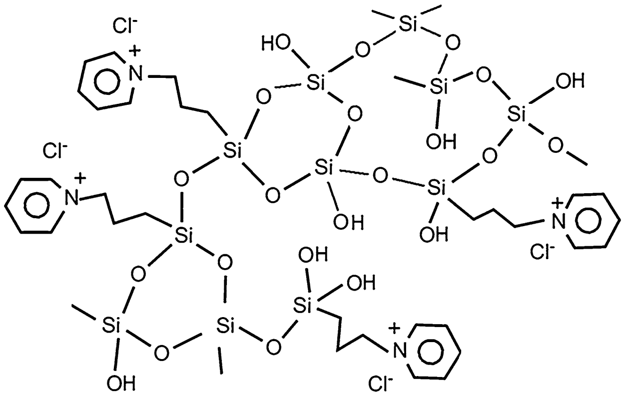

Fig. 2 Schematic representation of *SiPy* material

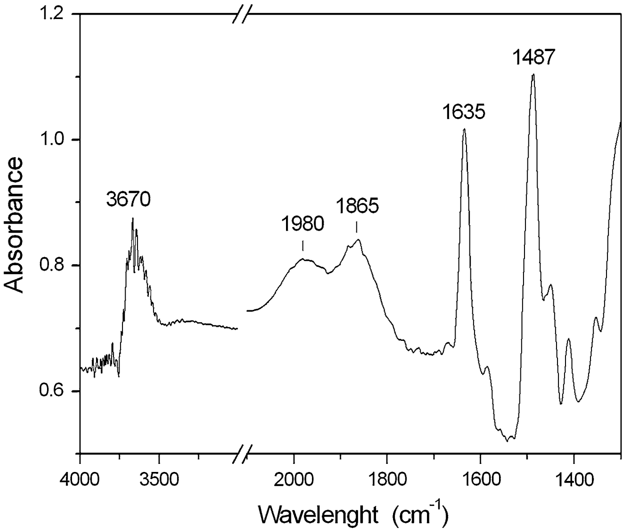

Fig. 3 Infrared absorption spectrum of *SiPy* material obtained at room temperature, after heat treatment at 200 °C, in vacuum

elemental analyses (CHN and chloride potentiometric analysis), were very similar, near to 1.0 mmol of pyridinium group per gram of *SiPy*.

The structure of the silica based hybrid material was confirmed by the infrared analysis shown in Fig. 3. It can be observed a typical spectrum of hybrid material, with both components, organic and inorganic moieties. The inorganic component can be identified by the typical silica overtone bands at 1980 and 1865 cm^{-1} (Maniar et al. 1990) and the silanol stretching bands at 3670 cm^{-1} (Costa et al. 1997). The organic component is clearly identified by the bands at 1635 and 1487 cm^{-1} corresponding to the pyridine ring modes (Benvenutti et al. 1992). The presence of pyridinium ion bands in the spectrum of the *SiPy* material, heat treated at 200 °C, under vacuum, is an

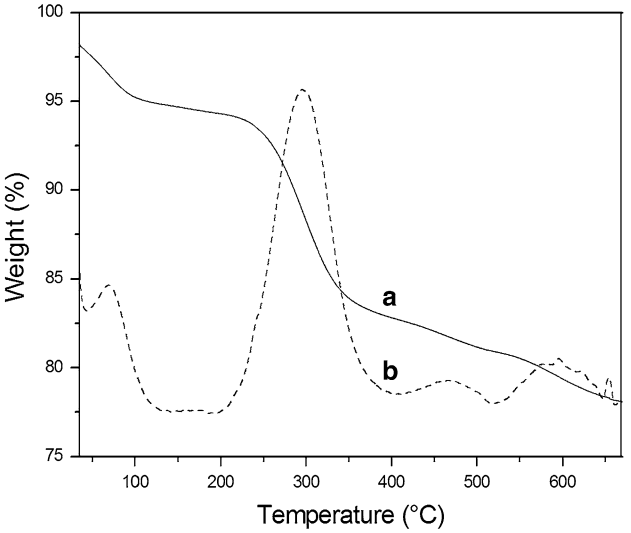

Fig. 4 Thermogravimetric analysis of *SiPy*. **a** TGA curve, **b** DTG curve

evidence of the high thermal stability of the organic group, confirming that the pyridine group is covalently bonded on the *SiPy* surface (de Menezes et al. 2012).

The *SiPy* material was also submitted to thermogravimetric analysis. The obtained TGA and DTG curves are presented in the Fig. 4. It can be observed two main events. The first, a weight loss that appears between room temperature and 100 °C, which was assigned to the water desorption. According to Arenas et al. (2003) ionic silica based hybrid materials can absorb larger amounts of water, due to the ion–dipole interactions. The second one is a major weight loss that occurs between 200 and 370 °C, and it was assigned to the organic moiety desorption or decomposition. Therefore, the *SiPy* material showed a good thermal stability up to 200 °C, in accordance to the infrared analysis.

In the Fig. 5a, it is presented the textural analysis of *SiPy*. It is possible to observe that the adsorption/desorption isotherm is type IV, typical of mesoporous material. The BET specific surface area was 155 ± 5 $m^2\ g^{-1}$ and the BJH pore volume was 0.47 ± 0.01 $cm^3\ g^{-1}$. The pore size distribution curve is shown in the Fig. 5b. It can be seen that the *SiPy* material presents a narrow pore size distribution with a maximum near to 10 nm. These characteristics are desirable and allow the use of *SiPy* as adsorbent material.

3.2 Acid compounds recovery from standard mixture

The results obtained by eluation of the standard acid mixture using *SiPy* as stationary phase are shown in the Fig. 6.

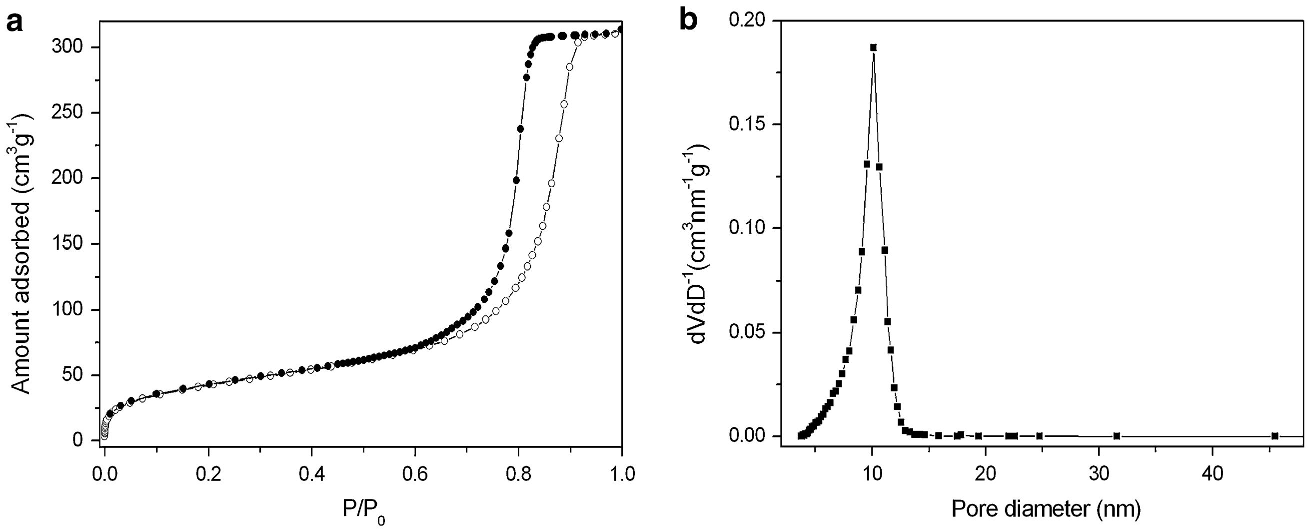

Fig. 5 Textural analysis of *SiPy*: **a** adsorption/desorption isotherm and; **b** BJH pore size distribution

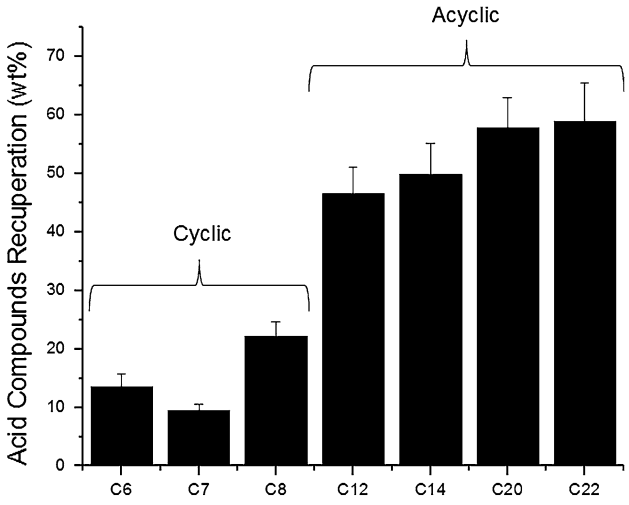

Fig. 6 Percentage of the acid compounds recovery from the standard mixture

As seen in the Fig. 6, the acyclic acid recovery was better than the cyclic acid in mass base (wt%). This result was expected because the cyclic acid has more interaction with the stationary phase due to its lower pKa compared with the acyclic acids (de Conto et al. 2012). According to Leenheer et al. (1995) cyclic acids have lower pKa when compared with acyclic acids with the same number of carbons, so the adsorption of the cyclic acid in the ionic exchange stationary phase has higher interaction force than the acyclic acid. This fact decreases the cyclic acid recovery. Within cyclic acids the pKa decreases with the ring size, i.e. the cyclichexanecarboxylic acid (C_7) have pKa value lower than cyclicpentanecarboxylic acid (C_6). This fact explains the lower recuperation of the C_7, due to its higher interaction with the stationary phase, hindering the recuperation of this acid (Bhat et al. 1978). Furthermore, the presence of electron-donor groups, as–CH_3, decreases the acidity of cyclic acids, so C_8 has the pKa value higher than C_6 and C_7 acids and presents lower interaction with the stationary phase, which increases its recuperation from stationary phase.

The acyclic acids recovery was close to 50 % for acid compounds that contain carbon chains of C_{12}, C_{14} and close to 60 % for acid compounds C_{20} and C_{22}. In the work of Jones et al. 2001 it was shown an acid compounds recovery of 98 ± 10 % for C_{14} and 81 ± 12 % for C_{22}, using SPE technique and SAX (commercial phase) as stationary phase. One can verify that the percentage of the acids recovery in Jones's work was higher than the one obtained in the present work. However, it is important to emphasize that, in the present work, only 0.5 g of stationary phase and 20 mL of solvent were used, while in that work, it was used used 10 g and 55 mL, respectively. Therefore, the *SiPy* material showed efficiency in the acid compounds recovery.

In previous report, de Conto et al. (2012) used three different stationary phases (SAX, NH_2 and Dab-Al_2O_3) for acid compounds recovery, using the same amount of solid phase and solvent of the present work. Comparing with that report, the acid recovery was higher in the present work, almost twice as much for C_6, C_7, C_8. This fact should be emphasized, because the cyclic naphthenic acids recovery is a challenge in the field of analytical chemistry due to the strong adsorption on the stationary phase and consequently, making difficult the elution of these compounds.

Regarding the acyclic acids, the percentage of recovery in the present work was similar to the results found by de Conto et al. (2012). However, it is important to emphasize

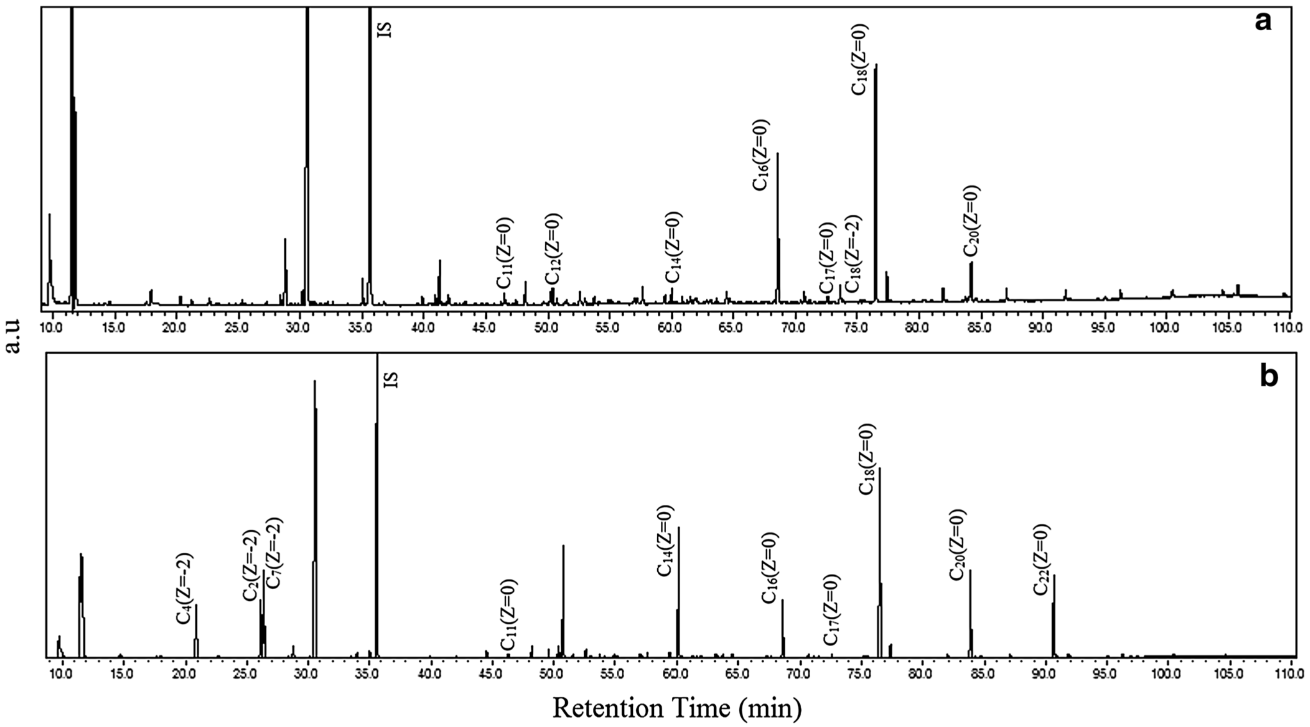

Fig. 7 Chromatograms obtained by GC/MS of petroleum resins samples: **a** RF and; **b** RF spiked with standard mixture of acid compounds, eluted by *SiPy* stationary phase

that the surface area of *SiPy* material used here, is lower than the surface area of SAX, NH_2 and Dab-Al_2O_3 solid phases.

3.3 Acid compounds recovery from petroleum

The extraction of acid compounds in the petroleum matrix was performed by SPE, using the resins fraction (RF) obtained from the pre-fractionation (SARA). The extraction of acid compounds was performed with pure RF and RF spiked with a mixture of standard acids, so that the matrix effect could be evaluated. Figure 7 shows the chromatograms obtained by GC/MS analysis of the extracts from both samples, RF and RF spiked, using the stationary phase *SiPy*.

The chromatogram of Fig. 7a shows that it was possible to extract seven acyclic acids (C_{11} to C_{18}, except the C_{15}) and only one monocyclic acid (C_{18}) by SPE process and using *SiPy* as stationary phase. In the Fig. 7b, it can be observed that the standard acids added in the sample were identified.

The recovery of the standard acids added in the petroleum sample was 25–48 % for the cyclic acids, and 55–83 % for the acyclic acids. These results show that the other compounds present in the petroleum matrix do not influence the recovery of acidic compounds in this fraction of petroleum.

4 Conclusion

The silica based hybrid material, *SiPy*, which contains the ionic pyridinium group, was successfully synthesized. The organic moiety is very thermally stable, at least to heat treatment at 200 °C. The *SiPy* material can be classified as mesoporous adsorbent that allows its use as stationary phase for acidic compounds recovery from petroleum resins fraction. The use of *SiPy* as stationary phase, to recover cyclic and acyclic acid compounds, showed satisfactory results, regarding their identification and quantification, in the standard mixture, as well as, in the resin fraction from petroleum. This result is promising because the recovery of cyclic acid, mainly those with short chain and high polarity, from complex matrixes is a challenge to the analytical chemistry.

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References

Arenas, L.T., Langaro, A., Gushikem, Y., Moro, C.C., Benvenutti, E.V., Costa, T.M.H.: 3-n-Propyl-1-azonia-4-azabicyclo[2.2.2] octanechloride Silsesquioxane: A New Water Soluble Polymer. J. Sol–gel Sci. Technol. **28**, 51–56 (2003)

Benvenutti, E.V., Gushikem, Y., Davanzo, C.U., de Castro, S.C., Torriani, I.L.: Antimony(v) Oxide grafted onto a Silica Gel Surface: Acidic Properties and Thermal Stability. J. Chem. Soc. Faraday Trans. **88**, 3193–3196 (1992)

Bhat, S.N., Rao, R., Ranganayakulu, K.: pKa values of protonated α,β-unsaturated cyclic carboxylic acids. Effect of ring size on acidities. Can. J. Chem. **56**, 2003–2007 (1978)

Borgund, A.E., Erstad, K., Barth, T.: Fractionation of Crude Oil Acids by HPLC and Characterization of Their Properties and Effects on Gas Hydrate Surfaces. Energy Fuels **21**, 2816–2826 (2007)

Campos, M.C.V., Oliveira, E.C., Filho, P.J.S., Piatnicki, C.M.S., Caramão, E.B.: Analysis of tert-butyldimethylsilyl derivatives in heavy gas oil from brazilian naphthenic acids by gas chromatography coupled to mass spectrometry with electron impact ionization. J. Chromatogr. A **1105**, 95–105 (2006)

Clemente, J.S., Fedorak, P.M.: A review of the occurrence, analyses, toxicity, and biodegradation of naphthenic acids. Chemosphere **60**, 585–600 (2005)

Clemente, J.S., Fedorak, P.M.: Evaluation of the analyses of tert-butyldimethylsilyl derivatives of naphthenic acids by gas chromatography – electron impact mass spectrometry. J. Chromatogr. A **1047**, 117–128 (2004)

Costa, T.M.H., Gallas, M.R., Benvenutti, E.V., Jornada, J.A.H.: Infrared and thermogravimetric study of high pressure consolidation in alkoxide silica gel powders. J. Non-Cryst. Solids **220**, 195–201 (1997)

Damasceno, F.C., Gruber, L.D.A., Geller, A.M., de Campos, M.C.V., Gomes, A.O., Regina, C.L., Guimarães, R.C.L., Péres, V.F., Jacques, R.A., Caramão, E.B.: Characterization of naphthenic acids using mass spectroscopy and chromatographic techniques: study of technical mixtures. Anal. Methods **6**, 807–816 (2014)

de Conto, J.F., Nascimento, J.S., de Souza, D.M.B., Costa, L.P., Egues, S.M.S., Freitas, L.S., Benvenutti, E.V.: Solid phase extraction of petroleum carboxylic acids using a functionalized alumina as stationary phase. J. Sep. Sci. **35**, 1044–1049 (2012)

de Menezes, E.W., Lima, E.C., Royer, B., De Souza, F.E., Dos Santos, B.D., Gregório, J.R., Costa, T.M.H., Gushikem, Y., Benvenutti, E.V.: Ionic silica based hybrid material containing the pyridinium group used as an adsorbent for textile dye. J. Colloid Interface Sci. **378**, 10–20 (2012)

Gregg, S.J., Sing, K.S.W.: Adsorption, surface area and porosity. Academic Press, London (1982)

Gruber, L.D.A., Damasceno, F.C., Caramão, E.B., Jacques, R.A., Geller, A.M., Campos, M.C.V.: Ácidos Naftênicos no Petróleo. Quim. Nova **35**, 1423–1433 (2012)

Gushikem, Y., Benvenutti, E.V., Kholin, Y.V.: Synthesis and applications of functionalized silsesquioxane polymers attached to organic and inorganic matrices. Pure Appl. Chem. **80**, 1593–1611 (2008)

Jones, D.M., Watson, J.S., Meredith, W., Chen, M., Bennett, B.: Determination of Naphthenic Acids in Crude Oils Using Nonaqueous Ion Exchange Solid-Phase Extraction. Anal. Chem. **73**(3), 703–707 (2001)

Kharrat, A.M., Zacharia, J., Cherian, V.J., Anyatonwu, A.: Issues with Comparing SARA Methodologies. Energy Fuels **21**, 3618–3621 (2007)

Leenheer, J.A., Wershaw, L.R., Reddy, M.M.: Strong-acid, carboxyl group structures in fulvic-acid from the Suwannee River, Georgia. Major Structures. Environ. Sci. Technol. **29**, 399–405 (1995)

Maniar, P.D., Navrotsky, A., Rabinovich, E.M., Ying, J.Y., Benziger, J.B.: Energetics and structure of sol-gel silicas. J. Non-Cryst. Solids **124**, 101–111 (1990)

Nielsen, K.E., Dittmer, J., Malmendal, A., Nielsen, N.C.: Quantitative Analysis of Constituents in Heavy Fuel Oil by 1H Nuclear Magnetic Resonance (NMR) Spectroscopy and Multivariate Data Analysis. Energy Fuels **22**, 4070–4076 (2008)

Pavan, F.A., Gobbi, S.A., Costa, T.M.H., Benvenutti, E.V.: FTIR thermal analysis on anilinepropylsilica xerogel. J. Therm. Anal. Calorim. **68**, 199–206 (2002)

Purcell, J.M., Juyal, P., Kim, D.G., Rodgers, R.P., Hendrickson, C.L., Marshall, A.G.: Sulfur speciation in petroleum: atmospheric pressure photoionization or chemical derivatization and electrospray ionization fourier transform ion cyclotron resonance mass spectrometry. Energy Fuels **21**, 2869–2874 (2007)

Thomas, J.E.A.P., Triggia, A.A., Correia, C.A., Verotti, C., Xavier, J.A.D., Machado, J.A.D., Souza, J.E.S., Paula, J.L., Rossi, N.C.M., Pitombo, N.E.S., Gouvêa, P.C.V.M., Carvalho, R.S., Barragan, R.V.: Fundamentos de Engenharia de Petróleo. Interciência, Rio de Janeiro (2004)

Wu, X., Jing, H., Zheng, Y., Yao, Z., Ke, W.: Erosion–corrosion of various oil-refining materials in naphthenic acid. Wear **256**, 133–144 (2004)