



REMOVAL OF NAPHTENIC ACIDITY OF JET FUEL BY ADSORPTION WITH MCM-41 MOLECULAR SIEVE

Genilson A. da Silva¹, Antônio S. Araújo², Monica S. A. Abreu³, Cesar A. M. de Abreu³,
Celmy M. B. M. Barbosa³

¹ Petroleo Brasileiro SA, Petrobras, SP, Brazil

² Department of Chemistry, Federal University of Rio Grande do Norte, RN, Brazil

³ Department of Chemical Engineering, Federal University of Pernambuco, PE, Brazil

Email: celmy@ufpe.br(Celmy M. B. M. Barbosa), genilson_antonio@hotmail.com(Genilson A. da Silva), asa-ufn@usa.net(Antônio S. Araújo), cesar@ufpe.br(Cesar A. M. de Abreu)

Abstract

The removal of naphthenic acid was carried out with mesoporous molecular sieves, types MCM-41 and MgMCM-41. These materials were synthesized and characterized, and employed as adsorbents for the removal of n-dodecanoic acid from a jet fuel model solution with n-dodecane. Different concentrations of n-dodecanoic acid in the initial solutions showed different equilibrium concentrations, highlighting data that were represented by isotherms of type IV BET. The capacity of the molecular sieve for n-dodecanoic acid adsorption was improved, circa 130 %, when magnesium was incorporated in the structure. The maximum adsorption capacities reached values of 0.62 g/g for MCM-41 and 1.48 g/g for MgMCM-41. In adsorption experiments, at 300 K, n-dodecanoic acid removals of 28.02 % and 42.67 % were obtained with MCM-41 and MgMCM-41, respectively.

Keywords: MCM-41 molecular sieve, mesoporous, adsorption, jet fuel, naphthenic acid removal.

INTRODUCTION

Naphthenic acids are contaminants present in heavy oils, identified with the emulsification of water and oil in refineries, and corrosion effects [15, 8]. Classified as carboxylic acids, these acids have saturated ring structures with a single carboxyl group [5, 14]. They occur as natural constituents of bitumen, and are present in oil and in some of its distilled fractions. The naphthenic acid corrosion occurs mostly in units of atmospheric and vacuum distillation, and to a lesser extent in catalytic and thermal cracking operations [3]. In refineries the naphthenic corrosion rate is influenced by type of acid, sulfur content, high temperatures and fluid flows [4, 16]. The jet fuel, obtained in intermediate cuts from oil atmospheric distillation contains naphthenic acids. Possible solutions to the problem of naphthenic acidity include the treatment of heavy oil prior to refining by thermal processes, catalytic hydrotreating of petroleum fractions, or the neutralization of desalted oil, where a gas stream of ammonia, produces low acidity oils. These ways of mitigating naphthenic corrosion, however, can cause problems of an operational and economic order, motivating the search for new solutions.

The separation of naphthenic acids by adsorption may be applied to dilute solutions of hydrocarbons, in the case of jet fuel. The adsorption allows separation and recovery of naphthenic acids, and additionally can improve the economic viability of the process through potential uses (i.e., additives, stabilizer, and ester production, [11]). For the purpose of adsorption use, attention must be paid to the choice of adsorbent. Some types of adsorbents such as zeolites, aluminosilicates, molecular sieves and silica gel [9, 15] are best, due to their characteristics of adsorption affinity with acids.

Mesoporous materials have characteristics that promote a series of surface interactions with organic solutes coming from the petrochemical and oil refining. The mesoporous molecular sieve MCM-41 (Mobil Composition of Mater, 1992) has been indicated for various applications in the petrochemical industry, particularly in the processing of heavy residues [6]. The sieve's system of ordered pores, and adjustable size, between 15-100 Å, and its high surface area indicate its potential for the mentioned removals.

The MCM materials are combined according to the modular structure of MCM-41 systems (channels), MCM-48 (pores) and MCM-50 (interlamellar space) and may cover a wide range

of mesoporosity [10]. The synthesis of MCM-41 type materials usually employs a solvent, a molecule surfactant as a structural director and a silica source. The incorporation or impregnation of other elements may improve the adsorptive and catalytic properties of the material [12,7]. Souza et al. (2006) studied the acidic properties of Al-MCM-41 (Bronsted acid sites) obtained by the incorporation of aluminum atoms. Molecular sieves and similar materials have been used as adsorbents with relative success. Wang et al. (2008) studied the desulfurization of jet fuel via adsorption using MCM-41 and SBA-15 as support for metal halide.

In this study, the formulation of the MCM-41 and MgMCM-4 materials via synthesis with magnesium acetate and silica gel was performed. Characterizations were made in terms of their morphological and textural properties, and chemical and physical characteristics. The materials were evaluated for efficacy in the removal of the jet fuel acidity. The adsorption performances for the removal of naphthenic acid were quantified through adsorption kinetics, and equilibrium. The influence of magnesium incorporation into the MCM-41 adsorbent, due to creation of surface basic sites, was observed by increasing the adsorptive capacity of the material.

EXPERIMENTAL

Formulation of the adsorbents

The adsorbents MCM-41 and MgMCM-41 were synthesized by a hydrothermal method using silica gel (Merck, 95.5% weight), sodium silicate (Riedel Haeh, 63.0 % wt. of SiO₂ and 18% wt. of Na₂O), magnesium acetate (C₄H₆MgO₄.4H₂O, 98.0% wt., Vetec), and cetyltrimethylammonium bromide (CTMABr, 98% wt., Vetec). During the synthesis, the reagents were mixed in stoichiometrical proportions: 1.0 CTMABr: 4.0 SiO₂: 1.0 NO₂: xMgO: 200.0 H₂O to obtain gels with Si/Mg ratios equal to 20 and 34, for MCM-41 and MgMCM-41, respectively. For the production of the gels, silica was added to the sodium silicate and stirred for 2 hours at 60 °C. Then, an aqueous solution of CTMABr, operating as the structural driver, was added, and stirring continued for 1 hour at 300 K. The pH of the mixture was adjusted (9.5 - 10.0) every 24 hours with a solution of acetic acid (30 % wt.). The solution was washed with distilled water and then with hydrochloric acid (2 %wt.) in ethanol to remove residual surfactant. Finally, the resulting solids of the crystallization process were dried at 373 K for 6 hours. These materials were calcined in a nitrogen atmosphere (5 cm³/min, 300 K - 773 K, 5

K/min) to remove the structural driver. The inert atmosphere was maintained for 1 hour, at 773 K, then the nitrogen flow was exchanged for synthetic air (100 cm³/min, 1 hr).

The materials were characterized by atomic absorption spectrophotometry (AAS, Varian Model AA220FS), scanning electron microscopy (SEM, JEOL JSM 6360 LV model), energy dispersive spectroscopy and microscopy scanning electron (SEM-EDS), XRD (Siemens D5000 Digital, CuK, 40kV, 40mA) and textural analysis (BET, Micromeritics Model ASAP 2010).

XRD data allow to estimate structural characteristics of adsorbents (hexagonal lattice parameter, a_0 ; thickness of the wall of the channels, W_t) by applying the correlations as: $W_t = a_0 - D_p$; $a_0 = 2d_{100}/\sqrt{3}$, $d_{100} = n\lambda / 2\sin\theta$ (Bragg's law), where D_p is the average pore diameter (BJH method, BET-N₂).

Equilibrium and kinetics of adsorption

Adsorption equilibrium measurements were performed at 300 K by taking samples (0.30 mL) in solutions of n-dodecanoic acid in dodecane (mass of adsorbent/solution volume ratio = 0.01) after contact with the adsorbents (MCM-41, MgMCM-41). The n-dodecanoic acid solutions in dodecane were prepared at concentrations of 0%, 0.3%, 0.6%, 0.9%, 1.2%, 1.5%, 1.8%, 2.1%, 2.4%, 2.7%, 3.0%, 5.0% and 7.0%, by weight. The samples were taken from each solution after 8 hours of contact, time, considered to reach equilibrium. The evolution of the adsorption process, from initial liquid-solid contact to equilibrium (0 – 930 min), was evaluated by adsorption kinetics experiments.

Residual contents of n-dodecanoic acid in dodecane solutions were quantified by gas chromatography using a GC chromatograph Master (GC Inst. Cient., Br), with a CG745 Carbowax column (30 m x 0.53 mm x 1 μ m) and a FID detector.

RESULTS AND DISCUSSION

Synthesis and characterization of adsorbents

The preparation procedure of the adsorbents was evaluated by thermal analysis (TG, DTG), where mass losses were observed resulting from the following events: desorption of water (303 – 393 K), decomposition of the surfactant (393 – 633 K), and condensation of silanol groups (633 – 843 K). A greater loss of organic material was observed in MgMCM-41,

possibly due to the magnesium acetate removal, occurring together with the structural driver (CTAMBr).

Samples of the materials (precursors) taken before and after calcination were analyzed by infrared spectroscopy (FTIR). Spectra are shown in Figure 1.

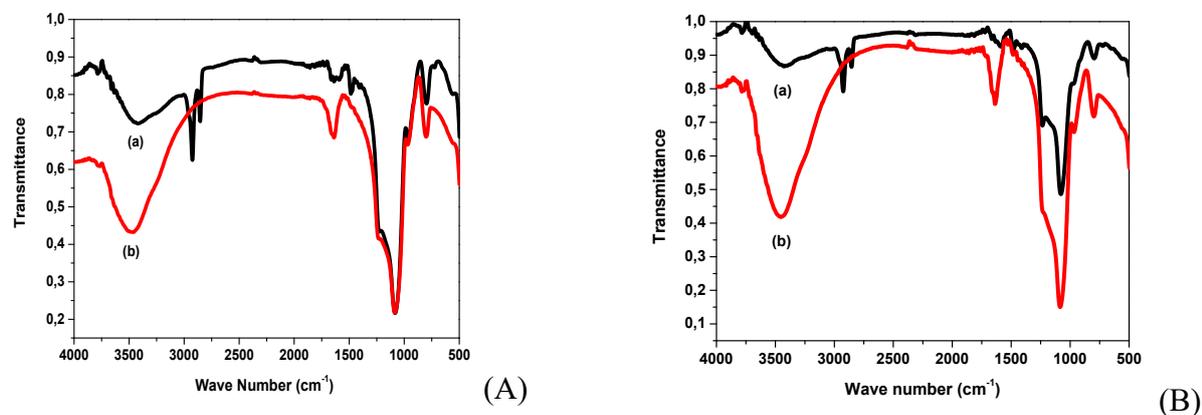


Figure 1. FTIR spectra of the adsorbent materials. (A) MCM-41: before calcination (a), after calcination (b); (B) MgMCM-41: before calcination (a), after calcination (b).

The spectra show a broad absorption band at 3400 cm⁻¹ corresponding to the stretching of the OH water bond. Groups of the structural driver agent appear in the region of the 2921 and 2851 cm⁻¹ bands, due to CH stretching of the CH₂ and CH₃. In the range 1400 - 700 cm⁻¹, there is a band due to fundamental vibrations of the network, in accordance with literature data [13]. After calcination at 773 K, the bands due to the driver agent disappear, indicating that the calcination process was effective in removing this compound.

An EDX analysis indicated the presence of silicon with higher intensity and the presence of oxygen and sodium, characteristic constituents of mesoporous materials MCM-41. In the adsorbent MgMCM-41 magnesium (SAA analysis) was found with an additional content of 0.64% by weight. In this material, the Si/Mg ratio, formulated in the synthesis as 20 and reaching a value of 17.55, showed a sufficient incorporation of magnesium.

Figure 2 shows the XRD patterns of the adsorbent MgMCM-41 uncalcined and calcined and the XRD pattern of the calcined MCM-41 obtained by Beck et al. (1992). The synthesized material showed an XRD pattern consistent with that reported in the literature for mesoporous materials of the type MCM-41 [2].

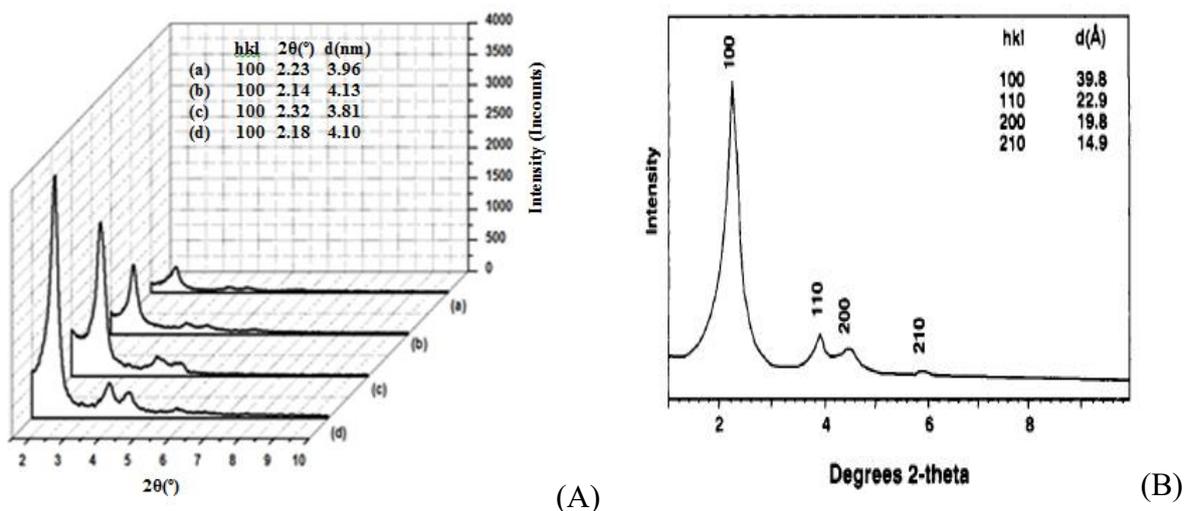


Figure 2. XRD analysis of the adsorbents. (A) MgMCM-41 non-calcined (a), MCM-41 non-calcined (b), MCM-41 calcined (c), MgMCM-41 calcined (d); (B) MCM-41 standard XRD (Beck et al., 1992).

The characteristic peaks of the MCM-41 materials were observed at low angles: $2\theta = 1.0 - 8.0^\circ$, and were well arranged in crystallographic planes (100), (110), (200) and (210). Comparing the XRD patterns of the materials prepared (Figure 2A (c) and (d)) with the pattern found in the literature (Figure 2B) planes and characteristic peaks were observed, meaning that the incorporation of magnesium and the calcination process did not affect the structure of the material. It was also observed that the diffraction pattern of the sample modified with magnesium (Figure 2A (a) and (d)) was similar to the pattern of the MCM-41 [2]. In the XRD patterns of the calcined sample higher peak intensities (100) were found, suggesting an improvement in their level of organization.

The values of the structure parameters (a_0 , D_p , W_t) are considered as indicators of the adsorbent formulation process. Their orders of magnitude have been estimated based on XRD analysis (Table 1).

Table 1. Structural characteristics of adsorbents.

Adsorbent	a_0 (nm)	D_p (nm)	W_t (nm)
MCM-41	4.76	3.61	1.15
MCM-41 (calcined)	4.40	3.63	0.94
MgMCM-41	4.57	3.70	0.70
MgMCM-41 (calcined)	4.73	3.95	0.78

XRD analysis shows peaks at $2\theta = 2.14^\circ$ for MCM-41 and $2\theta = 2.23^\circ$ for MgMCM-41, providing a_0 values of 4.76 nm and 4.57 nm for MCM-41 and MgMCM-41 non-calcined, respectively. As a result, it was found that for the material after calcination with magnesium had a lattice contraction, as revealed by the decrease of the a_0 values. This occurred with a decrease in structural organization, indicated by a reduction in peak intensity (100). After calcination, the MCM-41 showed $a_0 = 4.40$ nm, less than $a_0 = 4.76$ nm of the initial material. Removal of CTMABr driver promoted contraction of the crystal lattice, while maintaining the wall thickness of the material. With MgMCM-41 system expansion and growth of the pore diameter and wall thickness occurred.

The tubular typical morphology of these materials was verified by micrographs (SEM), where fused particles were identified, some interconnected in the form of tubes and plates. Cheng et al. (1995) proposed a mechanism describing the formation of these structures in the form of imperfect and irregular hexagonal plates.

Textural analysis of the materials by nitrogen adsorption isotherms (Figure 3) were made, allowing their IUPAC classification as type IV, characteristic of mesoporous materials. In the measurements evolutions were observed depending on the gas pressure, identified with the monolayer adsorption and capillary condensation inside the mesopores, and multilayer adsorption on the outer surface of the material.

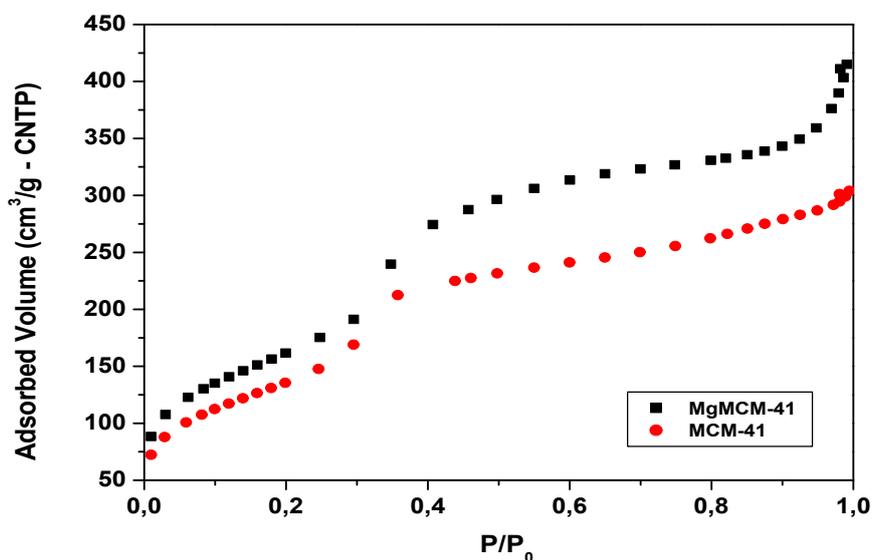


Figure 3. Nitrogen adsorption equilibrium isotherms. Conditions: adsorbents, MCM-41, MgMCM-41.

The textural characteristics of MgMCM-41 and MCM-41 were quantified in terms of the superficial area and mesopore volumes of $497.41 \text{ m}^2\text{g}^{-1}$, $0.52 \text{ cm}^3\text{g}^{-1}$ and $589.45 \text{ m}^2\text{g}^{-1}$, $0.69 \text{ cm}^3\text{g}^{-1}$, respectively. The superficial area of MgMCM-41 was shown to be compatible with the analysis result of XRD, which showed a more intense characteristic peak (100), indicating a higher level of organization than that of MCM-41. A comparison reveals that the isotherms MgMCM-41 adsorbed a greater volume of N_2 .

Kinetics and adsorption equilibrium

The reduction of naphthenic acid (AC) in the mixture n-dodecanoic acid/dodecane (Figure 4) occurred at an adsorption equilibrium time of approximately 180 min and 240 min with MgMCM and MCM-41, respectively. In these cases, there were acidity reductions of 28.02% and 42.67%, respectively, meaning adsorption capacities $0.62 \text{ g}_{\text{AC}}/\text{g}$ and $0.97 \text{ g}_{\text{AC}}/\text{g}$. The longest time to reach adsorption equilibrium with MgMCM-41 was consistent with higher adsorption capacity observed, approximately 56% higher. In fact, the adsorbent with magnesium content added basic characteristics to MCM-41 material, while their textural properties (S_p , V_{mp}) were orders of a higher magnitude. These aspects allowed an expansion of its capacity to reduce the naphthenic acidity of the solution more effectively.

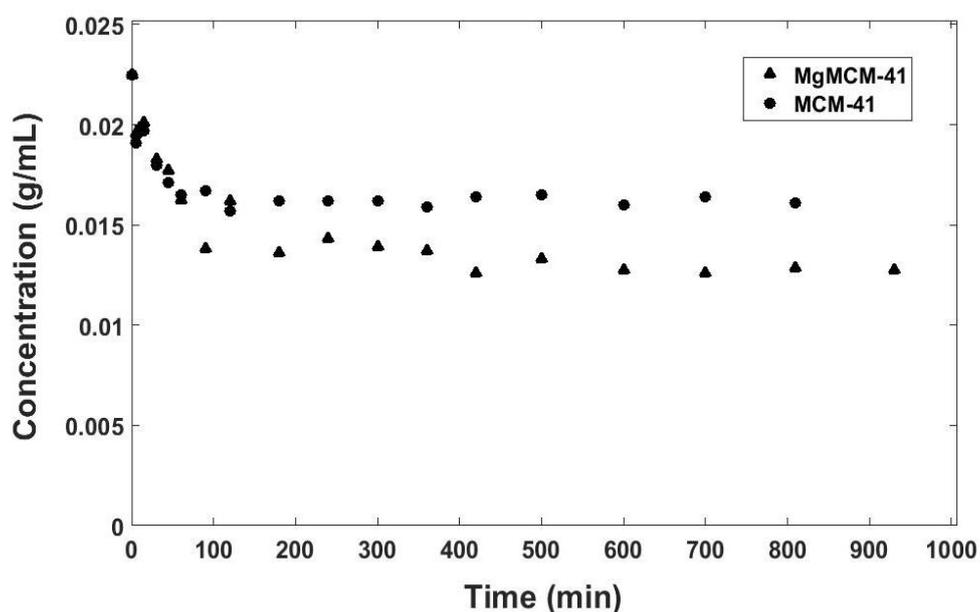


Figure 4. Kinetics of naphthenic acidity removal by adsorption. Conditions: C_0 (acid n-dodecanoico) = 3.0% wt., n-dodecanoic acid/dodecane solution 0.05 L, $m_{\text{ads}} = 0.50 \text{ g}$, 300 K.

Experiments carried out with n-dodecanoic acid solutions in dodecane at different initial concentrations (0.0, 0.3, 0.6, 0.9, 1.2, 1.5, 1.8, 2.1, 2.4, 2.7, 3.0, 5.0, 7.0 % wt.) provided equilibrium concentrations for the adsorption isotherms. Experimental evidence revealed by the isotherms of n-dodecanoic acid with the MCM-41 adsorbents indicated possibilities of their representation by BET isotherms of types IV or V. Thus, for the equilibrium model formulation the following assumptions were adopted:

- adsorption occurs between the layers of adsorbate molecules, with the maximum number of layers being $2n-1$, including the contact layer with the adsorbent;
- adsorption interactions are the Langmuir type for each layer.

To describe the adsorption equilibrium between the n-dodecanoic (Ac) acid and the MCM-41 adsorbents, the BET isotherm of type IV expressed by Equation 1 was employed.

$$q_{Ac} = \frac{q_{Acs} b C_{Ac}}{C_{Acs}} \frac{(ng/2 - n)(C/C_{Acs})^{n-1} - (ng - n + 1)(C/C_{Acs})^n + (ng/2)(C/C_{Acs})^{n+1}}{1 + (b-1)(C/C_{Acs}) + (bg/2 - b)(C/C_{Acs})^n - (bg/2)(C/C_{Acs})^{n+1}} \quad (1)$$

where q_{Acs} is the maximum adsorption capacity at monolayer of the adsorbents for the n-dodecanoic acid, and C_{Acs} is the corresponding acid concentration in the liquid phase. b is the interaction parameter between the adsorbate and the surface of the adsorbent, and g is the ratio between the kinetic constants of adsorption and desorption in each layer, expressed by $g = \exp(Q/RT)$, where Q is the extra energy related to the desorption of the adsorbate.

In the Figure 5, the results of equilibrium adsorption of n-dodecanedioic acid with the MCM-41 materials are represented by BET isotherms of type IV (Equation 1). These isotherms are characteristic of mesoporous material in which the pore diameters are larger than the diameter of the adsorbate (9).

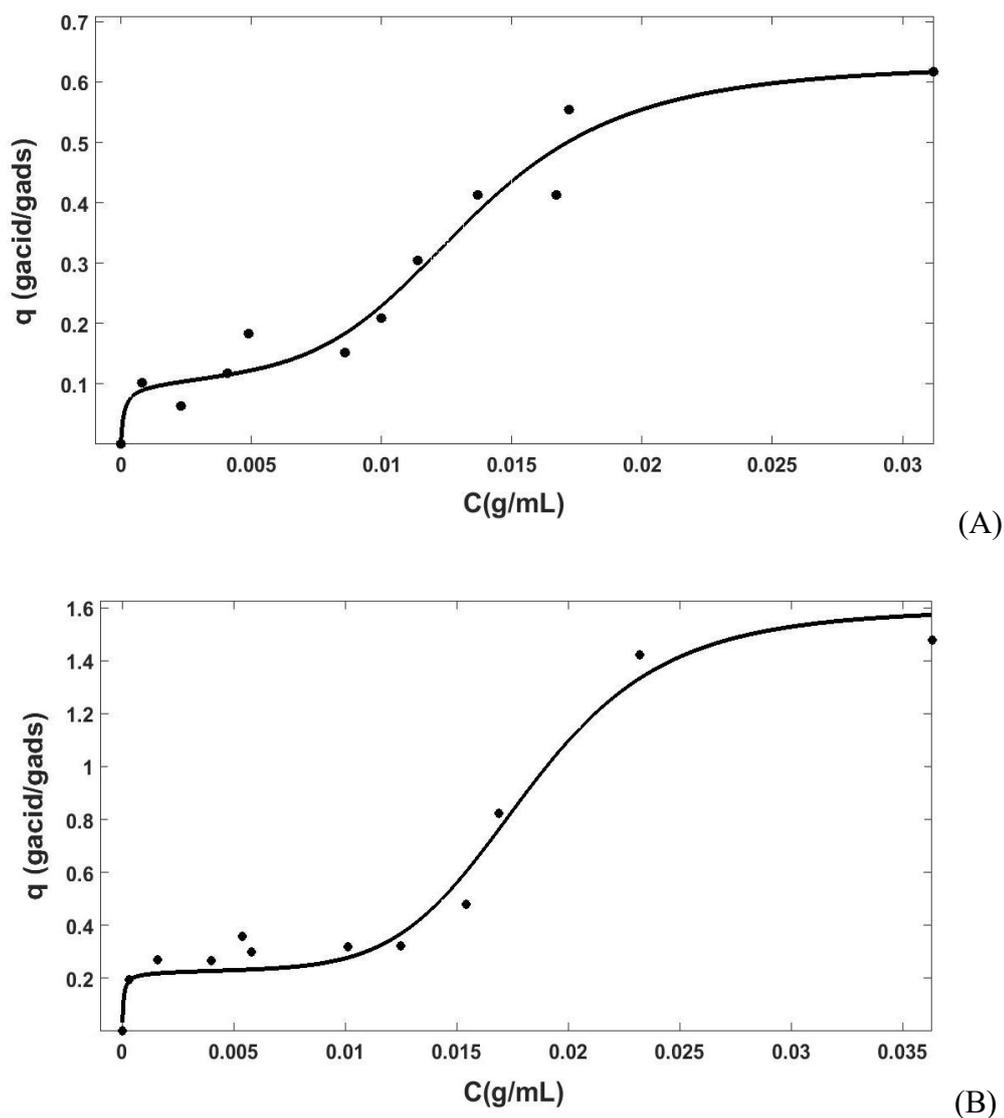


Figure 5. Isotherms of adsorption equilibrium of n-dodecanoic acid. Conditions: n-dodecanoic acid/dodecane solution, 0.05 L, $m_{ads} = 0.50$ g, 300 K. Adsorbents (A) MCM-41, (B) MgMCM-41.

In Table 2 are listed values of the equilibrium parameters, obtained by adjusting the isotherms of n-dodecanoic acid obtained with each of the adsorbent materials.

Table 2. Equilibrium model parameters (BET isothermal type IV). Conditions: n-dodecanoic acid/dodecane solution, 0.05 L, $m_{ads} = 0.50$ g, 300 K.

Adsorbent	q_{Acs} (g_{Ac}/g_{ads})	b	n	g
MCM-41	9.81×10^{-2}	22.53	6.44	0.98×10^2
MgMCM-41	2.23×10^{-1}	2.22	7.15	2.86×10^5

Correlation levels of the data adjustments for both adsorbents, obtained experimentally and estimated via the model are in the domain of -10% to + 10%. The MCM-41 presented a monolayer adsorption capacity of about ten times that of MCM-41, indicating greater ability to remove the n-dodecanoic acid by direct contact between the acid and the adsorbent. The maximum adsorption capacities (q_{Ac_s}), calculated from the highest levels of removal of the acid in the liquid phase (MCM-41, 28.02%; MgMCM-41, 42.67%), were 0.62 g_{Ac}/g_{ads} and 1.48 g_{Ac}/g_{ads}, respectively. These values were considerably higher than those obtained in monolayer adsorption, especially for MgMCM-41 adsorbent, indicating adsorption in multiple layers.

The parameter b ($b > 1$; BET isotherm type IV), which quantifies the affinity of the adsorbent by the acid in monolayer was about ten times higher for MgMCM-41 compared to MCM-41. This is consistent with the results found for the monolayer adsorption capacities (q_{Ac_s}).

The increase in adsorptive capacity of MgMCM-41, with improving in the removal of acidity due to the n-dodecanoic acid, may be associated with modifications on the surface of the mesoporous material, related to its basic characteristics.

From the values of the thermodynamic parameter g , the Q values were estimated with the orders of magnitude of 11.5 kJ/mol and 31.5 kJ/mol for MCM-41 and MgMCM-41, respectively. For MgMCM-41 the extra energy involved in the interaction acid-adsorbent was estimated to be three times that obtained with the MCM-41 adsorbent.

CONCLUSIONS

Molecular sieve adsorbents (MCM-41) were synthesized and assessed for removal of naphthenic acids by adsorption of n-dodecanoic acid in a dodecane solution. The solid showed predominant formation of mesopores with structural organization and morphology typical. Magnesium was incorporated into the matrix with the structural ordering in hexagonal phase being maintained in the adsorbent MgMCM-41 (Si/Mg \approx 20).

Adsorption equilibrium isotherms of n-dodecanoic acid showed behaviors of BET isotherms of type IV, favorable for the removal of the naphthenic acid from n-dodecanoic solutions. The BET model was fitted to the experimental data of adsorption isotherms at 300 K providing orders of magnitude of the equilibrium parameters. The values of monolayer adsorption capacities were 9.81×10^{-2} g of acid/g and 2.23×10^{-1} g of acid/g, while the adsorption

maximum capacities were 0.62 g of acid/g, and 1.48 g of acid/g for MCM-41 and MgMCM-41, respectively. The removal of naphthenic acid with MgMCM-41 adsorbent was about 1.5 higher than that obtained with MCM-41.

ACKNOWLEDGEMENTS

The authors acknowledge financial support from MCT/ANP (PRH-28) and PETROBRAS.

The English text of this paper has been revised by Sidney Pratt, Canadian, MAT (The Johns Hopkins University), RSAdip - TESL (Cambridge University).

REFERENCES

- [1] Beck, J.S., Vartuli, J.C., Roth, W.J., Leonowicz, M.E., Kresge, C.T., Schmitt, K. D., Chu, C. T. W., Olson, D. H., Sheppard, E. W., Mccullen, S. B., Higgins, Y. B., Schelenker, I. L., *Journal of American Chemical Society*, v.114, p.10834-10843, 1992.
- [2] Cheng, C. F.; He, H.; Zhou, W.; Klinowski, J., *Crystal Morphology Supports the Liquid-Crystal Formation Mechanism for the Mesoporous Molecular-Sieve MCM-41*, *Chem. Phys. Lett.*, v. 244, p. 117, 1995.
- [3] Cristina, F.; Galasso, L.; Montanari, L., Gennaro, M. E. *Evolution of naphthenic acids during the corrosion process*. *Energy & Fuels*, v.28(3), p.1701-1708, 2013.
- [4] DO, D. D. *Adsorption Analysis: Equilibria and Kinetics*, London, Imperial College Press, v.2, 1998.
- [5] Gruber, L. D. A., Damasceno, F. C., Camarão, E. B., Jacques, R. A., Geller, A. M., Campos, M. C. V. Ácidos naftênicos no petróleo. *Química Nova*, v.35(7), p. 1423-1433, 2012.
- [6] Huang, T.; WangLiang, L.; QingFen, L.; LiLi, G.; JiaQing, S.; JianMin, X.; HuiZhou, L., *Adsorptive desulfurization of diesel with mesoporous aluminosilicates*, v.52(3), p. 276-281, 2009.
- [7] Jung, H., Jeon, S., Jo, D.H., Huh, J. and Kim, S.H. *Effect of crosslinking on the CO₂ adsorption of polyethyleneimine-impregnated sorbents*. *Chemical Engineering Journal*, 307, pp.836-844, 2017.
- [8] Shah, S. N.; Mutalib, M. I. A.; Pilus, R. B. M.; Lethesh, K. C. *Separation of naphthenic acid using hydroxide based ionic liquids*. *Appl. Mech. Mater.*, 625, 570–573, 2014.

- [9] Shi Q, Zhao S, Xu Z, Chung KH, Zhang Y, Xu C, *Distribution of acids and neutral nitrogen compounds in a Chinese crude oil and its fractions: Characterized by negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. Energ Fuel*, v.24(7), p. 4005–4011, 2010.
- [10] Slavcheva, E. F.; Shone, B.; Turnbull, A. *Review of naphthenic acid corrosion in oil refining. British Corrosion Journal*, v.34, n.2, p.125-131, 1999.
- [11] Souza, M.J.B., Araújo, A.S., Pedrosa, A.M.G., Marinkovic, B.A., Jardim, P.M., Morgado JR., E., *Textural features of highly ordered Al-MCM-41 molecular sieve studied by X-ray diffraction, nitrogen adsorption and transmission electron microscopy, Materials Letters*, v.60, p.2682-2685, 2006.
- [12] Vinu, A.; Ariga, K.; Saravanamurugan, S.; Hartmann, M.; Murugesan, V. *Synthesis of highly acidic and well ordered MgAl-MCM-41 and its catalytic performance on the isopropylation of m-cresol, Microporous and Mesoporous Materials*, v.76, p.91–98, 2004.
- [13] Wang Y., Yang R. T., Heinzl J. M., *Desulfurization of jet fuel by Π -complexation adsorption with metal halides supported on MCM-41 and SBA-15 mesoporous materials, Chemical Engineering Science*, v.63(2), p.356-365, 2008.
- [14] Wang, B.; Wan, Y.; Gao, Y.; Zheng, G.; Yang, M.; Wu, S.; Hu, J. *Occurrences and behaviors of naphthenic acids in a petroleum refinery wastewater treatment plant. Environmental science & technology*, v.49(9), p. 5796-5804, 2015.
- [15] Wen, J., Zhang, J., Wang, Z. and Zhang, Y. *Correlations between emulsification behaviors of crude oil-water systems and crude oil compositions. Journal of Petroleum Science and Engineering*, 146, pp.1-9, 2016.
- [16] Zhang Y, Shi Q, Li A, Chung KH, Zhao S, Xu C. *Partitioning of crude oil acidic compounds into subfractions by extrography and identification of isoprenoidyl phenols and tocopherols. Energ Fuel*, v.25(11), p.5083–5089, 2011.