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Acid Treatments of Montmorillonite-rich Clay for Fe Removal Using a Factorial Design Method

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Montmorillonite clays are of great interest for industrial processes such as catalysis and adsorption. The textural properties of clays can be modified in an attempt to increase their uses. This paper describes the acid treatment of natural montmorillonite clay. The materials were characterized using X-ray diffraction (XRD), atomic absorption spectroscopy (AA) and BET surface area measurements. Three different acids (HCl, HNO_3 and H_2SO_4) were tested, and HCl and H_2SO_4 were more efficient for removing Fe from the clay. The results indicate that HCl better preserves the material structure because less Al is removed. A central composite design (CCD) 2^2 was applied to evaluate the treatment using HCl. The temperature and concentration presented positive effects on the removal of Fe, Al and Mg. Combinations of the HCl acid solution concentration and temperature, such as 4 $mol.L^{-1}$/50 °C and 1 $mol.L^{-1}$/75 °C, assured that Fe was removed with less damage to the structure.

Keywords: *acid treatment, clay, montmorillonite, Fe removal, central composite design*

1. Introduction

Smectite clays consist of layers of two silica tetrahedral sheets surrounding a central alumina octahedral sheet. In montmorillonites, which belong to this group, isomorphic substitutions occur in which the resulting negative charge is compensated by the adsorption of hydrated cations into the interlayer region[1,2]. These properties are useful for different industrial applications, such as in catalysis and adsorption, and can be modified using the pillarization process with aluminum polioxocations, which provides a permanent porosity and a Lewis acid characteristic to the material[3]. Acid treatments also result in an increase of the porosity in clays. With increasing concentration, higher surface areas are observed and the shape of the pores is modified from the slit-shaped type to the spheroidal or bottle type[4]. In the acid, the activation force and the number of acidic sites increase. However, as noted by Pushpletha et al. (1999)[5], the maximum increase is obtained in the intermediate acid concentration range. The authors used a maximum acidity of 1.5 N for the samples treated with H_2SO_4 or HCl. The increased aggressiveness of the acid treatment decreases the catalytic activity of clays because of the impairment of the octahedral layers, which reflects a decrease in the Brönsted acidity and is higher in acid-treated materials at lower concentrations[6]. These treatments yield catalytic materials that have high porosities, surface areas, acidity and thermal stability.

The natural clays have different compositions, and the presence of some types of minerals can frequently be a problem for some applications[7]. For example, in pillared clays for acid-base catalysis, the presence of Fe can reduce the thermal stability[8].

Acid treatments are efficient for removing Fe, but other cations, such as Ca, Mg and Na, can also be removed. Depending on the variables tested in the treatment, a partial or total degradation of the structure of the material can occur. The treatment using hydrochloric acid for a long period of time (days) resulted in the amorphization of the structure[9] and a decrease in the cationic exchange capacity[4,5]. Adsorption of methylene blue on acid-treated clay minerals confirmed reduction in layer charge. From decreased values of cation exchange capacity (CEC) upon HCl attack was confirmed that clay with higher content of swelling layers were more stable in HCl[10].

The resistance to acid treatment is also influenced by the mineralogical composition. Nguetnkam et al. (2011)[11] observed that activation destroys preferentially smectites particles, kaolinite particles seem to be more resistant. After acid treatment the samples still exhibit OH stretching vibrations of kaolinite.

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Some previous studies[5,12] using sulfuric acid and hydrochloric acid report reductions of approximately 75% to 40% in the Fe_2O_3 content, depending on the type of acid used and the temperature of the treatment. Higher concentrations and higher temperatures result in greater removals. Sulfuric acid removes a higher percentage of iron compared to the same conditions in HCl. The parameters, such as acid concentration, contact time[13,14], clay/acid ratio[13] and temperature[14], were studied and applied to an oil cleaning process[13-15]. Acid treatments were also used during the catalytic synthesis for the benzylation of benzene with similar activity of commercial clays (K10 and KSF)[4].

Those K10 and KSF commercial montmorillonite-rich clays, obtained by treatment with sulfuric acid at different temperatures, were used during the pillarization process[16]. The KSF clay that was obtained using a soft treatment exhibited a higher adaptability for the pillarization process. Therefore, an acid treatment study seems necessary, and the optimization of the experimental parameters is crucial for obtaining materials with low Fe levels while maintaining their structural integrity. These materials might then be used in their activated or pillared forms.

The main aim of this work is to test different acids during the treatment of a selected iron-rich montmorillonitic clay and then optimize the removal of Fe without structural degradation by using the most effective acid and adjusting the temperature and acid concentrations. A factorial design tool was used for this purpose.

2. Material and methods

2.1. *Materials*

The natural montmorillonite clay was supplied by Colorminas Colorifício e Mineração S/A, Içara, Brazil, and was called Clay A.

The material was treated with sulfuric acid P.A. 98% (Quimex), hydrochloric acid P.A. 37% (Vetec) and nitric acid P.A. 65% (Quimex).

2.2. *Leaching using different acids.*

The samples were treated with the three different acids, which were each at a concentration of 4 mol.L^{-1}. The reaction time was 6 h, and the temperature was 50 °C. The solid/liquid ratio was 1 g of solid to 30 mL of solution. All of the treated samples were washed until the pH ≥ 5, and they were dried at 95 *°C* for 12 h.

2.3. *Experimental design for leaching with HCl*

After selecting the acid (hydrochloric acid), a central composite design (CCD) 2^2 was constructed. The independent variables studied were temperature (25 and 75 °C) and HCl concentration (1 and 7 mol.L^{-1}) (Table 1). The reaction time was fixed at 6 h, and the Clay/HCl ratio was maintained at 1 g to 30 mL. The data were statistically analyzed using the Statistica 6.0 software package (Statsoft Inc, Tulsa, USA).

2.4. *Characterization of samples*

The obtained materials were characterized using X-ray diffraction (XRD) and specific surface area adsorption (BET) and X-ray fluorescence (XRF). The liquid phase was analyzed using atomic absorption spectroscopy (AA) to quantify the extracted amounts of Mg, Fe and Al.

The X-ray diffraction measurements were performed on a Siemens D5000 diffractometer equipped with a Ni filter and a Cu Kα X-ray source (λ = 1.54Å) interval of 2θ = 2° to 65° and scanning pace of 0.02°. A Varian model AA spectrometer was used for the atomic absorption measurements. The surface area measurements were performed using nitrogen adsorption data employing a *QuantaChrome NovaWin 2* instrument. The samples were analyzed by infrared spectroscopy using a FT-IR Bruker alpha-p equipment without pretreatment.

3. Results and Discussion

3.1. *Leaching with different acids*

Table 2 presents the chemical analysis data (FRX) of Clay A. The sample presents a low concentration of Fe_2O_3 (2.37%). Fe in smectite clays can be as isolated oxides or in an isomorphic substitution in the crystal network[8]. The material contained montmorillonite (2θ = 5.8°; 17.7°; 19.8° and 35.1°), quartz and mica (see Figure 1).

After the leaching treatment, the recovered material and the control sample were analyzed using XRD. Figure 1 presents the results of leaching with different acids at a concentration of 4 mol.L^{-1} at 50 °C. It was observed that the intensity of the 001 peak decreased. This loss of intensity likely occurs because of a lamellar distortion that causes a partial decomposition of the structure.

Table 1. Matrix of CCD 2^2 (real and coded values) used and responses in terms of mass of cations dissolved during acid treatment.

Run	T (°C)	[ ] mol.L^{-1}	Mg^{2+}	Fe^{2+}	Al^{3+}
1	25 (-1)	1 (–1)	3.61	0.66	2.68
2	25 (-1)	7 (+1)	3.72	0.87	3.34
3	75 (+1)	1 (-1)	4.97	3.27	10.13
4	75 (+1)	7 (+1)	10.96	9.93	26.76
5*	50 (0)	4 (0)	5.98	4.82	4.05
6*	50 (0)	4 (0)	6.05	5.04	4.58
7*	50 (0)	4 (0)	5.52	4.31	3.73

* central points.

Table 2. Clay A mass composition (wet sample).

Compound	Mass (%)
SiO_2	63.29
Al_2O_3	17.26
Fe_2O_3	2.37
CaO	2.47
Na_2O	0.15
K_2O	0.38
MnO	0.45
TiO_2	0.14
MgO	5.08
P_2O_5	0.02
LOI	8.37

In addition, the 001 peak is shifted. Before the acidic treatment, the d_{001} of the clay was 15.12 Å. After treatment with HCl, H_2SO_4 and HNO_3, the d_{001} changed to 12.56, 14.73 and 12.60 Å, respectively. This peak shift is more pronounced after treatment with hydrochloric and nitric acids, and it indicates a decrease of the interlayer region. Table 3 presents the the amount of metal removed after acid leaching.

The decrease in the interlayer region resulting from the acid treatments with HCl and HNO_3 can be attributed to the exchange of the Ca^{2+} cation with H^+ (H_3O^+). Pushpletha et al. (2005)[5] reported that the basal spacing of samples treated with H_2SO_4 also decreased. In our samples, a re-hydration process may have occurred because with the acid treatment, the samples lose only approximately 20% of their swelling capacity compared to natural clay[17.] All of the acids removed cations, namely Al, Mg and Fe, from the octahedral layer of the clay. After the acid treatment of metakaolinite and natural kaolinite, Sabu et al. (1999)[18] observed that H_2SO_4 was more efficient in the removal of Fe. In montmorillonite-rich clays, H_2SO_4 strongly removed the Al^{3+} species, which resulted in partial degradation of the structure[5,12]. The removal of magnesium was similar for all of the different acid treatments. Finally, nitric acid did not remove Fe from the material.

All of the samples that were treated with different acids were analyzed using N_2 adsorption measurements, and Table 4 presents the measured surface areas. As expected, the surface areas increased after the acid treatment, which is a probable consequence of removing cations from the clay structure, thereby promoting porosity.

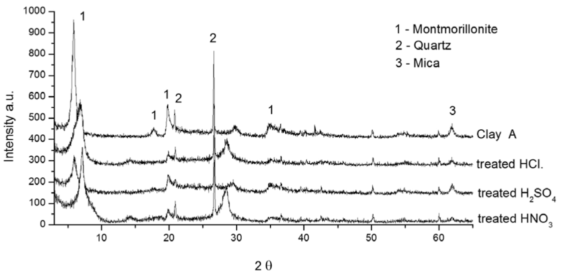

Figure 1. Diffractogram of Clay A treated with HCl, H_2SO_4 and HNO_3 with 4 mol/L at 50 °C for 6 h.

Table 3. Mass of cations dissolved during acid treatment at a concentration of 4 $mol.L^{-1}$ at 50 °C for 6 h (mg of cation/g of clay).

Acids	Fe^{2+}	Mg^{2+}	Ca^{2+}	Al^{3+}
HCl	5.03	6.05	15.33	4.58
H_2SO_4	6.29	6.75	0.33	12.68
HNO_3	1.76	6.61	13.37	9.00

Table 4. Surface areas (BET) for samples leached with HCl, H_2SO_4 and HNO_3 with 4 $mol.L^{-1}$ at 50 °C for 6 h.

Sample	S_{BET} (m^2/g)
Clay A	63
Leached HCl	124
Leached H_2SO_4	138
Leached HNO_3	99

The increase of in the specific surface area has been reported for different materials, for example, KSF and K10 clays that were treated with sulfuric acid[19]. For the KSF clay, the surface area values were lower (9 m^2/g) than for K10 clay, and micropores were not observed, which reveals that the structural elements (Al, Fe and Mg) were weakly extracted. This clay was treated at room temperature. In contrast, the acidic treatment of the K10 clay was stronger and performed at higher temperatures, which resulted in the extraction of Al. The K10 clay presented a large surface area (229 m^2/g) with a major contribution from the mesopores.

3.2. *Experimental design for leaching with HCl*

The central composite design (CCD) using hydrochloric acid was constructed to verify the removal of Fe and other species. Because the sample treated with HCl, at first, have a smaller disorganization, than the sample treated with H_2SO_4. Atomic absorption spectroscopy was used to determine the amounts of Mg^{2+}, Fe^{2+} and Al^{3+} in the liquid phase. Table 1 presents the evaluated variables, the experimental results and the response to the acid treatment in terms of cation removal (mg of cation/g of clay).

The main and interaction effects of each evaluated variable are presented in Figure 2. Mg can be present in the interlayer space of the clay structure, but it can also be exchangeable or isomorphically substituted into the crystalline network[1]. The Pareto chart presented in Figure 2a shows that either an increase in temperature or acid concentration enhances the removal of Mg^{2+}. However, the effect of temperature appears to be more relevant. In fact, at low temperatures, the removal is incipient, irrespective of the acid concentration.

The effects of temperature and acid concentration on the removal of Fe are shown in the Pareto chart presented in Figure 2b, and one can observe that the concentration of acid enhances the removal of Fe when the temperature is higher than 30 °C. This result is in agreement with previously reported results[13] that revealed that the removal of Fe^{2+} does not occur when temperature is 30 °C or below.

During the extraction of aluminum, both parameters (temperature and concentration) showed significant (main and interactive) effects, as observed in Figure 2c. Higher temperatures and acid concentrations enhance the removal of Al^{3+}, but the temperature exerts a major influence on the evaluated response. As observed with the other species, an increase in the acid concentration during the test performed at room temperature did not promote a strong extraction of Al^{3+}.

Table 5 presents the empirical models that predict the removal of cations (mg of cation/g of clay) as a function of temperature and HCl concentration. One can observe, based on the variance analysis presented in Table 6, that the coded models related to the removal of Mg^{2+} and Fe^{2+} were validated. However, the model related to the removal of Al^{3+} was not validated considering the 95% confidence level. In this situation, an analysis of the Pareto chart of effects should be followed. The determination coefficients were 99%, 96% and 83% for the Mg^{2+}, Fe^{2+} and Al^{3+} cations, respectively.

Infrared analyses of the natural and leached samples were performed (Figure 3) to examine the influence of the acid treatments on the crystalline compositions. The bands at

3405 and 1635 cm^{-1} (adsorbed water) become more diffuse when the severity of the treatment is increased[14].

The natural and acid treated samples exhibit absorption bands that are characteristic of dioctahedral smectites (3629 cm^{-1} – stretching vibration of Al-OH-Al, and 920 cm^{-1} – deformation vibration of Al-OH-Al)[5,14]. These bands and the band observed at 1116 cm^{-1} (Al-OH)[4] decrease after Al is removed during the acid treatment. The absorption bands also become more diffuse when the severity of the treatment is increased. The absorption band at 1116 cm^{-1} from the samples treated with the 7 mol.L^{-1} solution at 75 °C was almost eliminated. This result indicates that the acidic

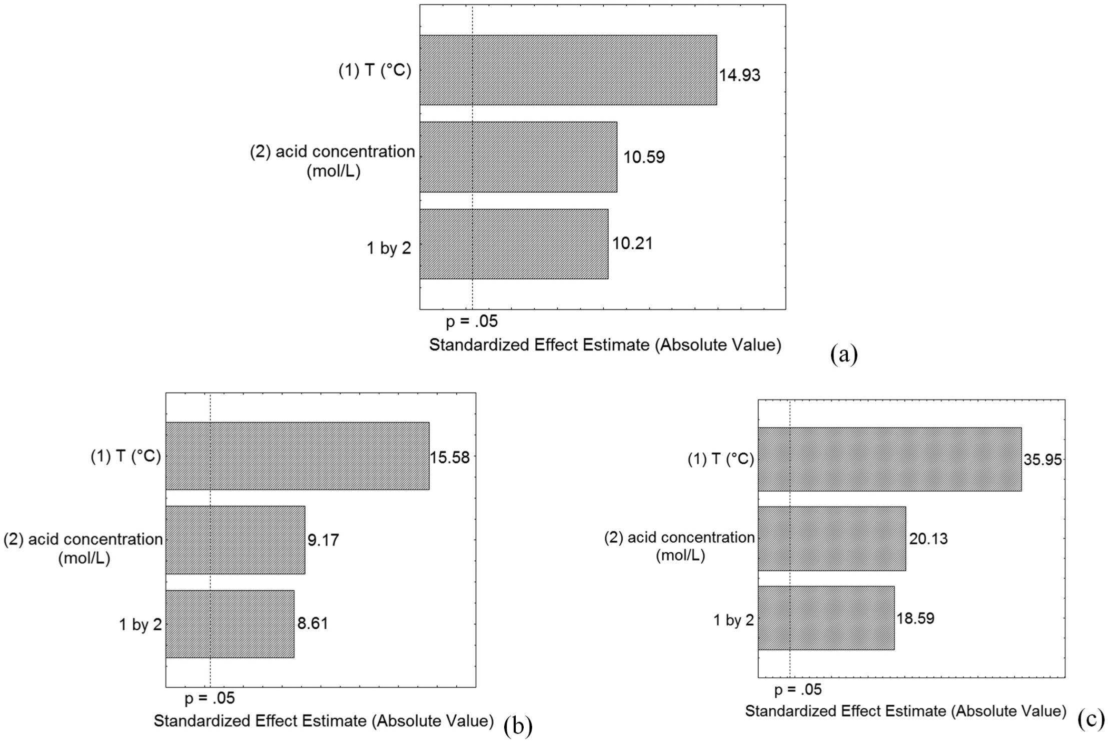

Figure 2. Pareto charts of the main and interaction effects of the independent variables on the removal of (a) Mg^{2+}, (b) Fe^{2+} and (c) Al^{3+} during acid treatment.

Table 5. Empirical models that predict the removal of cations (mg of cation/g of Clay) as a function of temperature and HCl concentration for each cation evaluated.

Cation	Coded model
Mg^{2+}	$5.83 - 2.15.T + 1.53.HCl_{concentration} + 1.47.T.HCl_{concentration}$
Fe^{2+}	$4.12 + 2.92.T\ (°C) + 1.72.HCl_{concentration} + 1.61.T\ (°C).HCl_{concentration}$
Al^{3+}	$7.89 + 7.72.T\ (°C) + 4.32.HCl_{concentration} + 3.99.T\ (°C).HCl_{concentration}$

Table 6. Analysis of variance for each model presented in Table 5.

Cation		Sum of squares	Degrees of freedom	Mean of squares	F calculated
Mg^{2+}	Regression	36.44	3.00	12.15	217.01
	Residues	0.17	3.00	0.06	
	Total	36.60	6.00		
Fe^{2+}	Regression	56.25	3.00	18.75	26.31
	Residues	2.14	3.00	0.71	
	Total	58.38	6.00		
Al^{3+}	Regression	376.74	3.00	125.58	5.01
	Residues	75.21	3.00	25.07	
	Total	451.95	6.00		

Listed $F_{3;3;\,0.95}$= 9.27.

treatment preferentially attacks the octahedral layers of the clay. However, the intensity decreases of the 997 cm^{-1} (Si-O-Si stretching) and 518 cm^{-1} (Si-O deformation) bands after leaching indicates that tetrahedral structure was also affected by the acid treatment[4].

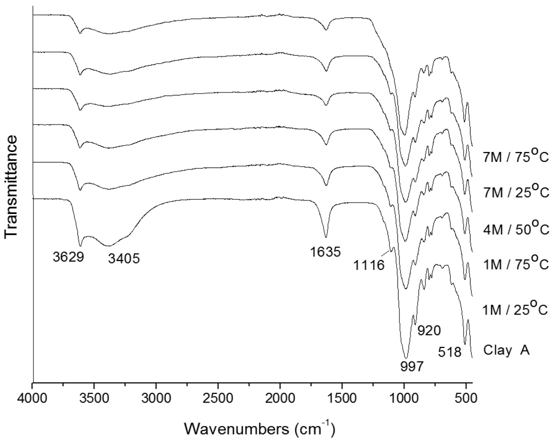

Figure 3. FTIR spectra of leached samples.

Table 7. BET surface areas for samples treated with HCl using the experimental design methodology.

Run	S_{BET} (m^2/g)	Temperature (°C)	Concentration (mol.L^{-1})
1	73	25	1
2	69	25	7
3	126	75	1
4	176	75	7
6 *	124	50	4

* central point.

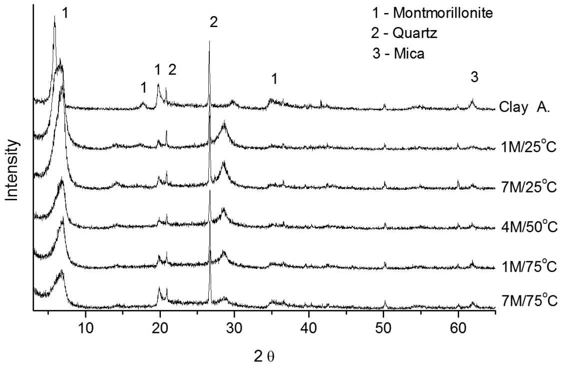

Figure 4. XRD patterns of Clay A and samples treated with HCl at concentrations of 1, 4 and 7 mol.L^{-1} at 25, 50 and 75 °C for 6 h.

Table 7 presents the surface area values for the samples treated for 6 h with HCl (1, 4 and 7 mol.L^{-1}) at 25, 50 and 75 °C. Previous reports[4,5,13] indicate that an increases in the acid concentration promotes the removal of cations from the tetrahedral and octahedral layers, which results in an increase of the surface areas. Before treatment, the clay presents a surface area of 63 m^2/g. In this work, an increase in the surface area was not observed for the samples treated at 25 °C. The tendency for the surface area to increase was confirmed only at higher temperatures, even when using diluted acid solutions (1 mol.L^{-1}).

Changes in the mineralogical composition, which were revealed in the XRD measurements presented in Figure 4, are in agreement with the variations in the specific surface area data. All of the samples treated at 25 °C present almost constant structural features because the removal of Fe and Al is low. The displacement of the 001 reflection (from 15.12 Å in the natural clay to 13.4 Å and 12.83 Å for the samples treated with 1 and 7 mol/L, respectively) is likely caused by a Ca^{2+} cationic exchange, as noted in a previous study[5].

At higher temperatures, a significant decrease in the intensity of the diffraction peaks is observed. The major decrease in the diffraction peak intensity occurs after treating with 7 mol.L^{-1} of HCl at 75 °C.

4. Conclusions

Sulfuric and hydrochloric acids were efficient in the removal of Fe from the montmorillonite-rich clay used in this work. These acids also promoted the extraction of the Al and Ca species, respectively. In contrast, the use of nitric acid for the removal of Fe was inefficient. The acid treatment enhanced the specific surface area of the material, thereby revealing the partial degradation of the structure. Also evidenced by the decrease in intensity of the diffraction peaks 001 in samples treated. The use of the experimental design methodology might be useful in helping to define such conditions, and to explain the influence of temperature and HCl acid concentration on the extraction of Fe, Mg and Al. The temperature has a more effect on the removal of Al compared removal of Fe and Mg.

The combinations 4 mol.L^{-1} HCl / 50 °C and 1 mol.L^{-1} HCl / 75 °C assured the best results for removal of Fe without affecting the structure of the material.

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References

1. Gomes CF. *Argilas:* O que são e para que servem. Lisboa: Fundação Galouste Gulbenkian; 1988.
2. Pergher SBC, Corma A and Fornes V. Materiales Laminares Pilareados: Preparación y Propiedades *Quimica Nova*. 1999a; 22:693-709. http://dx.doi.org/10.1590/S0100-40421999000500013
3. Pergher SBC, Corma A and Fornes V. Preparación y Propiedades de una Arcilla Montmorillonita Pilareada con Polihidroxicationes de Aluminio. *Quimica Nova*. 1999b; 22:649-653. http://dx.doi.org/10.1590/S0100-40421999000500004
4. Kumar P, Jasra RV and Bhat TSG. Evolution of porosity and surface acidity in montmorillonita clay an acid activation, *Industrial e Engineering Chemistry Research*. 1995; 34:1440-1448. http://dx.doi.org/10.1021/ie00043a053
5. Pushpletha P, Rugmini S and Lalithambika M. Correlation between surface properties and catalytic actividy. *Applied Clay Science*. 2005; 30:141-153. http://dx.doi.org/10.1016/j.clay.2005.03.011
6. Komadel P. Chemically modified smectites. *Clay Minerals*. 2003; 38:127-138. http://dx.doi.org/10.1180/0009855033810083
7. Araújo CS and Silva LRD. Influência da Calcinação sobre a Remoção de Ferro da Caulinita e Ilita e seus Efeitos sobre a Acidez. *Quimica Nova*. 2003; 26:161-164. http://dx.doi.org/10.1590/S0100-40422003000200003
8. Leite SQM, Colodete CHA and Dieguez LC. Extração de Ferro de Esmectita Brasileira com Emprego do Método Ditionito-Citrato-Bicarbonato. *Quimica Nova*. 2000; 23:297-302. http://dx.doi.org/10.1590/S0100-40422000000300002
9. Rodrigues MGF, Pereira KRO and Valenzuela-Diaz FR. Obtenção e caracterização de materiais argilosos quimicamente ativados para utilização em catálise. *Cerâmica*. 2006; 52:260-263. http://dx.doi.org/10.1590/S0366-69132006000400008
10. Pentrák M, Czímerová A, Madejová J and Komadel P. Changes in layer charge of clay minerals upon acid treatment as obtained from their interactions with methylene blue. *Applied Clay Science*. 2012; 55:100-107. http://dx.doi.org/10.1016/j.clay.2011.10.012
11. Nguetnkam JP, Kamga R, Villiéras F, Ekodeck GE, Razafitianamaharavo A and Yvon J. Alteration of cameroonian clays under acid treatment. Comparison with industrial adsorbents. *Applied Clay Science*. 2011; 52:122-132. http://dx.doi.org/10.1016/j.clay.2011.02.009
12. Folleto EL, Morgado AF and Porto LM. Influência do tipo de ácido usado e da sua concentração na ativação de uma argila bentonitica. *Cerâmica*. 2001; 47:208-211.
13. Didi MA, Makhoukhi B, Azzouz A and Villemin D. Colza oil bleaching through optimized acid activation of bentonite. A comparative study. *Applied Clay Science*. 2009; 42:336-344. http://dx.doi.org/10.1016/j.clay.2008.03.014
14. Christidis GE, Scott PW and Dunham AC. Acid activation and bleaching capacity of bentonites from the islands of Milos and Chios, Aegean, Greece. *Applied Clay Science*. 1997; 12:329-347. http://dx.doi.org/10.1016/S0169-1317(97)00017-3
15. Woumfo D, Kamga R, Figueras F and Njopwouo D. Acid activation and bleaching capacity of some Cameroonian smectite soil clays. *Applied Clay Sci*ence. 2007; 37:149-156. http://dx.doi.org/10.1016/j.clay.2006.12.008
16. Rossa V, Spazzini ST, Schwanke AJ, Penha FG and Pergher SCB. Pilarização de Argilas Montmorillonitas Comerciais. In: *Anais 30ª Reunião Anual da Sociedade Brasileira de Química*; 2007; São Paulo. São Paulo; 2007.
17. Önal M. Swelling and cation exchange capacity relationship for the samples obtained from a bentonite by acid activations and heat treatments. *Applied Clay Science*. 2007; 37:74-80. http://dx.doi.org/10.1016/j.clay.2006.12.004
18. Sabu KR., Sukumar R, Rekha R and Latithambika M. A comparative study on H_2SO_4, HNO_3 and $HClO_4$ treated metakaolinite of a natural Kaolinite as Friedel-Crafts alkylation catalyst. *Catalysis Today*. 1999; 49:321-326. http://dx.doi.org/10.1016/S0920-5861(98)00439-8
19. Cseri T, Békássy S, Figueras F, Cseke E, Menorval L and Dutartre R. Characterization of clay-based K catalysts and their application in Friedel-Crafts alkylation of aromatics. *Applied Catalysis A*: General. 1995; 132:141-155. http://dx.doi.org/10.1016/0926-860X(95)00158-1