

# EVALUATION OF STRUCTURAL MODIFICATION OF ORGANOCCLAY BY ADSORPTION OF BTX

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**ABSTRACT** – Aromatic hydrocarbons, as benzene, toluene and xylene were removed by adsorption into a commercial organoclay as an alternative for wastewater treatment and the aim of this study was to evaluate modifications on the structure of the organoclay due to the adsorption process of BTX, which is relevant for the next studies of regeneration of this adsorbent. From mercury porosimetry analysis it was observed that the largest number of pores of organoclay occurs to a diameter close to  $200 \times 10^3$  nm. EDS results showed that basic elements of clays of smectite group derived from the structure of phyllosilicate are found in significant amounts, such as Si, Al, Mg, Fe, and O. The analysis of infrared spectroscopy in Fourier showed functional groups present in the structures of clays. Two endothermic peaks and one endothermic peak were identified by thermal analysis (DSC). Diffraction patterns (XRD) showed that the organoclay is not characterized by a highly crystalline structure and the reduction in interlayer spacing after BTX adsorption can be indicative of a decrease in the number of layers of water in the interspaces.

## 1. INTRODUCTION

Soil and/or water contamination by aromatic hydrocarbons from leaking storage tanks, effluent of petrochemical and chemical industries and improper disposal of hazardous wastes are of concern worldwide. These contaminants have highly toxic to human health and the environment properties. Benzene, for example, even accounting for only 2 % of the oil, is considered the most toxic, a fact that is directly related to its carcinogenic and mutagenic potential (El Brihi *et al.*, 2002).

Also, another factor that aggravates the contamination to these hydrocarbons is higher water solubility than other organic compounds that are present in this kind of effluent. Generally, solubility of benzene, toluene, xylene and gasoline in water are respectively 18, 25, 3, 20, 50–100 ppm when gasoline is introduced into water (Kermanshahi-pour *et al.*, 2005). Maximum levels for monoaromatic compounds in effluent are 1.2 ppm for benzene and toluene, and  $1.6 \text{ mg.L}^{-1}$  for xylene, according to the National Council of the Environment in Brazil (CONAMA 430, 2011). Furthermore, maximum levels in potable water are 5, 170 and  $300 \text{ }\mu\text{g.L}^{-1}$ , for benzene, toluene and xylene, respectively (Ministry of Health in Brazil, 1995).

There are different methods for monoaromatic compounds removal from groundwater, such as physical techniques (pump and treat, air sparging, carbon and zeolite adsorption, and filtration) (Nourmoradi *et al.*, 2012; Souza *et al.*, 2012; Vidal *et al.*, 2012; Zenasni *et al.*, 2011; Yang *et al.*, 2005) chemical methods (advanced oxidation processes, photo catalysis remediation) (Tiburtius *et al.*, 2005) and biological processes (bioremediation, biodegradation in reactors) (Dou *et al.*, 2008; Jiin-Shuh *et al.*, 2008). Among these processes, the adsorption became promising for reaching the low limits set by environmental legislation.

In search of alternative adsorbent having good removal efficiency and with the aim of reducing waste residue generation in industrial processes and improving reuse of these in the production process, companies are investing more in research in order to transform them into commercially interesting by-products. Thus, this study made use of a commercial organoclay supplied by Brazilian industry Spectrochem for adsorption of benzene, toluene and xylene. In order to identify structural group, characteristics and structural changes occurred after adsorption, this study aimed to evaluate structural modifications of organoclay by adsorption of BTX, which is important for the next studies of regeneration of this adsorbent.

## 2. MATERIALS AND METHODS

The commercial organoclay named Spectrogel type C<sup>®</sup> used in this study was kindly provided by Brazilian company SpectroChem. For preparation of the adsorbent, this was sieved for 20 minutes, being used the fraction between sieves of 24 and 28 Tyler mesh to obtain particles with size of 0.655 mm of average diameter.

The commercial organoclay and the organoclays contaminated with organic compounds (BTX) were characterized by porosimetry of Hg, energy-dispersive X-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and x-ray diffraction (XRD). Table 1 shows the methodology of each analysis.

Table 1 – Characterization methods.

Analysis	Equipment	Parameters
Porosimetry of Hg	AutoPore IV Mercury Porosimeter Micromeritics	Pressure evacuation of 50 $\mu\text{mHg}$ , time of 5 min and equilibrium time of 10 sec.
X-ray diffraction (XRD)	Philips Analytical X Ray, X'Pert-MPD.	Copper Ka radiation with a wavelength of 1.54 angstrom, voltage 40 kV, current of 40 pA, step size of 0.02 degrees, 0.02 Speed graus.seg <sup>-1</sup> .
Differential scanning calorimetry (DSC)	Mettler-Toledo, DSC1	Flow 50 mL.min <sup>-1</sup> from room temperature to 500 °C and a heating rate of 10 °C.min <sup>-1</sup> in nitrogen atmosphere.
Fourier transform infrared spectroscopy (FTIR)	Thermo Scientific, Nicolet 6700	Wavelength in the range 4000-400 cm <sup>-1</sup> with samples in the form of pressed KBr pellets.
Energy-dispersive X-ray spectroscopy (EDS)	Sputter Coater POLARON, SC7620, VG Microtech.	Accelerating voltage equal to 20 kV and 600 pA for obtaining spectra of X-ray and metal coating of gold.

The organoclays contaminated with organic compounds were obtained from batch tests by contacting 1 g of commercial organoclay with 100 mL of solution having different initial concentrations ( $0.03$  to  $1.6 \text{ mmol.L}^{-1}$ ) for each contaminant, separately. The samples were agitated in water bath at a constant speed of 200 rpm for 3 h (equilibrium time obtained by kinetic study) at  $25^\circ\text{C}$ .

### 3. RESULTS AND DISCUSSION

Figure 1 shows the pore size distribution according to mercury porosimetry analysis for the commercial organoclay, as well as, organoclay contaminated with benzene, toluene and xylene.

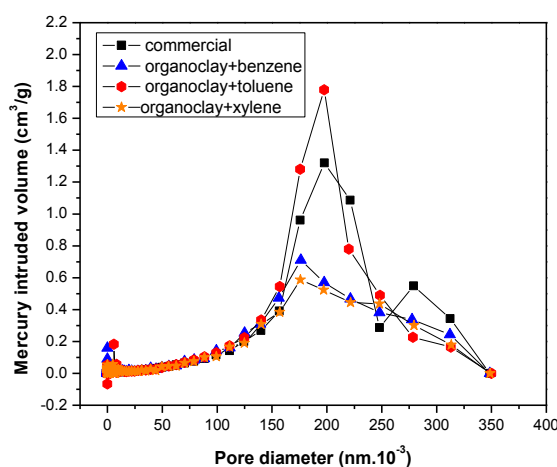


Figure 1 - Pore size distribution for commercial organoclay and organoclay after BTX adsorption process.

It is observed that the largest number of pores of organoclay occurs to a diameter close to  $200 \cdot 10^3 \text{ nm}$ , however, the volume of mercury intruded is small, which means that the adsorbent material is not highly porous. Comparing the pore distribution among all samples, it is observed that there is a distribution profile of pores similar to the organoclays. For diameter values between  $150$  and  $250 \text{ nm} \cdot 10^3$  it was noted a difference in the volume of intruded mercury. However, this is a very small scale, being about  $1.4 \text{ cm}^3 \cdot \text{g}^{-1}$  in the increased adsorption. Due to this profile pores are very similar among the samples before and after adsorption, it emerged the hypothesis that the BTX molecules are adsorbed on the adsorbent surface and not into the macropores.

Table 2 shows the chemical composition of the samples according to the analysis of Energy-dispersive X-ray spectroscopy. Basic elements of clays of smectite group derived from the structure of phyllosilicate are found in significant amounts, such as Si, Al, Mg, Fe, and O. The components  $\text{Na}^+$  and  $\text{Ca}^{2+}$  are present in the interlamellar spaces in the clay and they are exchangeable cations in the process of organophilization. Thus the presence of these two elements in the commercial organoclay may indicate that the process of organophilization, made by Spectrochem industry, was carried out with a low amount of water. Small traces of Ti come from the titanium oxide. The presence of Cl and C is due to the decomposition of the salt used in organophilization, which is not known since this is a commercial organoclay. Similar compositions for different types of organoclays have been found by Martin *et al.* (2011) and Silva *et al.* (2007).

Table 2 – Chemical composition of commercial organoclay and organoclay after BTX adsorption process by EDS.

Sample	Composition (%)										
	Na	Mg	Al	Si	Ca	Ti	Fe	O	Cl	C	S
Commercial	2.02	0.90	5.06	13.80	0.16	0.15	1.71	43.08	1.44	31.44	0.21
+ B	0.28	0.93	5.28	14.16	0.12	0.17	1.57	44.62	0*	32.76	0.09
+ T	0.31	1.04	5.40	14.60	0.16	0.18	1.54	44.82	0.11	31.84	0*
+ X	0.30	0.97	5.37	14.63	0.15	0.16	1.99	43.84	0.10	32.49	0*

\*: not identified by EDS analysis

The decrease of the cations Na and the absence or near absence of Cl for samples of organoclays contaminated may indicate the removal of the salt for the entrance of the adsorbed organic compounds.

Figure 2 shows the curves obtained from the DSC analysis for commercial organoclay and organoclays contaminated with BTX. Analyzing the curve of commercial organoclay, it is observed one endothermic peak below 200 °C related to dehydration (interlayer or external water) (Martin *et al.*, 2011). A second endothermic peak near 200 °C is due to thermal reactions of organic matter, characteristic of evaporation and decomposition of the organic compounds when exposed to an inert atmosphere. The third peak above 400 °C is related to the dehydroxylation of the organoclay (Santos and Silva, 2012).

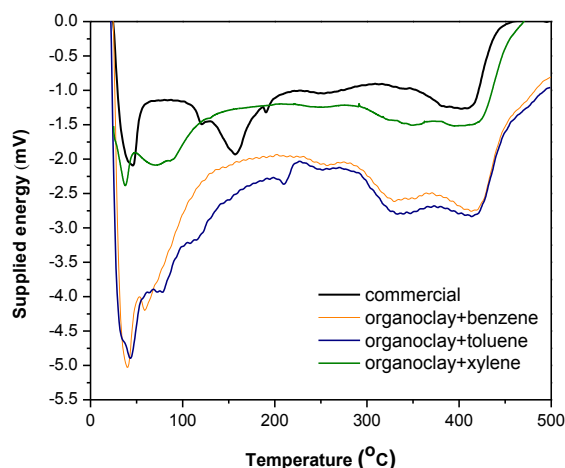


Figure 2 – DSC of the commercial organoclay and contaminated organoclays.

The contaminated organoclays have one more peak than the commercial organoclay at below 100 °C. The contaminated organoclays have higher amount of water than the commercial organoclay due to water molecules adsorbed along with the contaminants in the adsorption process. Therefore, the contaminated organoclays showed an extra peak due to water loss. However, contaminated organoclays do not have a peak near 200 °C which is related to the evaporation and decomposition of the salt used in organophilization process. Furthermore, they have one more peak than the commercial organoclay, at temperature near 350 °C, which may be due to decomposition/evaporation of BTX compounds adsorbed. Again

it was concluded that during the adsorption occurred the removal of the molecules of salts present in the interlayer spaces for input of the adsorbed compounds.

Figure 3 shows the infrared spectroscopy with Fourier transform for the commercial organoclay and organoclays contaminated with BTX.

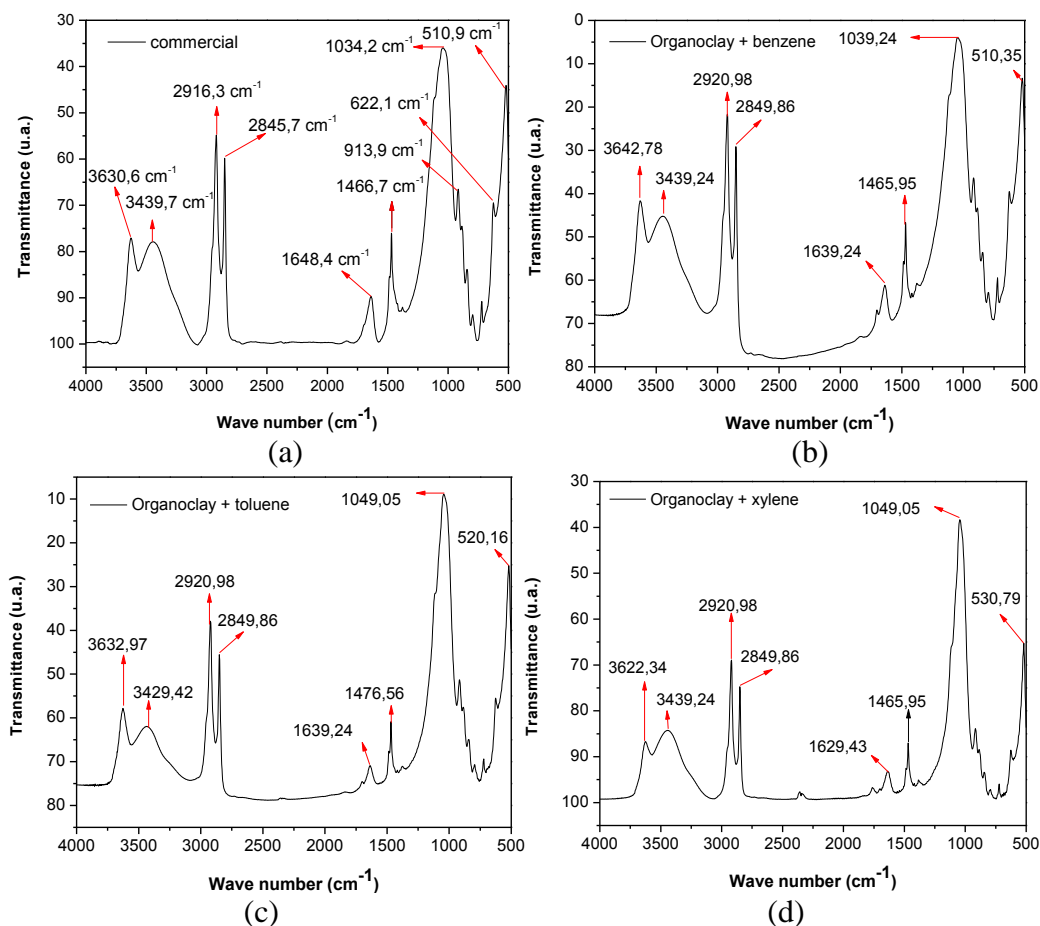


Figure 3 - Infrared spectroscopy spectra for organoclays (a) commercial (b) contaminated with benzene, (c) contaminated with toluene and (d) contaminated with xylene.

For the commercial organoclay, the bands  $3630.6 \text{ cm}^{-1}$  and  $3439.7 \text{ cm}^{-1}$  correspond to the asymmetrical stretching O-H and the symmetric stretch O-H, respectively. The band  $1648.4 \text{ cm}^{-1}$  is related to the angular deformation H-O-H (Santos and Silva, 2012; Bala *et al.*, 2000). It is also observed the appearance of the vibrational stretching of C-H linking from the organic cations, as evidenced by the bands  $2916.3 \text{ cm}^{-1}$  and  $2845.7 \text{ cm}^{-1}$  corresponding to asymmetric and symmetric stretching, respectively. The band  $1466.7 \text{ cm}^{-1}$  is related to the angular deformation  $\text{CH}_2$  (Vaia *et al.*, 1994). The band  $1034.2 \text{ cm}^{-1}$  corresponds to Si-O stretching and the bands between  $622.1$  and  $913.9 \text{ cm}^{-1}$  are due to the layers of octahedral (Zhang *et al.* 2003). Finally, the band of  $510.9 \text{ cm}^{-1}$  corresponds to the phyllosilicate structure associated with stretching and angular deformation of Si-O-Si and Si-O-Al. These vibrations occur within the crystal structure without being affected by intercalated cations (Li *et al.*, 2008).

It can be seen that all the peaks present in the commercial organoclay are also present in the organoclays contaminated with small variations in the intensities of the bands. These very small changes in the intensity of the bands among commercial and contaminated organoclays suggest that BTX/organoclay complex has a microscopic structure that is not very different from the commercial organoclay (before the removal process). The validation of these results requires the application of advanced structural techniques.

The XRD patterns of the commercial organoclay and contaminated organoclays are shown in Figure 4.

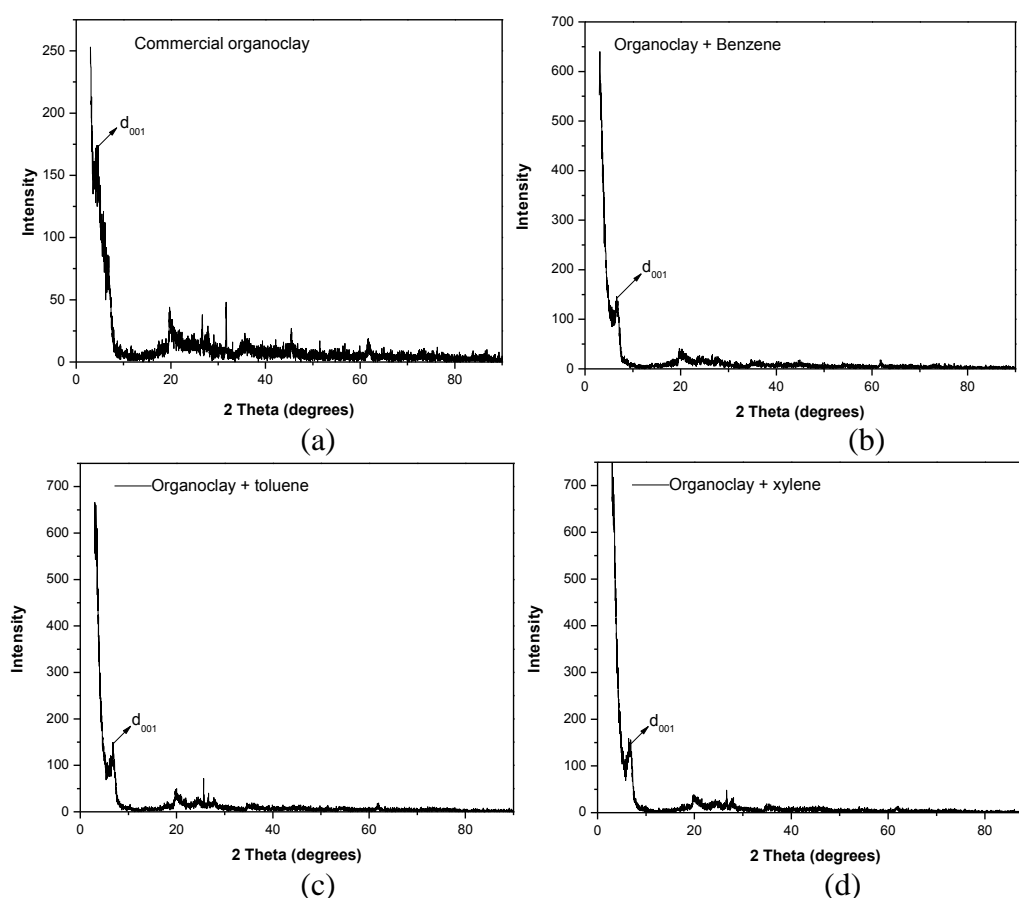


Figure 4 - XRD for the organoclay (a) commercial (b) contaminated with benzene, (c) contaminated with toluene and (d) contaminated with xylene.

According to the diffractograms, the commercial organoclay is not characterized by a highly crystalline structure, which is typical for mineral clays. The peak respect to the plane 001 is located at  $2\theta = 4.51$  degrees, which provides a basal spacing of  $21.74 \text{ \AA}$ . This occurrence of a peak before  $2\theta = 10^\circ$  is representative of the basal spacing,  $d_{001}$ , of the smectite clay (Moore and Reynolds, 1997). The low value of  $2\theta$  respect to the plane 001 and, thus, a high value of basal spacing when compared with no organophilic clays, are related to the salt which was inserted in the organophilization process of the clay, which promotes the advance angle  $2\theta$  due to the changes caused in the clay structure (Paiva and Morales, 2012).

For contaminated organoclays, it is observed a very similar diffraction patterns, with the basal plane distance 001 that it is equal for three samples of contaminated organoclays,  $14.28$



Å at  $2\theta = 6.87$ . This basal spacing was smaller than that for commercial organoclay ( $d_{001} = 21.74$  Å) at  $2\theta = 4.51$ . The reduction of the interlayer spacing can be indicative of the removal of the salt used in the organophilization process for input of adsorbed compounds.

## 4. CONCLUSIONS

The organoclay adsorbent is not highly porous material and BTX molecules may have been adsorbed onto the adsorbent surface rather than into macropores. EDS analysis indicated the effective adsorption of BTX due to the changes of the elements present in the samples before and after adsorption. The DSC analysis revealed the presence or absence of different peaks when compared to the commercial organoclay sample with the contaminated organoclays samples. The FTIR spectra showed that BTX/organoclay complexes have a microscopic structure that is not very different from the commercial organoclays. The diffractograms showed a difference in the basal spacing among commercial organoclay and contaminated organoclays. Again, the reduction in interlayer spacing can be indicative of the removal of the salt used in the organophilization process for input of adsorbed compounds. This study will help in the next essays for the regeneration of this adsorbent.

## 5. ACKNOWLEDGEMENT

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## 6. REFERENCES

- BALA, P.; SAMANTARAY, B.K.; SRIVASTAVA S.K. Synthesis and characterization of Na-montmorillonite-alkylammonium intercalation compounds. *Materials Research Bulletin*, v. 35, p. 1717-172, 2000.
- CONAMA, Brazilian Ministry of Environment, Conditions and standards for wastewaters discharge. Resolution N°. 430, May 13, 2011. (In Portuguese).
- DOU, J.; LIU, X; HU, Z. Anaerobic BTEX degradation in soil bioaugmented with mixed consortia under nitrate reducing conditions. *Journal of Environmental Sciences*, v.20, p.585–592, 2008.
- EL BRIHI, T.; JAUBERT, J.N.; BARTH, D.; PERRIN L. Determining volatile organic compounds' adsorption isotherms on dealuminated Y zeolite and correlation with different models. *J. Chem. Eng. Data*, v.47, p.1553-1557, 2002.
- JIIN-SHUH, J.; MING-KUO, L.; SHIH-MING, W.; PABITR, C.; JYOTI PRAKASH, M. Effects of inorganic nutrient levels on the biodegradation of benzene, toluene, and xylene (BTX) by *Pseudomonas* spp. in a laboratory porous media sand aquifer model. *Bioresource Technology*, v.99, p.7807–7815, 2008.
- KERMANS SHAHI-POUR, A.; KARAMANEV, D.; MARGARITIS, A. Biodegradation of petroleum hydrocarbons in an immobilized cell airlift bioreactor, *Water Res.*, v.39, p.3704–3714, 2005.
- LI, Z.; JIANG, W.-T.; HONG, H. An FTIR investigation of hexadecyltrimethylammonium intercalation into rectorite. *Spectrochimica Acta Part A*, v.71, p.1525-1534, 2008.
- MARTIN, D. C. R.; MOLINA, J.P.C.; VIEIRA, M.G.A.; TOMAZ, E. Characterization of organophilic clay fluidgel for application as adsorbent for aromatic hydrocarbons. In: XXX Brazilian Congress of Particulate Systems (ENEMP), Vassouras-RJ, Brazil, 2011. (In Portuguese).

- MINISTRY OF LABOR, Bureau of Safety and Health at Work. Decree N° 14, December 20, 1995. (In Portuguese).
- MOORE, D M; REYNOLDS, JR., R.C. X-Ray diffraction and identification and analysis of clay minerals. 2. ed. New York: Oxford University Press, p.378, 1997.
- NOURMORADI, H.; NIKAEEN, M.; KHIADANI M. Removal of benzene, toluene, ethylbenzene and xylene (BTEX) from aqueous solutions by montmorillonite modified with nonionic surfactant: Equilibrium, kinetic and thermodynamic study. Chem. Eng., v.191, p.341-348, 2012.
- PAIVA, L.B.; MORALES, A.R. Organophilic bentonites based on argentinean and brazilian bentonites. Part 1: Influence of intrinsic properties of sodium bentonites on the final properties of organophilic bentonites prepared by solid-liquid and semisolid reactions. Chem. Eng., v.29. n.3. p.525-536, 2012.
- SANTOS, O.A. A.; SILVA, M.G.C. Thermal characterization of organoclays for the removal of fuel oils. In: VI Brazilian Conference on Heat Treatment Issues, Atibaia-SP, Brazil. June 17 to 20, 2012. (In Portuguese).
- SILVA, A.A.; VALENZUELA-DIAZ, F.R; MARTINS, G.S.V.; RODRIGUES, M.G.F. Preparation of organoclays using different concentrations of quaternary ammonium salt. Ceramics, v.53, p.417-422, 2007. (In Portuguese).
- SOUZA, S.M.A.G.U.; LUZ, A.D.; SILVA, A. Removal of Mono- and Multicomponent BTX Compounds from Effluents Using Activated Carbon from Coconut Shell as the Adsorbent. Ind. Eng. Chem. Res., v.51, p.6461-6469, 2012.
- TIBURTIUS, E.R.L.; PERALTA-ZAMORA, P.; EMMEL, A. Treatment of gasoline contaminated waters by advanced oxidation processes, Journal of Hazardous Materials, B126, p.86-90, 2005.
- VAIA, R.A.; TEUKOLSKY, R.K.; GIANNELIS, E.P. Interlayer structure and molecular environment of alkylammonium layered silicates. Chemistry of Materials, v.6, n.7, p.1017-1022, 1994.
- VIDAL, C.B.; RAULINO, G.S.C.; BARROS, A.L.; LIMA, A.C.A.; RIBEIRO J.P; PIRE, M.J.R.; NASCIMENTO, R.F. BTEX removal from aqueous solutions by HDTMA-modified Y zeolite. J. of Environmental Management, v.112, p.178-185, 2012.
- YANG, X.; AL-DURI, B. Kinetic modeling of liquid-phase adsorption of reactive dyes on activated carbon. Colloid and Interface Science, v.287, p. 25-34, 2005.
- ZENASNI, M.A.; BENFARHI, S.; MANSRI, A.; BENMEHDI, H.; MEROUFEL, B.; DESBRIERES, J.; DEDRIVERES, R. Influence of pH on the uptake of toluene from water by the composite poly (4-vinylpyridinium)-maghnite. African Journal of Pure and Applied Chemistry, v. 5(15), p. 486-493, 2011.
- ZHANG, W.A.; CHEN, D. Z.; XU, H.Y.; SHEN, X.F.; FANG, Y.E. Influence of four different types of organophilic clay on the morphology and thermal properties of polystyrene/clay nanocomposites prepared by using the  $\gamma$ -ray irradiation technique. European Polymer J., v.39, p.2323-2328, 2003.