CHEMICAL ENGINEERING TRANSACTIONS

VOL. 32, 2013

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet

Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-23-5; **ISSN** 1974-9791

DOI: 10.3303/CET1332053

Adsorption of Toluene in Batch System in Natural Clay and Organoclay

Sidmara Bedin[a], Maria F. Oliveira[a], Melissa G. A. Vieira[a],
Onélia A. Andreo dos Santos[b], Meuris C. G. da Silva*[a]

[a]School of Chemical Engineering, University of Campinas (UNICAMP), Cidade Universitária Zeferino Vaz, P.O. Box, 6066, 13083-970, Campinas-São Paulo, Brazil
[b]Chemical Engineering Department, University of Maringá. Av. Colombo, 5790, Jardim Universitário, 87020-900, Maringá-Paraná, Brazil
meuris@feq.unicamp.br

This study aimed to evaluate the adsorption of toluene in two forms of sodium smectite national clays called Fluidgel and produced in northeastern Brazil: commercial and chemically modified with quaternary ammonium salt (hexadecyltrimethylammonium bromide) by the process of organophilization. The commercial Fluidgel and organoclay were characterized by a physical-chemical study evaluating their adsorptive properties and quality from the process of organophilization on the morphology and chemical composition, in relation to their affinity for volatile organic compounds in processes such as BTX adsorption. Toluene adsorption onto clays, commercial and organoclay, with particle diameter of 0.55 mm was carried out in batch system at room temperature with constant stirring. The adsorption study was conducted at initial toluene concentration of 100 ppm, 10 g of clay per liter of effluent and at initial pH of about 6. For kinetic data fitting, pseudo-first-order, pseudo-second-order and intraparticle diffusion models were applied. The results obtained with the characterization analyses showed the efficiency of organophilization process. The adsorption kinetics process showed that the kinetic model of pseudo-second-order was the best fit to experimental data. The adsorption study presented a percentage removal of toluene from about 96 % to equilibrium time of 180 min.

1. Introduction

Benzene, toluene and xylene are volatile and flammable monocyclic aromatic hydrocarbons capable of causing adverse effects to human health and the environment, which may be carcinogenic and / or mutagenic effects. Thus their presence in water flow even at low concentrations is of serious environmental concern and its removal from water is essential to ensure the safety of water supply (Nourmoradi et al, 2012). The difficulty in meeting the parameters required by law, the high costs and operational complexity increase interest in alternative technologies for removing pollutants, among which we can highlight the adsorption, because in addition to the advantages already mentioned, this process allows regenerate the adsorbent (Zhou et al. 2008). In recent years, organoclays, an alternative adsorbent, has become the subject of study by many researchers (Bertagnolli, 2011). The organoclays contain organic molecules sandwiched between its layers which are structural or adsorbed on surfaces. The insertion of these molecules causes an expansion of their plans d_{001}, changing its hydrophobic to hydrophilic and / or organophilic nature. The most natural clays used in the preparation of organoclays are smectite group due to the small size of their crystals, high cationic exchange capacity and swelling capacity in water that cause the intercalation of organic compounds used in the synthesis rapid and full (Paiva et al., 2008). Thus, this work aims to prepare, characterize and evaluate the performance of organoclays in the treatment of water contaminated with toluene.

Please cite this article as: Bedin S., Fernanda Oliveira M., Vieira M.G.A., Andreo Dos Santos O. A., da Silva M. G. C. , 2013, Adsorption of toluene in batch system in natural clay and organoclay, Chemical Engineering Transactions, 32, 313-318 DOI: 10.3303/CET1332053

2. Experimental

2.1 Preparation of Organoclay

The preparation of organoclay was performed with sodium smectite clays from Boa Vista - Paraiba - Brazil, marketed as Fluidgel and processed by Dolomil Ltda. The technique consisted of organophilization cation exchange of sodium present in commercial clay, with the quaternary ammonium salt, in case the hexadecyltrimethylammonium bromide, defined from the cation exchange capacity of commercial clay (171 meq/100 g clay). Initially, 100 g of commercial clay dispersed in 1L of deionized water were kept under constant magnetic stirring for about 30 min. Thereafter, 62.59 g of hexadecyltrimethylammonium bromide was added, keeping the mixture magnetically stirred for a period of 4 hours. The resulting solution was vacuum-filtered and washed with deionized water until complete removal of organic materials and residual unreacted salt. The agglomerates were dried in an oven at 55 ± 5 ˚C for 48 h, ground and granulometrically separated to obtain particles of average diameter dp of 0.55 mm.

2.2 Characterization of the adsorbent

The specific surface area of adsorbent material (Sg) and total volume (Vp) and average pore diameter (dp) were determined on a Quantachrome equipment New Model 1200, equipped with software for data analysis from measures adsorption-desorption of N_2. Before analysis, samples were subjected to heat treatment at 60 ° C under vacuum for 48 hours to remove the water adsorbed during handling and possible condensate existing in the pores of the solids. The surface areas of the clays were calculated by the BET method (Brunauer, Emmett and Teller) and pore parameters were determined based on calculations BJH (Barrett-Joyner-Halenda). The porosity, pore size distribution and density of the adsorbent material were obtained by mercury porosimetry (Autopore II brand Micromeritics). The thermal stability of the adsorbent material was determined by thermal analysis (TG / DTG) (Shimadzu-TGA-50) in which samples of clay were subjected to programmed increase of temperature from room temperature to 1000 °C with a heating ratio of 10 °C / min.

Analyses of X-ray diffraction allowed us to evaluate and measure the basal spacing from the clay mineral forming the bentonite, since each plane of a crystal can behave as a reflecting surface for X-rays. The equipment used was from Shimadzu XDR 7000 Kα radiation of copper lambda (λ) = 1.54 Å, which provided the diffraction angles 2 theta (2θ) on a sample in powder form. The basal spacing was obtained due to changes in intensity over the angle 2 theta (2θ) and the distance (d) determined in the first peak intensity less than 10 °, to the studied clays. The baseline distances were calculated using Bragg's Law, described Equation 1.

$$d = \frac{n\lambda}{2sen(\theta)} \tag{1}$$

Where: d is the baseline distance (nm), n is a positive integer, λ is the wavelength of X-rays (nm) and θ is the angle of diffraction (degrees).

2.3 Adsorption Tests

The kinetic removal employing commercial and organoclays were conducted to an initial toluene concentration of 100 ppm. The kinetics of removal was evaluated in a beaker containing 500 mL of aqueous dopant and 5 g of clay (10 gL^{-1} effluent), at initial pH of about 6. Aliquots of solution were collected at intervals of predetermined times. Then the samples were filtered through Millex membranes (0.22 µm) and analyzed by high performance liquid chromatography (HPLC) with a C18 column, mobile phase 28 % acetonitrile, 35 % methanol and 37 % water milli-Q, to determine the amount adsorbed. Kinetic models of pseudo-first order (Lagergren, 1898), pseudo-second order (Ho and McKay, 1999) and intraparticle diffusion (Weber and Morris, 1962), were fitted to the data. To obtain the adsorption isotherms, aqueous solutions of 50 mL of toluene with concentrations varying from 3 to 400 mg / L were mixed with 0.5 g of clay, placed in flasks and subjected to constant stirring (200 rpm) for 4 hours (equilibrium time). Temperature values analyzed were of 25 and 35 ºC. Subsequently, aliquots of solution were collected, filtered and analyzed in (HPLC). Langmuir and Freundlich models were used to evaluate and fit the isotherm data.

3. Results and Discussion

3.1 Characterization of Clays

In Table 1 are shown the values of specific surface area, total volume and average pore diameter of commercial and organophilic clays.

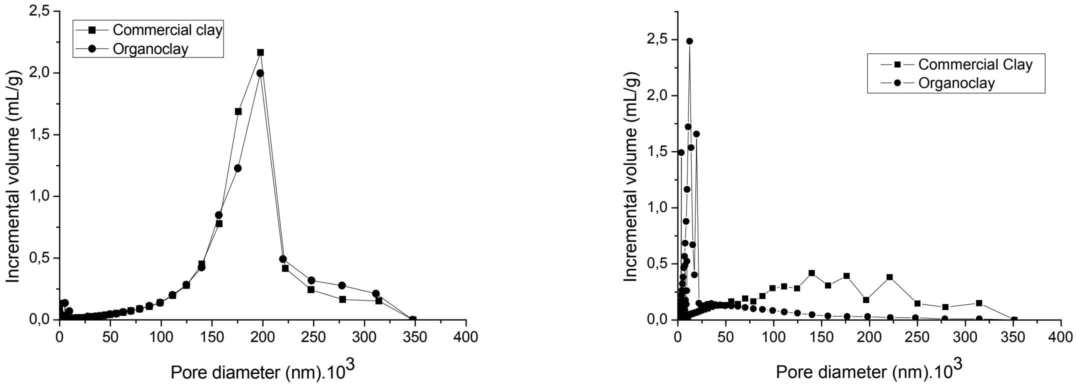
Table 1: Specific surface area and pore parameters of clays

Fluidgel Clay*	Sg (m^2/g)	Vp (cm^3/g)	dp (Å)
Commercial	59.87	0.08630	40.17
Organoclay	6.23	0.01331	26.64

*dp = 0.85mm

After the process of organophilization, there is a significant reduction in the total volume and the average pore diameter of Fluidgel clay, evidenced by a sharp reduction in surface area. This decrease can be attributed to intercalation of the quaternary salt in the organoclay microstructures, which causes an interlayer expansion thereof, such that the cations of the salt can block this space inhibiting the passage of molecules N_2 (Bertagnolli, 2011).

Figure 1 shows the analysis results of mercury porosimetry on samples of clay in powder form and particle.

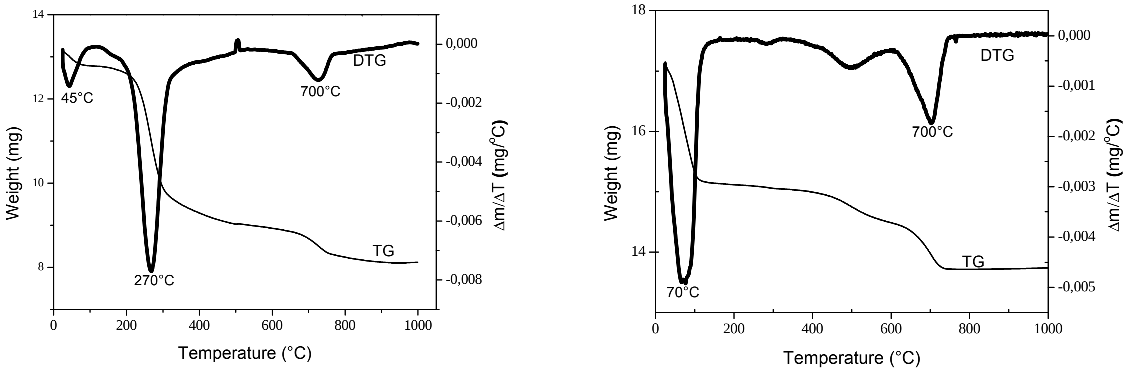


Clay particles (0.55mm)

Clay powder

Figure 1: Mercury porosimetry in samples of clays in the forms of powder and particle

For material in particulate form, both as commercial and organoclay exhibit a concentrated region of macropores between 125,000 and 225,000 nm. As for the clay in powder form, the organoclay has macropores in the region between 5,000 and 25,000 nm and commercial clay between 100,000 and 250,000 nm. The results obtained by the thermogravimetric analysis, as presented in Figure 2, show a region of weight loss between 25 and 150 °C, with a maximum temperature of 45 °C for the organoclay and 70 °C for the commercial clay, attributed to the loss of adsorbed water on the surface of the adsorbent and the water of hydration around the exchangeable cations, whose presence depends on the number of hydrated cations (Na^+, K^+ and Ca^{2+}) in the interlayer. It was also observed that the first peak is significantly less for the organoclay due to the change of connections between the structure of clay and water, caused by organic matter adsorbed, causing the dehydration peak which appears at lower temperatures and with lower intensity. The second region of mass loss observed for the organoclay is between 150 and 550 °C, with a maximum temperature of 270 °C, attributed to the combustion of the organic part derived from quaternary ammonium salt. The third region of weight loss for both clays is between 550 and 800 °C, with a maximum temperature of 700 °C, attributed to the dehydroxylation of the clay mineral structure. These results agree with those reported by Bertagnolli (2011). The values of total weight loss were approximately 20 % for the commercial clay and 38 % for the organoclay. The increase in total mass loss observed for organophilic material can be attributed to the burning of the organic radicals intercalated in the clay structure due to its preparation process.



Organoclay

Commercial clay

Figure 2: Thermogravimetric analysis of organoclay and commercial clay

The results with the XRD for both clays, shown in Figure 3, indicate that the clays are not characterized by a highly crystalline structure, as identified by the diffraction peaks that are not well defined and a peak relative to the plane (001) that has extended format, typical of clay minerals. The occurrence of a peak before $2\theta = 10$ ° is representative of the basal distance d_{001} of smectite clays and tends to be intense, which enables their detection even in small quantities (Bertagnolli, 2011). The peaks at 20 ° and 27 ° are related to smectite and quartz, respectively. The hexadecyltrimethylammonium bromide promotes the modification of the clay structure with the advance angle 2θ, of 6.92 in the commercial clay to 4.29 in the organoclay and, consequently, an increase in basal spacing of 12.76 Å - 20.58 Å calculated by Bragg's Law, after the process of organophilization, This interleaving may show effective quaternary ammonium cations interlamellar layers, increasing the spacing between the clay layers.

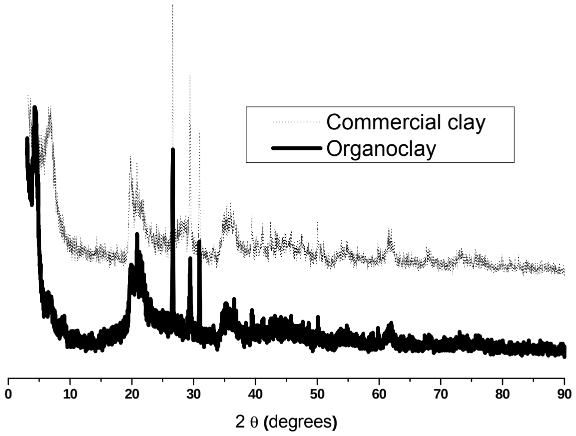


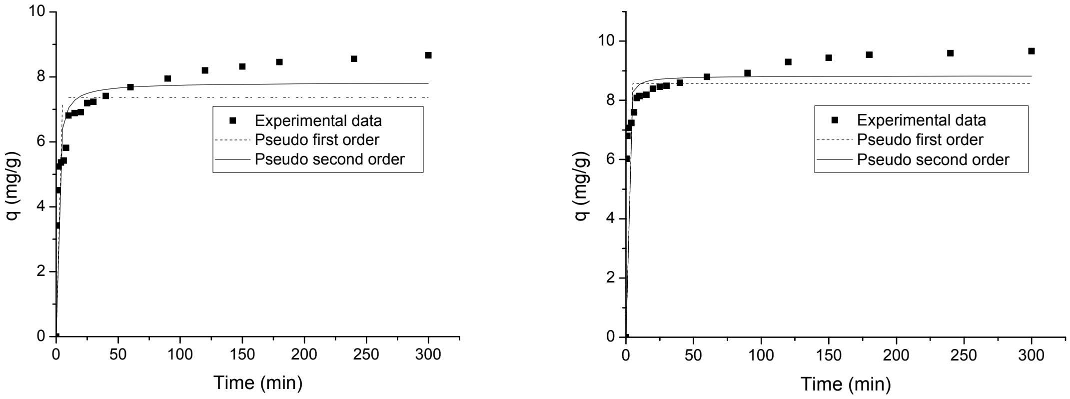
Figure 3: Diffractograms of organoclay and commercial clay

3.2 Adsorption Kinetics

Toluene adsorption kinetic onto Fluidgel and organoclay with their respective fits are shown in Table 2 and Figure 4. It is observed from Figure 4 that the adsorption of toluene increased rapidly during the first hour and sparingly during the contact time remaining, probably due to reduced number of adsorptive sites of beginning of process. The percentage removal of toluene to an equilibrium time of 180 min was 96 % for both clays. However, for commercial clay we observed the formation of a gel when in contact with toluene, hindering an indication of the separation process and their application in dynamic fixed bed system. The kinetic model that best fitted the experimental data obtained for both clays was the pseudo second order model, showing only one active site available for adsorption. Similar results were observed by Moura et al., (2011) evaluating the adsorption of BTX compounds in organo-mesoporous silica, Souza et al., (2011) in adsorption studies of organic compost and Vidal et al., (2012), investigating the removal of BTX compounds in zeolite Y modified with hexadecyltrimethylammonium bromide.

Table 2: Pseudo first order, second order and intraparticle diffusion models parameters

Fluidgel Clay	Pseudo First Order			Pseudo Second Order		
	q_e (mg.g^{-1})	K_1 (min^{-1})	R^2	q_e (mg.g^{-1})	K_2 (min^{-1})	R^2
Commercial	8.57	1.94	0.88	8.83	0.34	0.94
Organoclay	7.36	0.74	0.79	7.83	0.11	0.91
	Intraparticle Diffusion					
	K_{dif} (mg.g^{-1}.min$^{-1/2}$)			C (mg.g^{-1})	R^2	
Commercial	0.76			5.79	0.81	
Organoclay	0.61			4.25	0.84	



Organoclay

Commercial clay

Figure 4: Toluene adsorption kinetics onto organoclay and commercial clay

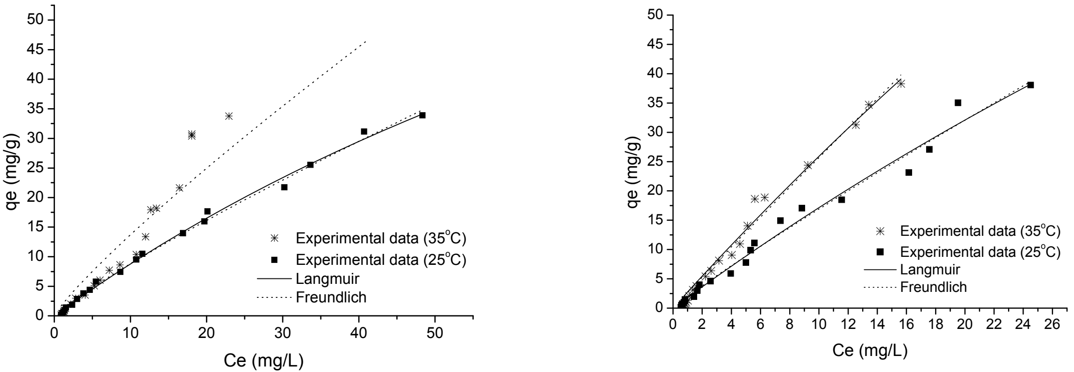
3.3 Adsorption Isotherms

The adsorption isotherms were gotten at temperatures of 25 and 35 ° C. The model fitting to the equilibrium experimental data is shown in Figure 5 and the model parameters are shown in Table 3.

Table 3: Langmuir and Freundlich parameters

Fluidgel Clay	Langmuir							
	25 ºC				35 ºC			
	q_{exp} (mg.g^{-1})	q_{max} (mg.g^{-1})	K (L.mg^{-1})	R^2	q_{exp} (mg.g^{-1})	$q_{máx}$ (mg.g^{-1})	K (L.mg^{-1})	R^2
Commercial	38.07	247.98	0.01	0.98	38.31	410.60	0.01	0.99
Organoclay	33.91	137.75	0.01	0.99	37.10	-	-	-
	Freundlich							
	25 ºC				35 ºC			
	K_F (L.mg^{-1})		n	R^2	K_F (L.mg^{-1})		n	R^2
Commercial	2.02		1.09	0.98	2.67		1.02	0.98
Organoclay	1.18		1.15	0.99	0.94		0.89	0.99

The curves of adsorption isotherms obtained are linear and indicate that the amount of toluene adsorbed (q_e) is proportional to the equilibrium concentration (C_e) of toluene in the fluid phase. Analyzing data, it appears that removal capability was reduced with decreasing temperature, suggesting that the adsorption is of endothermic nature. Comparing the isotherm models evaluated, it is observed that despite the high value of the correlation coefficients obtained with the model adjustment, they only describe well the experimental data for low concentrations of toluene. For higher concentrations, the experimental data cannot be adjusted by the models, which can be observed by the discrepancy between the experimental values (q_{exp}) and calculated values of q_{max} shown in Table 3.



Organoclay

Commercial clay

Figure 5: Adsorption isotherms for organoclay and commercial clay

4. Conclusions

This study demonstrated the potential application of the process of organophilization to improve the adsorption of toluene onto Fluidgel clay. The increased basal spacing and emergence of an additional step of mass loss during thermal analyzes confirm the organophilization of clay Fluidgel, changing its character naturally hydrophilic to hydrophobic and organophilic. The kinetic model of pseudo second order was the best fit to the data obtained for both forms of the clays, emphasizing only one active site available for adsorption process. Regarding the equilibrium data, despite the high value of the correlation coefficients obtained, Langmuir and Freundlich only describe well the experimental data for low concentrations of toluene.

Acknowledgements

The authors would like to acknowledge CNPq and FAPESP for the financial support.

References

Bertagnolli C., Araujo A.L.P., Kleinübing S.J., Silva M.G.C., 2011, Evaluation of Brazilian Organoclay Synthesized in the Laboratory and Commercial. Chemical Engineering Transaction, 24, 1537-1542.

Ho Y.S., McKay G., 1999, Pseudo-second Order Model for Sorption Processes. Process Biochemistry, 34, 451-465.

Lagergren S., 1898, About the Theory of So-called Adsorption of Soluble Substances. Kungliga Svenska Vetenskapsakademiens, Handlingar, 24, 1-39.

Moura C.P., Vidal C.B., Barros A.L., Costa L.S., Vasconcellos L.C.G., Dias F.S., Nascimento R.F., 2011, Adsorption of BTX (Benzene, Toluene, o-Xylene, and p-Xylene) from Aqueous Solutions by Modified Periodic Mesoporous Organosilica, Journal of Colloid and Interface Science, 363, 626-634.

Nourmoradi H., Nikaeen M., Hajian M.K., 2012, Removal of Benzene, Toluene, Ethylbenzene and Xylene (BTEX) from Aqueous Solutions by Montmorillonite Modified with Nonionic Surfactant: Equilibrium, Kinetic and Thermodynamic Study. Chemical Engineering Journal, 191, 341-348.

Paiva, L. B., Morales A. R., Díaz F. R. V., 2008. Organoclays: Properties, Preparation and Applications, Applied Clay Sci. 42, 8-24

Souza R.S., Didi H.S., Silva M.G.C., 2011, Removal of Benzene from Aqueous Solution Using Raw Red Mud. Chemical Engineering Transactions, 24, 1225-1230.

Vidal C.B., Raulino G.S.C., Barros A.L., Lima A.C.A., Ribeiro J.P., Pires M.J.R., Nascimento R.F., 2012, BTEX Removal from Aqueous Solution by HDTMA-modified Y Zeolite, Journal of Environmental Management, 112, 178-185.

Weber W.J., Morris J.C., 1962, Advances in Water Pollution Research: Removal of Biologically Resistant Pollutants from Waste Waters by Adsorption, in: Proceedings of International Conference on Water Pollution Symposium, Pergamon Press, Oxford, 2, 231-266.

Zhou Q., He H.P., Zhu J.X., Shen W., Frost R.L., Yuan P., 2008, Mechanism of p-Nitrophenol Adsorption from Aqueous Solution by HDTMA$^+$ Pillared Montmorillonite – Implications of Water Purifications. Journal of Hazardous Materials, 154, 1025-1032.