J Therm Anal Calorim (2011) 105:915–920
DOI 10.1007/s10973-011-1471-3

Partially exchanged organophilic bentonites

Part II. Phenol adsorption

Emerson Paes Barreto · Mariana Santos Lemos · Isabelle Bulhoes Aranha · Pedro Mauricio Büchler · Jo Dweck

ESTAC2010 Conference Special Issue

Abstract Phenol is a pollutant that has caused many problems even when present in low concentrations and still represents an environmental problem with difficult solution. This paper presents a study of phenol adsorption by organophilic clays, obtained from aVerde Claro bentonitic clay, from Bravo, Paraíba State, Brazil, at different partial cation exchange degrees with hexadecyltrimethylammonium (HDTMA) chloride, at increasing reacting ratios, from 20 to 120 mmol/100 g of clay, which were characterized in a previous paper. By using Freundlich isotherms obtained for each case, which presented the best correlation coefficients with experimental data, it can be seen that for equilibrium concentrations up to 0.53 mmol L^{-1} of phenol, the adsorptive capacity decreases for organophilic bentonites obtained at cation exchange degrees higher than 80 mmol/100 g of clay. This indicates that in these cases, the higher is the exchange by organic cation, the higher is the difficulty for the phenol diffusion and sorption in the interlayer space of the organophilic clays. For higher equilibrium concentrations, the maximum adsorption occurs for the organophilic bentonite obtained at 100 mmol/100 g of bentonite exchange.

Keywords Phenol · Organophilic clays · Partial cation exchange · Adsorption

E. P. Barreto · P. M. Büchler
Chemical Engineering Department, São Paulo State University, Avenida Professor Luciano, Gualberto 380, São Paulo, SP 05424-970, Brazil

M. S. Lemos · I. B. Aranha · J. Dweck (✉)
School of Chemistry, Rio de Janeiro Federal University, Bloco E do CT Sala E206, Rio de Janeiro, RJ 21949-900, Brazil
e-mail: jodweck@yahoo.com.br

Introduction

The result of systematic negligence of the environment for many years, and still likely to meet, face major problems with pollution of our soil, water, and air. Pollution affects directly the life quality of people, as it harms the health of people living in contaminated regions. The phenol is a pollutant that has caused many problems and even at low concentrations, it represents an environmental problem of difficult solution. Phenolic compounds are considered pollutants since 1975 [1]. Contaminants such as phenolic compounds are common in industrial effluents from the petrochemical industry and industries that use it, such as the manufacture of phenolic resins, epoxy resins and adhesives, and polyamide for various applications [2].

Bentonite clays are those which consist essentially of smectite and whose properties are dictated by the component minerals [3]. The clays possess negative surface charge due to isomorphic substitutions [4, 5]. Sodium bentonite are hydrophilic [6] and do not adsorb organic pollutants. Therefore, they need to be transformed into organophilic clays for that purpose. This transformation may be done through cation exchange of the metal original cations by organic cations from quaternary ammonium salts, which adsorb organic pollutants [6]. These salts may have from one to four hydrocarbon groups linked directly to the nitrogen atom of the organic cation. When added to aqueous dispersions of the sodium smectites obtained from original clays, these organic cations replace sodium cations and settle in the interlayer regions 2:1 of the smectite clay mineral turning it organophilic.

The replacement of the inorganic cations by quaternary ammonium cations reduces the hydration of the clay, increases the interlayer spacing and simultaneously decreases the surface area of aluminosilicates. Depending on the extent that the inorganic cation is replaced by organic cation, the properties change gradually from highly hydrophilic to increasingly hydrophobic [7]. The property of organoclays to adsorb organics, suggests its effective use in the retention of organic chemical pollutants that are present in hazardous wastes, industrial wastes, and effluents [8].

The removal of phenol from aqueous effluents is difficult because of several factors related to their properties as its high solubility in water at ambient temperature, low vapor pressure, and its tendency to oxidation. The processes used to remove phenol are: solvent extraction, adsorption on activated coal, chemical oxidation, electrochemical extraction, and the biological treatment. The most used is activated coal [9] and as it is very expensive, several non-conventional sorbent materials have been object of study as alternative ways for the removal of organic contaminants from aqueous solutions. These alternative sorbents must have appropriate characteristics for its use in industrial scale, such as high sorption capacity, abundance, and low cost. This is the reason for the use of organophilic clays [10].

The study of inorganic and organic pollutants removal by organophilic clays has aroused great environmental interest. Their use in adsorption of pollutants has been used in soil remediation through the adsorption of 2,4-dichlorophenol by organoclay/aquifer material mixtures [11], removal of 2-phenylphenol from aqueous solutions [12], treatment of emulsified oily wastewater [13], aquifer bioremediation through the adsorption of chlorobenzene [14], adsorption of phenol [15], treatment of phenol pollution in wastewater from oil refinery by dual cation modified bentonite [16], adsorption of organic contaminant and heavy metal [17], to enhance carbon filtration [18], adsorption of phenanthrene from distilled and saline water [19], and adsorption of phenthoate and acetochlor from polluted water [20].

This work has as main objective, to study the adsorption of phenol by organophilic clays obtained by partial and total exchange of the inorganic cations by hexadecyltrimethylammonium of a polycationic Verde Claro bentonite from Boa Vista, Paraíba State, Brazil, to study the process and mechanism of adsorption as a function of the degree of cation exchange.

Experimental

A Verde Claro bentonite (VC) was used, original from Boa Vista, Paraíba State, Brazil, provided by Bravo Mining Co, which has a greenish color. The original sample was milled into samples 100% passing in ASTM no. 200 sieve (74 μm). P.A. anhydrous sodium carbonate, provided by Casa Americana de Artigos para Laboratório LTDA, was used to obtain the respective sodium clay (VCNa) from original clay. Clariant S.A provided hexadecyltrimethylammonium chloride. P.A. phenol, provided by Casa Americana de Artigos para Laboratório Ltda, was used to prepare the aqueous solutions to simulate contaminated effluents.

Using the process developed by Valenzuela Diaz [21], the VCNa sodium bentonite was obtained by cation exchange through the addition of the 120 meq of sodium carbonate per 100 g of the original bentonite clay in aqueous dispersions containing 4% of clay. After resting for 24 h, reactions with $X = 20$, 40, 60, 80, 100, and 120 meq of hexadecyltrimethylammonium chloride were performed to obtain the respective VCX organophilic clays. After another rest for 24 h, these clays were obtained by filtering and washing with demineralized water until negative test of the filtrate with silver nitrate. Then the organoclay filter cakes were dried at 60 °C, followed by milling until obtaining particles 100% passing in ASTM no. 200 sieve.

XRD diffractograms were obtained in a Bruker-D4 endeavor equipment, already presented in part I.

The experiments of adsorption of phenol by organoclays were conducted in duplicate, by the method proposed by Büchler [22], and the presented data are average values. To simulate effluent conditions, phenol aqueous solutions were prepared at initial concentrations of 2.13, 4.26, 6.38, 8.51, and 10.64 mmol L^{-1}. Aliquots of the solutions were analyzed by total organic carbon (TOC) determination in a Shimadzu, model TOC-5000A equipment. To 20 mL aliquots of each initial phenol concentration solution, 0.5 g of organoclay was added, followed by agitation at constant temperature (25 °C) for 24 h.

At the end of this time, centrifugation for 30 min was promoted at 1000 rpm. Total organic carbon (TOC) determinations of the supernatant solutions were analyzed to determine the respective phenol equilibrium concentration. The corresponding amount of phenol in each solution was obtained by multiplying the TOC results by the ratio between the mass of one mol of phenol and its corresponding mass of carbon. The amount of phenol adsorbed by each organoclay was calculated from the difference between the initial and equilibrium concentrations, in mg L^{-1} of solution. This value, multiplied by the value of initial solution volume and divided by the used mass of clay, provides the mass of phenol adsorbed per mass of adsorbent clay, which was then converted in mmols of adsorbed phenol per 100 g of organophilic clay to be easier to compare the present results with results from other laboratories.

The analysis of the results of the phenol adsorption experiments by the partially exchanged organoclays, were performed by using Freundlich isotherms, which consider the non-uniformity of real surfaces [23], according to equation $\log \theta = \log kf + (1/n)\cdot\log C$, where θ is the mmols of phenol adsorbed per 100 g of clay; C is phenol equilibrium concentration in mmol L^{-1} of solution; n is reactivity of energetic sites of the clay, and kf is adsorption coefficient [23].

XRD characterization

As seen in Fig. 1, basal spacing of VCNa clay is lower than that of the original VC clay. The basal spacing of the VC20 and VC40 organoclays is practically equivalent, and from their value it seems that even at this degree of cation exchange, a single layer of organic radical is formed in the interlayer spacing of the clay. As the amount of quaternary salt available for exchange with sodium ion is increased, an inflection point occurs at the point correspondent to the use of 70 meq, after which the increase in basal spacing by increasing the amount of quaternary salt begins to decrease, reaching new values, in the order of 2.3 nm for VC100 and VC120 clays, characterizing the formation of a pseudo trilayered interlamelar spacing [24]. As was seen in part I, the actual mass of exchanged organic cation of VC120 clay is a little higher than that of VC100 clay, what explains their similar behavior and adsorbing properties as will be discussed in next items.

Analysis of the phenol adsorption process

The amount of phenol adsorbed changed according to its initial concentration in the solution and to the degree of cation exchange of the organoclay. In general, the higher is the adsorbed amount per unit mass of clay, the higher is the initial concentration of the solute and the higher is the degree of effective cation exchange [25–30]. In Fig. 2 the values of adsorbed phenol mass per unit mass of clay are shown as a function of the amount of quaternary ammonium salt used to obtain the different organoclays, for each initial concentration of phenol.

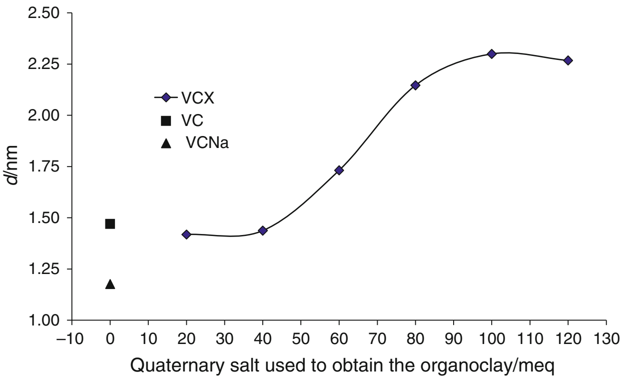

Fig. 1 Basal spacing of VCX organoclays as a function of quaternary ammonium salt used for the exchange

Phenol adsorption data follow Freundlich isotherm model, as shown in Fig. 3, where the mass of adsorbed phenol is shown as a function of the equilibrium concentration for each case. From the excellent linear correlation coefficients obtained for each case, the applicability of the Freundlich model is evidenced within the limits of initial phenol concentration used for the adsorption essays, which also indicates the non-uniformity of the adsorption areas [23].

Figure 4 curves shows the amount of phenol (in mmol) that can be adsorbed, as a function of the equilibrium concentration, per 100 g of each VCX organoclay clay, calculated from the respective Freundlich isotherm expression. It can be noticed that for equilibrium concentrations (C) greater than 1.17 mmol L^{-1}, generally, the higher is the number of milliequivalents (meq) of exchanged quaternary ammonium radical, the higher is the amount of adsorbed phenol. For equilibrium concentrations lesser than 1.17 mmol L^{-1} this does not occur and VC80 clay curve shows higher phenol adsorption than VC100 and VC120 clays, for values of $C < 0.85$ mmol L^{-1}. It is also observed for VC20 and VC60 cases an almost linear behavior of the amount of phenol adsorbed with equilibrium concentration, which does not happen for VC80, VC100, and VC120 clays.

From Freundlich equation, the higher is the equilibrium concentration, the higher is the amount of adsorbed phenol, which is also due to the greater concentration of phenol in the initial solution. However, the higher is the difference between the concentration of phenol in the external solution and the solution adhering to the surface of the particles of organoclay, the higher is the capacity and speed of diffusion of phenol to the sites where the adsorption occurs, which also depends on the free space available for this diffusion. This may explain the behavior of VC100 and VC120 clays with respect to VC80 clay for lower phenol equilibrium concentrations.

Figure 5 shows the phenol adsorbed by the organoclays, as a function of the different amounts of quaternary salt used for their synthesis, for a same equilibrium concentration of phenol. It is observed that in all cases from 20 to 80 meq of quaternary ammonium salt used to form the organoclay, the greater is the amount of cations of quaternary ammonium salt used and present in the organoclay, the greater is the amount of phenol adsorbed, indicating an apparent same adsorption capacity of the organic phase in these organoclays.

For equilibrium concentrations up to 0.53 mmol L^{-1} the adsorbed amount decreases for VC100 and VC120 organoclays indicating that in these cases, the largest amount of organic cation exchanged, promotes a greater difficulty for diffusion and adsorption of phenol in the available interlayer space of these organoclays. As the equilibrium concentration increases, as a consequence of a higher concentration of

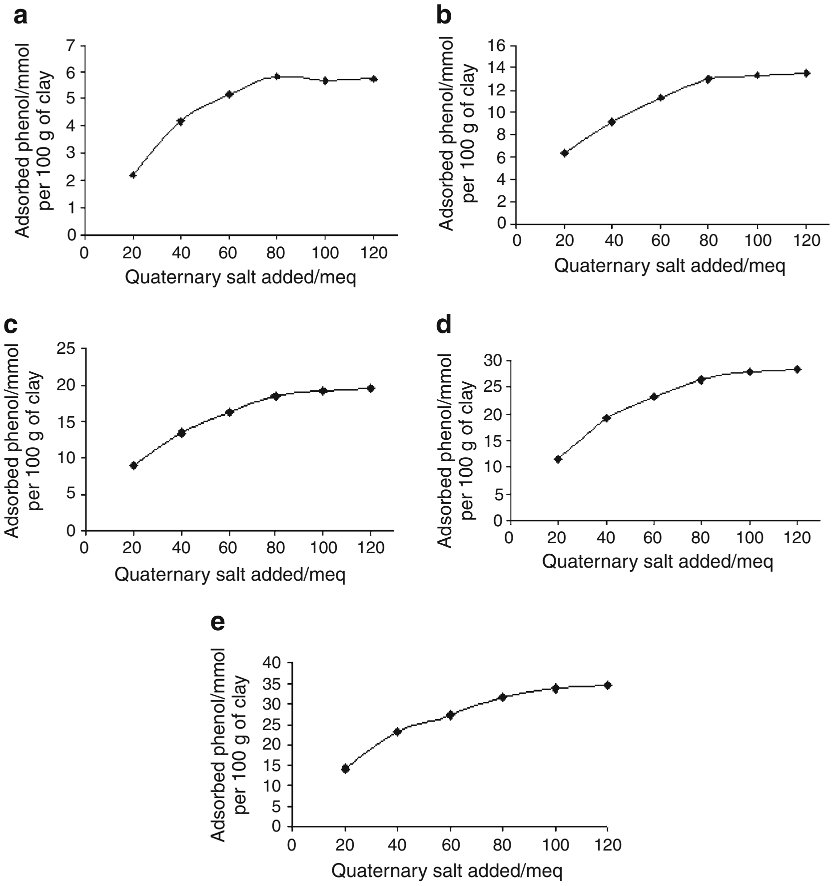

Fig. 2 Adsorbed phenol as a function of the cation exchange degree of the organoclay, for different initial phenol concentrations: **a** 2.13, **b** 4.26, **c** 6.38, **d** 8.51, **e** 10.64 mmol L^{-1}

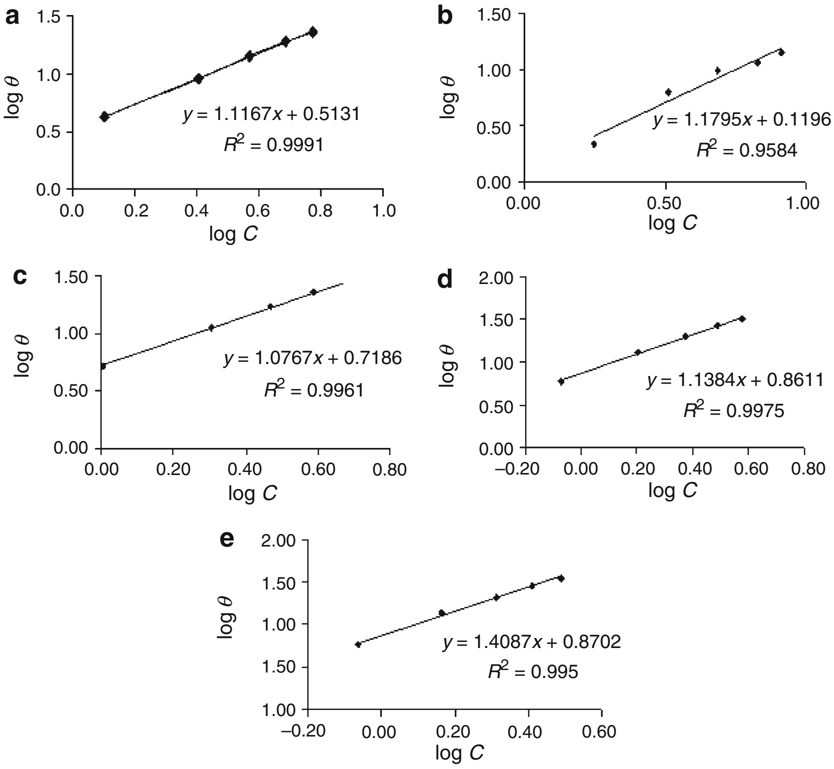

Fig. 3 Freundlich isotherms for the adsorption of phenol by different organoclays **a** VC20, **b** VC40, **c** VC60, **d** VC80, **e** VC100, **f** VC120

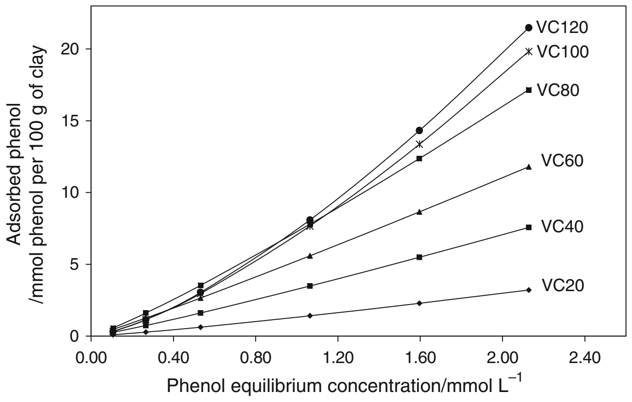

Fig. 4 Phenol adsorbed by differently exchanged organoclays, as a function of phenol equilibrium concentration

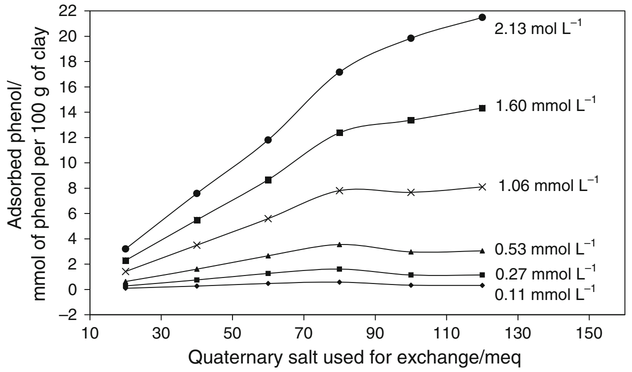

Fig. 5 Adsorption of phenol by the organoclays obtained at different exchange degrees as a function of phenol equilibrium concentration and the number of milliequivalents of quaternary ammonium salt used for the exchange

phenol in the original solution, at $C = 1.06$ mmol L^{-1} there is a limit on the maximum amount of phenol that can be adsorbed. For equilibrium concentrations greater than 1.06 mmol L^{-1}, the amount of phenol adsorbed increases with increasing equilibrium concentration, but with a smaller variation due to the increase of the quaternary ammonium salt present, when compared to what happened to the case of VC80 organoclay. This fact confirms the greater difficulty of adsorption for the organoclays obtained by exchange of more than 80 meq of organic cation. In cases of a greater amount adsorbed it may be occurring a secondary adsorption with weaker links on the outside surface of the organoclay particles.

Conclusions

- The Freundlich isotherms represent with good correlation coefficients the data of phenol adsorption by organoclays obtained from the Verde Claro bentonite with different degrees of substitution of cationic hexadecyltrimethylammonium.
- For a given equilibrium concentration, the amount of phenol adsorbed per unit mass of organoclay depends on the degree of substitution of the sodium ions by the organic radical.
- Analyses of the interplanar basal spacing by X-ray diffraction, indicate that a monolayer is formed in VC20 and VC40 organoclays, which increases gradually depending on the amount exchanged organic radical, to a new limit when a pseudo molecular trilayer is formed in the case of VC100 and VC120 organoclays, which present a same basal spacing.
- There is practically a same limit on the maximum phenol adsorption capacity for VC100 and VC 120 organoclays. For VC20 to VC80 organoclays, the higher is the amount of cations of quaternary ammonium salt present in the organoclay, the greater the amount of phenol adsorbed, indicating apparently the same adsorption capacity in these cases.
- As the equilibrium concentration increases, in the case of 1.06 mmol L^{-1}, there is a limit on the maximum amount of phenol that can be adsorbed.
- Although for equilibrium concentrations of phenol higher than 1.06 mmol L^{-1}, the amount of phenol adsorbed increases with increasing equilibrium concentration, with possible secondary adsorption, there is a minor variation of this increase with the increasing degree of cation exchange in the case of the organoclays obtained with 80 or higher meq of cation exchange.

Acknowledgements This study was performed with the financial support of the Brazilian National Research Council (CNPQ), Brazilian Ministry of Education (CAPES), and São Paulo State Research Foundation (FAPESP).

References

1. Villas-Bôas DMF. Microbiological study of activated sludge system with emphasis on phenol degrading bacteria. São Paulo, 1999. D.Sc. Thesis, Polytechnique School, São Paulo University.
2. Vianna MMG. Study in laboratory scale of the adsorption of vinasse components by organophilic clay, São Paulo, 2001. M.Sc. Thesis, Polytechnic School, São Paulo University.
3. Souza Santos P. Clay science and technology, vol. 3. 2nd ed. São Paulo: Edgar Blucher; 1992.
4. Rodríguez-Sarmiento DC, Pinzón-Bello JA. Adsorption of sodium dodecylbenzene sulfonate on organophilic bentonites. Appl Clay Sci. 2001;18:173–81.
5. Hower WF. Adsorption of surfactants on montmorillonite. Clays Clay Minerals. 1970;18:97–105.
6. Souza Santos P. Clay science and technology, vol. 1. 2nd ed. São Paulo: Edgar Blucher; 1989.

7. Nzegung VA, Voudrias EA, Nkedi-Kizza P, Wampler JM. Weaver CE organic cosolvent effects on sorption equilibrium of hydrophobic organic chemicals by organoclays. Environ Sci Technol. 1996;30:89–96.
8. Sharmasarkar S, Jaynes W, Vance G. BTEX sorption by montmorillonite organo-ckays: TMPA, ADAM, HDTMA. Water Air Soil Pollut. 2000;119:257–73.
9. Wilberg K, Assenhaimer C, Rubio J. Removal of aqueous phenol catalysed by a low purity soybean peroxidase. J Chem Technol Biotecnol. 2002;77:851–7.
10. Nunes DG, Léon ATD, Rubio J. Innovation in the removal of contaminants in adsorbent and unconventional reactors. Learning, creating and integration in undergraduate research proceeding of UFRGS. 2002; 37–50.
11. Pernyeszi T, Kasteel R, Witthuhn B, Klahre P, Vereecken H, Klumpp E. Organoclays for soil remediation: adsorption of 2,4-dichlorophenol on organoclay/aquifer material mixtures studied under static and flow conditions. Appl Clay Science. 2006; 32(3–4):179–89.
12. Seki Y, Ogawa M. The removal of 2-phenylphenol from aqueous solution by adsorption onto organoclays. Bull Chem Soc Jpn. 2010;83(6):712–5.
13. Yuan B, Wang L, Hua S, Jiang B. Complex organoclay adsorbent for treatment of emulsified oily wastewater. Huanjing Wuran Yu Fangzhi. 2006;28(6):448–51.
14. Witthuhn B, Klauth P, Pernyeszi T, Vereecken H, Klumpp E. Organoclays for aquifer bioremediation: adsorption of chlorobenzene on organoclays and its degradation by RHODOCOCCUS B528. Water Air Soil Pollut. 2006;6(3–4):317–29.
15. Cavalcanti JVFL, Abreu MCA, Motta Sobrinho MA, Barauna OS, Portela LAP. Preparation and use of a organophilic smectitic clay for adsorption of phenol. Quim Nova. 2009;32(8):2051–7.
16. Zhen W, Pang G, Qi X, Li Z. Study on treatment of phenol pollution in wastewater from oil refinery by dual cation modified bentonite. Feijinshukuang. 2006;29(6):58–60.
17. Lee J-J, Park JW. Organoclay as a dual sorbent for organic contaminant and heavy metal. Div Environ Chem. 2001;41(1): 296–300.
18. Alther G. Using organoclays to enhance carbon filtration. Waste Man. 2002;22(5):507–13.
19. El-Nahhal YZ, Safi JM. Adsorption of phenanthrene on organoclays from distilled and saline water. J Colloid Interface Sci. 2004;269(2):265–73.
20. Liao M, Xie X-M. Adsorption of phenthoate and acetochlor from water by clays and organoclays. J Environ Sci. 2004;16(5): 738–41.
21. Valenzuela Diaz FR. Preparation of organophilic clays from Brazilian smectitic clay. Key Eng Mater. 2001;189:203–7.
22. Buchler PM. Studies in laboratory scale, the adsorption of the organic components of vinasse in sodium smectites exchanged with tetramethylammonium cation, given its use in stabilization ponds. São Paulo, 1987. Thesis, Polytechnic School, University of São Paulo.
23. Sodré FF. Use of physical chemical models in the study adsorption behavior of copper. Clay Soils. 2001;24:324–30.
24. Boyd SA, Jaynes WF. Role of layer charge in organic contaminant sorption by organoclay. In: Layer charge characteristics of 2:1 silicate clay minerals, CMS Workshop Lectures. Vol. 6. Clay Mineral Society; 1994.
25. Saltzman S, Yariv S. Infrared study of the sorption of phenol and p-nitrophenol by montmorillonite. Soil Sci Soc Am Proc. 1975;39: 474–9.
26. Ovadyahu D, Yariv S, Lapides I. Mechanochemical adsorption of phenol by TOT swelling clay minerals. I. Thermo-IR-spectroscopy and X-ray study. J Therm Anal. 1998;51:415–30.
27. Vianna MMG, Dweck J, Kozievitch VJ, Valenzuela-Diaz FR, Büchler PM. Characterization and study of sorptive properties of differently prepared organoclays from a Brazilian natural bentonite. J Therm Anal Calorim. 2005;82:595–602.
28. Vianna MMG, Dweck J, Kozievitch VJ, Quina FH, Carvalho FMS, Nascimento CAO. Toluene and naphthalene sorption by iron oxide/clay composites part I. Materials characterization. J Therm Anal Calorim. 2010;100(3):889–96.
29. Vianna MMG, Dweck J, Kozievitch VJ, Quina FH, Carvalho FMS, Nascimento CAO. Toluene and naphthalene sorption by iron oxide/clay composites part II. Adsorption experiments. J Therm Anal Calorim. 2010;101(3):887–92.
30. Yermiyahu Z, Lapides I, Yariv S. Synthesis and thermo-XRD-analysis of the organo-clay color pigment. Naphthylazonaphthylamine–montmorillonite. J Therm Anal Calorim. 2007;88(3): 795–800.