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Evaluation of BTEX and phenol removal from aqueous solution by multi-solute adsorption onto smectite organoclay

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HIGHLIGHTS

- The removal process of BTEX and phenol was evaluated.
- Smectite clay was converted to organophilic adsorbent by Na_2CO_3 and HDTMA treatment.
- BTEX were removed from the liquid phase with approximately the same specific rates.
- Phenol was an exception, adsorbing slowly.
- The removal efficiencies in the multicomponent system was: $E > X > T > P \approx B$.

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ABSTRACT

The removal process of BTEX and phenol was evaluated. The smectite organoclay for single-solute system reached removal was evaluated by adsorption on smectite organoclay adsorbent by kinetic and equilibrium efficiencies between 55 and 90% while was reached between 30 and 90% for multi-solute system at 297 K and pH 9. The Langmuir–Freundlich model was used to fit the experimental data with correlation coefficient between 0.98 and 0.99 providing kinetic and equilibrium parameter values. Phenol and ethylbenzene presented high maximum adsorbed amount, 8.28 and 6.67 mg/g, respectively, compared to the other compounds for single-solute. Toluene and p-xylene presented high values of adsorption constant which indicates a high adsorption affinity of compounds to organoclay surface and high binding energy of adsorption. Phenol presented low kinetic adsorption constant value indicating slow rate of adsorption.

1. Introduction

Phenol and BTEX (benzene, toluene, ethylbenzene and xylenes) are often present in wastewater from chemical and petrochemical industries. Because of their high toxicity to human health and for the environment, stringent regulations have been imposed on concentration of these compounds inside wastewaters for the safe discharge [1]. Phenol and BTEX can be included in the list of organic compounds identified as hazardous chemicals due to adverse effects on human health at very low concentrations [2].

Different methods such as thermal oxidation, catalytic oxidation, absorption, condensation, membrane separation and adsorption have been used for removal of organic compounds from wastewaters. The combined processes also are widely used for the treatment of organic contaminants in wastewater. The combined carbon-activated sludge process has been used in order to improve the efficiency of this process [3] considering that the process has great potential to control effluent toxicity from oil refineries.

The adsorption process is one of the most efficient methods to remove pollutants in wastewater. This process is indicated as a secondary treatment for low level polluting liquids and through continuous process (fixed bed of adsorbent or moving bed of adsorbent) can be used to treat large volumes of liquid effluents. Removal of phenol and BTEX from chemical or petrochemical liquid effluents by adsorption can be evaluated as a multicomponent adsorption problem. Thus the solute–adsorbent interactions must be considered taking into account the different adsorbent sites and the adsorption selectivity of the solutes.

Attentions have been focused on adsorbent performances that depend on their natures and are related to adsorption capacity and regeneration. Some materials such as resin [1,3], *Moringa oleifera* pods [4], rice bran [5], and bagasse fly ash [6] have been used as adsorbent for removal of organic compound by adsorption.

Recently, there has been an increasing interest in the study of adsorption process for removing aqueous organics species using organoclays [7–22]. These adsorbent materials are obtained from

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Nomenclature

BTEX	benzene, toluene, ethylbenzene and xylenes
i	component: b (benzene); t (toluene); e (ethylbenzene); x (xylenes) and p (phenol)
CEC	cation exchange capacity
HDTMA	hexadecyl trimethyl ammonium chloride
XRD	X-ray diffraction
HPLC	high-performance liquid chromatography
C_{0i}	component initial concentration in the liquid phase (mg/L)
C_i	component concentration in the liquid phase (mg/L)
d_{001}	basal spacing (Å)
k_a	kinetic adsorption constant ($L^n/(g\,min\,mg^{n-1})$)
k_d	kinetic desorption constant (mg/(g min))
K	adsorption constant $(L/mg)^n$
K_d	multi-solute partition coefficient
K_{ow}	octanol–water partition coefficient
k_1	constant of pseudo-first-order adsorption rate (min^{-1})
k_2	constant of pseudo-second-order adsorption rate (g/mg)/min
m_s	mass of adsorbent (g)
n_i	heterogeneity factor
q	adsorbed amount (mg/g)
q_e	adsorbed amount at equilibrium (mg/g)
$q_{m,i}$	maximum BTEX and phenol amount adsorbed at saturation conditions (mg/g)
S_p	specific surface area (m^2/g)
T	temperature (K)
V_p	total pore volume (cm^3/g)

modifications to allow the development of organophilic properties of clay minerals. The organoclays are usually prepared using a quaternary ammonium cation $[(CH_3)3NR]^+$ or $[(CH_3)2NR_2]^+$, where R is an organic radical. The physical properties and adsorptive capacity of organoclays depend on the molecular size of the R group [23].

Some researchers [2,8,12,18–21] have published studies about phenol and BTEX adsorption by organoclays in which the affinity of these components is discussed.

The adsorption affinities of BTEX compounds for organoclays were studied and the preference order of adsorption was related to physicochemical properties of compounds: partition coefficient, hydrophobicity, polarity, structure and molecular size [18–21].

Smectite clays and their modified forms can present superficial characteristics that indicate a variety of different adsorption sites. Silanol groups, aluminum, silicon and organic radicals in organoclays can promote adsorption allowing interactions with nonionic polar organic compounds. Affinity interactions between the clay adsorbent and a different nonionic aromatic organic compound can be related to their polarities. The BTEX compounds can present polarity due to π electrons in an aromatic ring by adding inductive effects promoted by methyl and ethyl groups.

Adsorption isotherms of decolorization of maize oil follow the Freundlich equation, indicating the existence of heterogeneous adsorption sites on the solid's surface. Heterogeneity was attributed both to different active centers on the smectite surface (Brönsted and Lewis centers) and to the different phases present in the adsorbent bentonite, such as illitic layers and clinoptilolite, which also have active centers on their surfaces [24].

The present work investigated the removal of aromatic compounds, phenol and BTEX, by adsorption process through the contact between single-solute, multi-solute system and a smectite organoclay. Evaluations were performed considering kinetic and equilibrium approaches. The removal efficiencies were quantified and related to the pH of aqueous solution. The Langmuir–Freundlich model was used to fit the experimental data providing the values for kinetics and equilibrium parameters. Based on the order of magnitude of the parameters from single-solute system, predictions were made to justify the behavior of the multicomponent system.

2. Materials and methods

2.1. Preparation of adsorbent

The organoclay was synthesized by an ion exchange between smectite clay and quaternary ammonium salt. The smectite clay presenting cation exchange capacity (CEC) value of 78.3 mequiv./100 g was obtained from Paraiba, Brazil and ground to 200 mesh size for further use. The clay preliminary was converted into polycationic clay by adding sodium salt and then converted into organophilic by the treatment with the cationic surfactant hexadecyltrimethylammonium chloride (HDTMA).

Initially, 10 mL of an aqueous solution of sodium carbonate (5.00 mequiv. of sodium) was added to a dispersion formed by 50.0 g of clay and water. The mixture was placed in a glass batch reactor at 800 rpm stirring speed for 3 h at 318 K. After reaction the Na-saturated clay was vacuum filtered, washed with deionized water for removal of excess sodium and dried at 373 K for 12 h.

The organoclay was prepared by ion exchange between Na^+ and $HDTMA^+$ in relative concentration 150% CEC. Then, the material was dried at 333 K for 48 h, ground to 200 mesh and ready to be used as adsorbent.

2.2. Adsorbate solutions

Phenol and the BTEX chemicals (purity: 99.95–99.99 wt.%; Ultra Scientific, USA) were used to prepare the adsorbate stock solutions in 0.20 wt.% methanol. There is no meaningful interference from methanol on the adsorption measurements of the compounds studied over the concentration range [25]. The solutions were used for both kinetic and equilibrium isotherm experiments, in order to quantify the adsorbent capacity and process efficiency.

2.3. Analysis

Standard X-ray diffraction analysis (XRD) was performed for the samples of modified and ordinary smectite clay. The basal spacing (d_{001}) of surfactant-modified smectite was determined by a Rigaku diffractometer with Cu Kα radiation.

The quantitative analysis of BTEX and phenol aqueous solution was performed by high performance liquid chromatography (HPLC, Schimadzu, LC Solution) analysis using the following operational characteristics: 210 nm wavelength UV detector, 20 μL injection volume; C18 chromatographic column; 313 K column temperature, acetonitrile/methanol/water (28:35:37, v/v) mobile phase according to the method used by Breitkreitz et al. [26].

2.4. Effect of pH

The influence of pH was investigated on the removal of BTEX and phenol by the smectite organoclay. The system adsorbent/-adsorbate was evaluated at pH 4, 7 and 9 where the concentration of each compound in single-solute and in the mixture was equivalent to 10.0 mg/L. BTEX and phenol solutions were prepared at controlled temperature (296 ± 1 K) to avoid evaporation losses. The solutions were kept under constant stirring for 15 min to complete homogenization of the mixture. A volume of 50.0 mL of each solution was placed in contact with 1.0 g of organoclay. The pH