

Removal of BTEX from Aqueous Solution Using Organokaolinite

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Abstract

The effectiveness of hexadecyltrimethylammonium (HDTMA) cation exchanged with kaolinite clay (corresponding to 50% of the cation exchange capacity (CEC) of the clay) in the removal of BTEX (benzene, toluene, ethylbenzene and xylene) present in the water soluble fraction (WSF) of crude oil was studied using batch kinetic and isotherm studies. Laboratory batch kinetic and isotherm studies were carried out using various conditions of contact time and initial adsorbate concentrations at ambient temperature. The results of the BTEX adsorption experiments onto unmodified and surfactant-modified kaolinite (SMK) clay showed that SMK had higher capacity for removing BTEX from aqueous media. Kinetic studies followed pseudo-second-order kinetics and gave values of the rate constant for BTEX removal of the order of $4.5 \times 10^2 \text{ g/mg.min}^{-1}$. The Langmuir, Freundlich and Temkin models were used to evaluate the BTEX adsorption capacity by SMK. The Langmuir model was found to be more suitable in describing the adsorption process having a correlation coefficient value of 0.999.

Keywords: Benzene, Toluene, Ethylbenzene, Xylene, Adsorption, Organokaolin

Introduction

The Petroleum industry has witnessed increase in production in the last few decades. Due to their extensive and increasing application as both energy sources and raw materials in many industries, gasoline and its derivatives have been considered the main sources of environmental pollutants [1]. Gasoline is a mixture of many volatile

and semi-volatile hydrocarbons including benzene, toluene, ethylbenzene and o-, m-, and p-xylene (BTEX). These hazardous aromatic hydrocarbons are the major water-soluble constituents of gasoline that contaminate soils and natural waters [2]. These organic pollutants released from gasoline spills can lead to surface and ground water contamination which can be potentially hazardous to vegetation, biota and humans. Petrochemical wastewater is a complex mixture of hydrocarbon compounds, sulphur oxides, metals and numerous toxic organic compounds [3]. BTEX compounds have been classified as priority pollutants [4] as exposure leads to adverse health effects which include cancer, irritation of mucosal membranes, haematological changes, impairment of the central nervous system, respiratory problems and disruption of liver and kidney [4 – 6]. These compounds even in small concentrations cause chronic toxicity and may permanently damage the central nervous system [1]. It has been reported [4] that the maximum permissible concentrations of benzene, toluene, ethylbenzene and xylene in drinking water are 0.01, 0.7, 0.3 and 0.5 mg/l respectively. It is therefore essential to remove BTEX from water and wastewater using effective cleanup or containment methods.

Various methods have been reported for BTEX removal from aqueous solutions [1 – 4, 6, 7 – 10]. However, adsorption processes have been shown to offer a more efficient way to remove pollutants in wastewater before discharge into the environment. Organoclays, essentially 2:1 clays, have been widely used for the removal of BTEX compounds from aqueous solutions [2, 4, 6, 11 – 14]. The interest in the use of natural clay minerals in raw and modified forms (such as, montmorillonite, kaolinite and illite) for the removal of inorganic and organic contaminants from aqueous solutions has been on the increase in recent years on account of their relative low cost in comparison with activated carbons [15 – 18]. Many studies in literature have reported [2, 4, 16, 19-20] the use of montmorillonite (bentonite), which are 2:1 clays possessing two silica-oxygen tetrahedral sheets with a central alumina octahedral sheet, in the removal of organic contaminants from aqueous medium with little or no information on 1:1 clays (kaolinite) which are found in Nigeria.

Kaolinite clay is a 1:1 clay abundant locally, inexpensive, have high surface area, high adsorptive and ion-exchange properties. The nature of kaolinite clay can be modified for its use in various applications such as adsorbents, catalysts, polymer nanocomposites and photochemical reaction agents [11]. In a previous communication [21], the characterisation of SMK clay was extensively examined and reported. This present study aims to investigate the removal of the components of BTEX mixture in the water-soluble fraction of crude oil using kaolinite clay modified with hexadecyltrimethylammonium (HDTMA). Adsorption kinetics of the recovery process is also evaluated. This study is of importance as it provides useful information on the potential applications of 1:1 clays for the adsorption of organic molecules especially in contaminated sites and polluted waters.

Materials and Methods

Materials :

Crude oil was obtained from Escravos, Delta State, Nigeria. Hexadecyltrimethylammonium bromide (HDTMA-Br, C₁₉H₄₂BrN, MW 364.45, BDH chemicals) was used without further purification. The kaolinite clay obtained from a deposit located at Delta Central (Otedo), Delta State, situated at Longitude 5.9166 E and Latitude 5.4666 N was purified, organically modified and characterized as described previously [21].

Chemical Analysis :

The concentration of BTEX present in the water-soluble fraction of crude oil was quantitatively determined using gas chromatography equipped with flame ionisation detector (GC-FID) (Agilent GC, 7890A). Helium was used as the carrier gas.

Adsorption Kinetics Experiments :

Preliminary investigations at different time intervals of 5, 10, 30, 60, 90, 120 and 180 minutes were studied to determine the time required for the system to reach equilibrium. The sorption equilibrium was attained within 30 minutes. The optimum time was chosen and applied during the equilibrium experiments.

Batch Adsorption Equilibrium Studies :

Batch adsorption tests were carried out to assess the adsorption efficiency of the organokaolinite clay. The stock solution of the water-soluble fraction of crude oil was obtained by shaking vigorously 100 ml of crude oil in 1 litre of deionised water. The mixture was allowed to stand overnight and the water soluble extract separated from the oil phase using a separatory funnel. The water-soluble extract analyzed (a constant volume of 100 ml of water-soluble extract of crude oil gave the following initial concentrations: 9.202 mg/l benzene, 0.697 mg/l toluene, 0.147 mg/l ethylbenzene and 0.0422 mg/l xylene) was further diluted. All the adsorption experiments were conducted at room temperature (25°C) with single-bottle experiments having a fixed amount of the adsorbent (0.5g) and added to 100 ml of BTEX solution in 250 ml conical flasks (with sealed cap) and shaken with a rotary shaker (180 rpm). 0.5g of kaolinite organoclay was added to 100 ml of BTEX solution of varying concentrations and the suspension shaken until equilibrium reached. The suspension was filtered and the supernatant collected and immediately analyzed by GC-FID. The adsorption capacity of the organokaolinite for BTEX adsorption was calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where q_e is the amount of BTEX adsorbed (mg/g), C_o is the initial concentration of BTEX (mg/l); C_e is the equilibrium concentration of BTEX (mg/l); V is the volume of adsorbate solution (ml) m is the mass of adsorbent (g).

Results and Discussions

Adsorption studies :

Fig. 1 shows the variation in levels of equilibrium sorption on the organoclay material with initial concentration of BTEX. It would appear that the organophilic clay material has high capacity for removing BTEX from aqueous media. Quaternary ammonium cations containing long chain alkyl group are generally characterized by linear isotherms over a wide range of solute concentrations [22], due to the favourable interlayer microenvironment created by the long chain alkyl ammonium ions for the partitioning of organic molecules. The size of the alkyl chain and the charge density of the clay layer are responsible for the arrangement of the intercalated cations in the organoclays: usually as bilayers, pseudo-trimolecular arrangement or paraffin complexes [23]. The presence of multilayers of the organic cations in the interspace of clays may account for the relatively high adsorption capacity of organophilicised clay for BTEX.

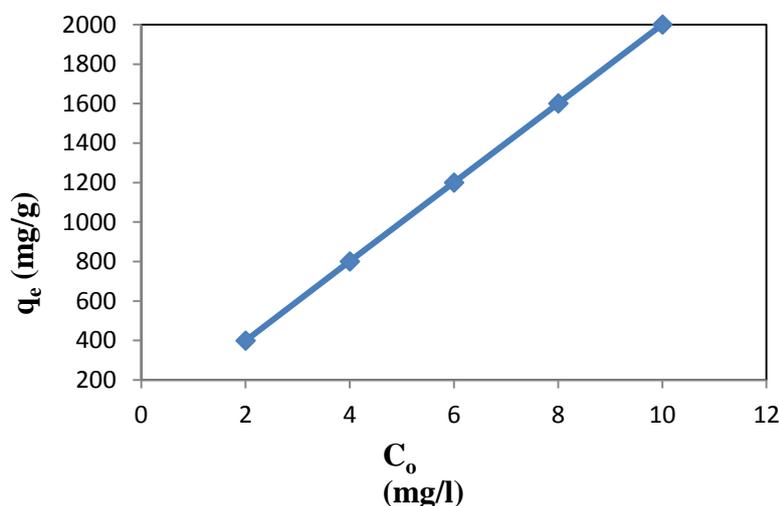


Figure 1: Adsorption isotherm of BTEX on organokaolinite

Adsorption isotherm models:

Adsorption processes are usually described using isotherms which indicates how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Such isotherms are useful for designing any sorption system. In this study, the Langmuir, Freundlich and Temkin isotherms were used in evaluating the relationship between the amounts of BTEX adsorbed onto the surface of organokaolinite at equilibrium.

The linearized form of the Langmuir isotherm (Eq. 2)

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max} K_l} \quad (2)$$

where C_e is the equilibrium concentration of BTEX adsorbate (mg/l), q_e is the amount of BTEX adsorbed at equilibrium (mg/g), q_{max} is the monolayer capacity of the BTEX (mg/g) and K_l is Langmuir's adsorption constant (L/mg); allows the values of

q_{max} and K_l to be obtained from the slope and intercept respectively of a linear plot of C_e/q_e versus C_e .

The Freundlich isotherm model considers that adsorption sites have different affinities for the adsorbate, that is, the adsorption occurs on a heterogeneous surface and so sites with stronger attractive forces are occupied [1]. The linearized form of the Freundlich model is given in Eq. (3).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where K_f and n are Freundlich isotherm constants and determined from the intercept and slope of $\log q_e$ against $\log C_e$. The value of K_f gives a relative measure of adsorption efficiency while the magnitude of n is an indication of the favourability of the adsorption process.

The Temkin model takes into account the effects of indirect adsorbate-adsorbate interactions on the adsorption isotherm and the heat of adsorption tends to decrease with increasing coverage due to these interactions [1]. The derivation of the Temkin model is based on the assumption that the decrease of the heat of adsorption with temperature is linear rather than logarithmic as implied by the Freundlich equation. The linear form of the Temkin model is given by Eq. (4).

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \quad (4)$$

where A ($\text{L}\cdot\text{mg}^{-1}$) and b are Temkin isotherm constants, $R = 0.0083\text{kJmol}^{-1} \text{K}^{-1}$ and T is temperature (K) of the experiment. A plot of q_e versus $\ln C_e$ is linear and the Temkin constants determined from the slope and intercept.

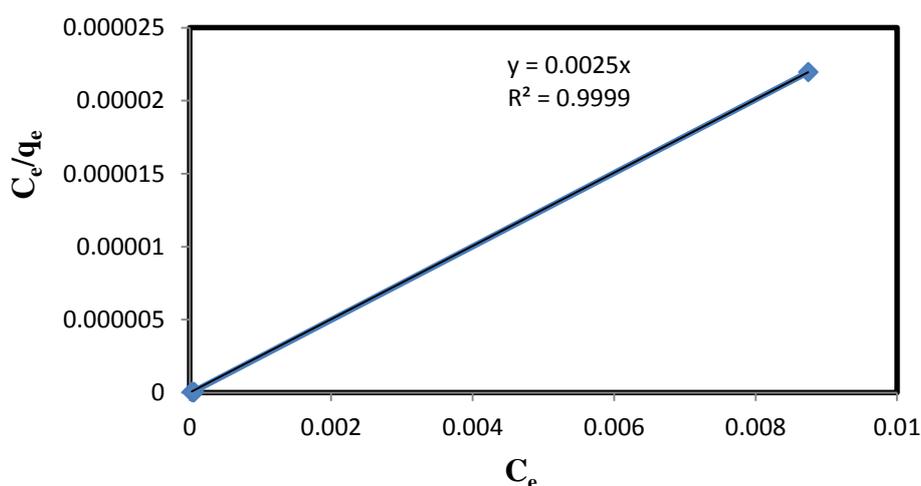


Figure 2: Langmuir isotherm plot for total BTEX adsorption onto organokaolinite

The data from this so fitted the Freundlich and Temkin's models rather poorly. Fig. 2 shows that the Langmuir model best described the sorption data. It has been reported [24] that adsorption conforms to Langmuir and/or Freundlich models when the value of the correlation coefficient (R^2) is greater than 0.89. The R^2 value obtained (0.999) is greater than 0.89 indicating the applicability of the Langmuir isotherm to the adsorption data and which implies that only a limited number of surface sites are adsorbing sites for the BTEX molecule under the experimental conditions studied. The q_{\max} and K_L values obtained from the linear plot were 396.42 mg/g and 1.27×10^3 L/mg respectively.

Kinetic Studies :

In this study, the adsorption data of BTEX by organokaolinite were fitted unto pseudo-first-order, known as the Lagergren equation and pseudo-second-order kinetic models (Eqs. 5 and 6 respectively).

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \quad (5)$$

where q_e is the amount of BTEX adsorbed at equilibrium (mg/g), q_t amount of BTEX adsorbed at any given time t (mg/g), k is the rate constant for the pseudo-first-order model. A plot of $\log(q_e - q_t)$ against t gives a linear slope from which the values of k_1 and q_e can be determined from the slope and intercept.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

k_2 is the rate constant for the pseudo-second-order model. A plot of $\frac{t}{q_t}$ versus t is linear and the slope equal to $\frac{1}{q_e}$ and intercept equal to $\frac{1}{k_2}$.

The kinetic plot for the pseudo-second order kinetic model (Fig. 3) gave a better fit for the experimental data.

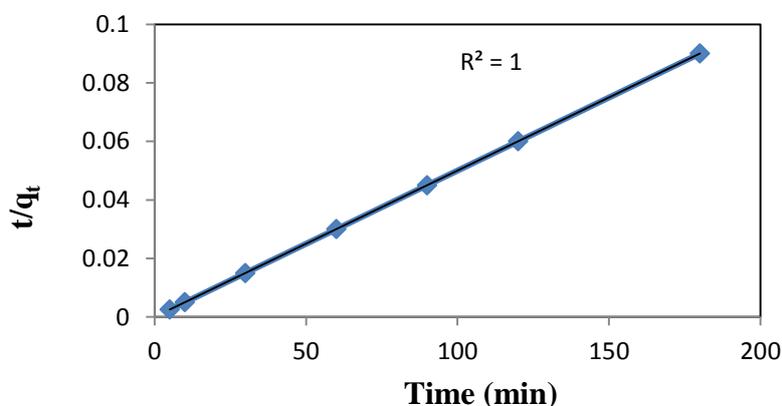


Figure 3: Pseudo-second-order kinetics for BTEX adsorption on organokaolinite

The pseudo-second-order model best described the adsorption mechanism in comparison with the pseudo-first-order model. The high linear correlation coefficient ($R^2 = 1.000$) of the pseudo-second-order kinetic model shows that the kinetic model fitted the data and is quite consistent with observations from previous studies [1, 4, 6, 10]. The value of the constant, k_2 , obtained from the linear plot is 4.5×10^2 g/mg/min. The apparent suggestion from these data explains that both the adsorbate concentration and the reactions of the solid-aqueous layer interface may be important in determining the capacity of adsorption.

Conclusion

Several studies on the sorption of BTEX on organoclay have treated the constituents of BTEX (benzene, toluene, ethylbenzene and xylene) as separate molecules. Adsorption data obtained from such studies may have considered competition by the components of BTEX on the basis of their relative polarities and molecular size insignificant in their uptake by organoclay. It would therefore seem that the procedure adopted in this study may provide more practical data for the removal of petroleum-related contaminants from aqueous medium.

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