

Research Article

Multi-Component Adsorption of Benzene, Toluene, Ethylbenzene, and Xylene from Aqueous Solutions by Montmorillonite Modified with Tetradecyl Trimethyl Ammonium Bromide

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Multicomponent adsorption of benzene, toluene, ethylbenzene, and xylene (BTEX) was assessed in aqueous solutions by montmorillonite modified with tetradecyl trimethyl ammonium bromide (TTAB-Mt). Batch experiments were conducted to determine the influences of parameters including loading rates of surfactant, contact time, pH, adsorbate concentration, and temperature on the adsorption efficiency. Scanning electron microscope (SEM) and X-ray diffractometer (XRD) were used to determine the adsorbent properties. Results showed that the modification of the adsorbent via the surfactant causes structural changes of the adsorbent. It was found that the optimum adsorption condition achieves with the surfactant loading rate of 200% of the cation exchange capacity (CEC) of the adsorbent for a period of 24 h. The sorption of BTEX by TTAB-Mt was in the order of $B < T < E < X$. The experimental data were fitted by many kinetic and isotherm models. The results also showed that the pseudo-second-order kinetic model and Freundlich isotherm model could, respectively, be fitted to the experimental data better than other available kinetic and isotherm models. The thermodynamic study indicated that the sorption of BTEX with TTAB-Mt was achieved spontaneously and the adsorption process was endothermic as well as physical in nature. The regeneration results of the adsorbent also showed that the adsorption capacity of adsorbent after one use was 51% to 70% of original TTAB-Mt.

1. Introduction

Petroleum hydrocarbons such as BTEX (benzene, toluene, ethylbenzene and xylene) are one of the most common pollutants that cause environmental pollution [1]. These compounds are volatile monoaromatic hydrocarbons that are present in petroleum, gasoline, and industrial solvents [2]. BTEX has been introduced in the environment through petrochemical wastewater, fuel leakage from storage tanks and transportation [3, 4].

BTEX has harmful effects on the human health that lead to cancer, mucosal membranes irritation, impairment of the central nervous system, and liver and kidney disruption [5, 6]. Due to these adverse health effects, removal of BTEX from water and wastewater is essential. Chemical

oxidation, biological treatment, air stripping, and adsorption have been successfully carried out for the removal of BTEX from aqueous solutions [5]. Adsorption process is one of the prominent treatment options for the removal of these pollutants from the aqueous mediums because it is possible to recover the adsorbent and adsorbate [4, 7]. Many adsorbents including activated carbon [8, 9], carbon nanotube [2, 10], macroporous resins [7], diatomite [1, 4, 5], and organoclay [11–17] have been used for adsorption of BTEX from aqueous solutions. Activated carbon is the most common material used extensively as an adsorbent for this purpose [9]; however, it is expensive and the regeneration cost is high [8, 18].

Clay, because of its high surface area, low cost, being eco-friendly, and nontoxicity, has a good efficacy in the

adsorption of various pollutants in aqueous solutions [19–22]. Raw clay, due to the hydration of inorganic cations in its active sites, has a hydrophilic property. Therefore, it is ineffective for the removal of nonpolar nonionic organic compounds such as BTEX. Hence, the modification of clay by a surfactant, especially the cationic type, shifts it from the hydrophilic nature to the organophilic one [23]. Many studies have been conducted by other researchers for the removal of BTEX with clay modified by cationic surfactants [11–17]. However, to the authors knowledge modification of clay with tetradecyl trimethyl ammonium bromide (TTAB) as a cationic surfactant has not been investigated. In this study montmorillonite, a type of clay, was modified by TTAB and used to remove BTEX from aqueous solution.

2. Materials and Methods

2.1. Materials

The montmorillonite (Mt) was purchased from Laviosa Co. (Italy). The cationic surfactant, tetradecyl trimethyl ammonium bromide (TTAB), ($\text{CH}_3(\text{CH}_2)_{13}\text{N}(\text{Br})(\text{CH}_3)_3$ with $\geq 99\%$ purity), was provided by Aldrich Co. Benzene ($\geq 99\%$), toluene (99.5%), ethylbenzene ($\geq 99\%$), and xylene (99.5%) were purchased from Merck Co. The BTEX standard solution (400 mg/L BTEX = 100 mg/L benzene + 100 mg/L toluene + 100 mg/L ethylbenzene + 100 mg/L xylene) was prepared in distilled water and kept at 4°C. The stock solution was diluted by distilled water as working solutions. Other chemicals used were of analytical grade.

2.2. Purification and Modification of the Adsorbent. In order to purify the clay, 30 g of the raw Mt was dissolved in 1 L distilled water and mixed with a mechanical stirrer (600 rpm for 24 h) at room temperature (25°C). The Mt impurities such as iron oxide and silica, because of higher density, were precipitated in the tube using a centrifuge rotating at 6000 rpm for 15 min [24]. The impurities were removed from the solution and high-purity Mt was then dried (110°C for 24 h), ground and sieved to a size of less than 125 μm . The cation exchange capacity of the raw Mt after purification was increased from 86 to 108 meq/100 g clay. The Na-montmorillonite (Na-Mt) was prepared by mixing the high purity Mt with 1 N NaCl using a mechanical stirrer (600 rpm for 24 h) at room temperature of 25°C. The Na-Mt was then separated and washed four times with distilled water to make sure all chloride was removed as confirmed by 1 M AgNO_3 [25].

The amount of 5 g of dried and pulverized Na-Mt was dissolved in 100 mL distilled water and modified with TTAB of 0.363 g, 0.908 g, 1.271 g, 1.816 g, 2.179 g, 2.725 g, 3.633 g, 5.449 g, and 7.266 g, respectively, equal to 0.2, 0.5, 0.7, 1, 1.2, 1.5, 2, 3, and 4 CEC of the clay. The suspensions were mixed by mechanical stirrer (600 rpm for 24 h), at 60°C. The TTAB-Mt was then centrifuged, washed (four times), dried (60°C for 24 h) and ground to <125 μm for subsequent use.

2.3. Characterization and Analysis. The surface area of the Na-Mt and TTAB-Mt was measured by Sear's method [26].

The cation exchange capacity of the adsorbent was determined by ammonium acetate procedure [27]. The morphology of the raw and modified adsorbent was specified by a scanning electron microscope (Seron, AIS-2100, Republic of Korea). The FTIR spectra and the composition of the raw and modified adsorbents were characterized using a FTIR spectrophotometer (JASCO, FT/IR-6300, Japan) in the range of 400–4000 cm^{-1} and X-ray diffractometer (Bruker, D8ADVANCE, Germany) using Ni-filtered $\text{Cu K}\alpha\alpha$ radiation (1.5406 Å), respectively. The concentration of BTEX in the solutions was measured by gas chromatography (Agilent GC, 7890A) equipped with flame ionization detector (GC-FID). The GC-FID method for determination of BTEX was optimized as follows:

- (i) Sampling method: head space;
- (ii) Injected sample volume: 250 μL ;
- (iii) Carrier gas: helium (purity 99.995%) with flow rate of 1.11 mL/min;
- (iv) Fuel gas: H_2 with flow rate of 30 mL/min;
- (v) GC column characteristic: Agilent 19091S-433: 30 m \times 250 μm \times 0.25 μm ;
- (vi) Detector temperature: 250°C;
- (vii) Oven temperature: 36°C for 1 min then increased to 90°C at a rate of 10°C/min with a subsequent increase to 150°C at rate of 25°C/min for a period of 6 min (total run time: 14.8 min).

2.4. Adsorption Experiments. All adsorption experiments (except the one for the effects of temperature on the adsorption) were carried out at room temperature (25°C) with 100 mL of BTEX solution into a 200 mL conical flask (with air tight cape) and shaken at 250 rpm for 24 h. After this, the suspensions were centrifuged (6000 rpm for 15 min) and the clear supernatant was analyzed for BTEX by GC-FID. Blank samples (BTEX solution without the adsorbent) were also used to determine the value of BTEX volatilization. The BTEX loss due to the volatilization was estimated to be in the range of 2–8%. The experimental data were corrected to account for volatilize BTEX. The adsorbent capacity of the TTAB-Mt for BTEX uptake was determined from

$$q_e = \frac{(C_0 - C_e)V}{m}, \quad (1)$$

where q_e (mg/g) is the adsorption capacity of the adsorbent, C_0 (mg/L) is the initial concentration of the adsorbate, C_e (mg/L) is the equilibrium concentration of the adsorbate in the solution, m (g) is the mass of the adsorbent, and V (L) is the volume of the solution.

2.4.1. Effect of the Surfactant Loading Rate. The effect of various loading rates of the surfactant onto the clay (0.2, 0.5, 0.7, 1, 1.2, 1.5, 2, 3, and 4 CEC of the clay) for BTEX removal was determined using 100 mL of a solution containing 0.5 g clay and 150 mg/L BTEX. The suspensions were mixed, centrifuged, and analyzed for the organic pollutants by GC-FID.

2.4.2. Effect of Contact Time and pH. The effect of contact time on the adsorption was carried out using 100 mL of a solution containing 0.5 g adsorbent and 150 mg/L BTEX at various contact times (0.5, 1, 2, 3, 4, 5, 8, 12, 16, 24 h). The pH experiments were also conducted with optimum contact time at various pH values ranging from 4 to 12. The adjustment of the pH solution was carried out with 0.1 M HCl and 0.1 M NaOH to the desired value.

2.4.3. Effect of Adsorbate Concentration and Temperature. In many industrial wastewaters the concentration of BTEX varies between 20 to 200 mg/L [2]. Hence, the effect of initial BTEX concentrations (10, 25, 50, 75, 100, 125, 150, and 200 mg/L) on the adsorption efficiency was evaluated at the optimum contact time and pH at 25°C. The effect of various temperatures (10, 20, 30, 40°C) on the adsorption at the optimum contact time and pH was also performed.

2.4.4. Regeneration of BTEX Saturated TTAB-Mt. The regeneration experiments were performed by heating. For this, the TTAB-Mt was subjected to the adsorption as follows. Initially 0.5 g of the adsorbent was equilibrated in 100 mL of 150 mg/L BTEX at the optimum contact time and pH at 25°C. After mixing, the supernatant was centrifuged and analyzed. The saturated clay was then separated and dried at room temperature for 48 h. The BTEX that saturated TTAB-Mt were then placed in oven at 150°C for 5, 10, and 20 min. The adsorption experiments were then conducted using the regenerated adsorbent.

3. Results and Discussion

3.1. Characterization of the Adsorbent

The physical and chemical characteristics of the adsorbent are presented in Table 1. The SEM images of the Raw-Mt and TTAB-Mt are presented in Figures 1(a) and 1(b). The surface structure of the adsorbent is changed by the modification with TTAB. It can be seen that the surface texture of the Raw-Mt is rough with irregular shapes. However, the surface morphology of the TTAB-Mt is smoother than Raw-Mt. This is due to the fact that the porous surface of Raw-Mt is filled with surfactant. The adsorbent modification by TTAB leads to reduction of the surface area from 32.6 m²/g to 26.2 m²/g for Raw-Mt and TTAB-Mt, respectively.

Figure 1(c) presents the FT-IR spectrums of the Na-Mt and TTAB-Mt. The results of infrared spectrum showed that the absorption bands are corresponding to the montmorillonite. As seen in this figure, the absorption band at 3627 cm⁻¹ is assigned to the stretching vibration of ⁻OH groups, which may be due to the isomorphous substitution in the Raw-Mt tetra- and octa-hedral layers [28]. The wide band at 3436 cm⁻¹ is attributed to H₂O stretching vibration [18]. The IR band of 1635 cm⁻¹ is also assigned to Al and Mg bound water molecules [29]. A broad band at 1037 cm⁻¹ is related to Si-O groups stretching vibration, whereas the bands at 525 cm⁻¹ and 468 cm⁻¹ are attributed to Al-O-Si and

TABLE 1: Composition of montmorillonite used in this study.

Chemical composition (%)	
SiO ₂	60
Al ₂ O ₃	20.03
Fe ₂ O ₃	2.31
Na ₂ O	3.02
MgO	4.02
P ₂ O ₅	0.05
K ₂ O	0.13
CaO	1.46
TiO ₂	0.23
MnO	0.03
H ₂ O	8.71
Mineralogical analysis (%)	
Montmorillonite	98
Feldspar	0.5–1
Quartz	0.5–1
Other	
CEC (meq/100 g)	108
Limit of ignition (%)	7.03

Si-O-Si vibrations, respectively [30]. The bands at 2851 cm⁻¹ and 2922 cm⁻¹ in the modified adsorbent are due to C-H stretching vibration.

The XRD patterns of Raw-Mt and TTAB-Mt samples are shown in Figure 1(d). The XRD basal spacing (*d*₀₀₁) of the Raw-Mt and TTAB-Mt were found to be 12.10 Å and 18.59 Å, respectively. Moreover, increasing the reflection intensity from 21.8% for Raw-Mt to 100% for TTAB-Mt showed that the surfactant modification has led to structural changes in the Raw-Mt. The interlamellar expansion in the modified adsorbent may be due to the penetration of TTAB into the layer of Raw-Mt.

3.2. Effect of the Surfactant Loading Rate. The influence of different loading rates of the surfactant onto the adsorbent was also assessed in the removing BTEX from aqueous solution. The results are shown in Figure 2. As can be seen, the sorption capacity (*q_e*) was increased by increasing the surfactant loading to 200% of CEC. Ma et al. (2011) reported that the adsorption capacity of HDTMA-bentonite for the anionic dyes (Orange II and Orange G) was increased by increasing the amounts of HDTMA to 200% of CEC [31]. The sorption capacity was then decreased by increasing the surfactant loading rate, exceeding from 200% of CEC of the clay. The higher surfactant loading rates, after 200% of CEC, may have caused to complete occupancy of the internal pores of the adsorbent, resulting in reduced BTEX penetration to these regions. Hence, TTAB-Mt with surfactant loading rate of 200% CEC was used for the remaining experiments.

3.3. Effect of Contact Time and Adsorption Kinetics. The adsorption data for BTEX uptake by TTAB-Mt are presented

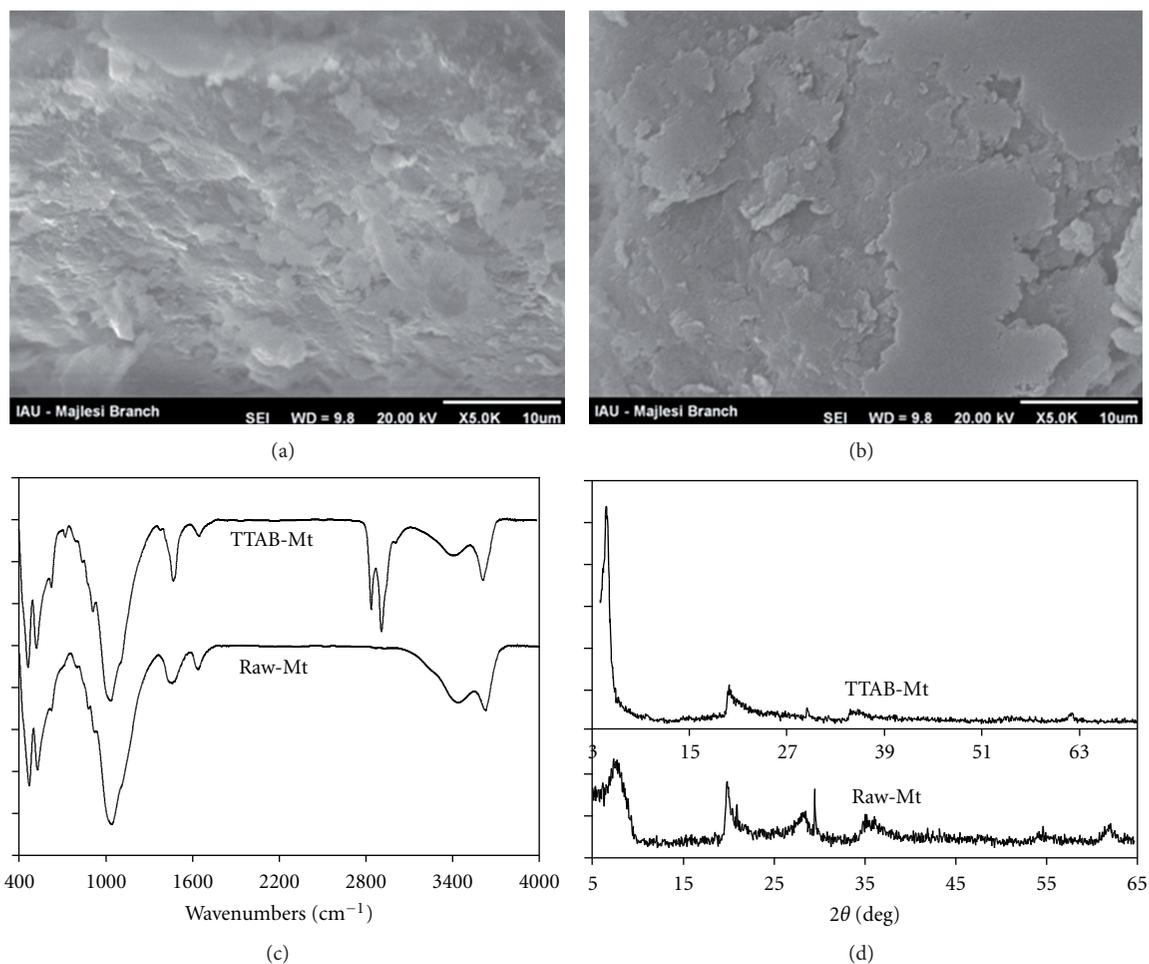


FIGURE 1: Characteristics of the adsorbent. SEM for (a) Raw-Mt and (b) TTAB-Mt. (c) FT-IR and (d) XRD of raw and modified adsorbent.

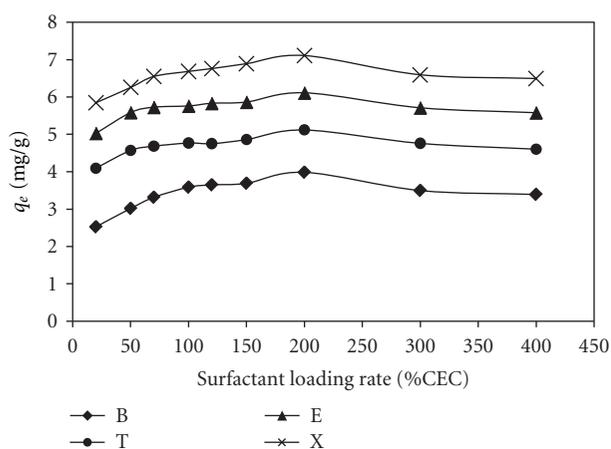


FIGURE 2: Effect of different loading rates of surfactant on adsorption of BTEX by TTAB-Mt (BTEX solution = 150 mg/L, initial pH = 7 ± 0.5, contact time = 24 h, and adsorbent conc. = 5 g/L).

in Figure 3(a). The adsorption capacity of BTEX using modified adsorbent has been rapidly increased at the beginning

of contact time which could be due to the availability of more adsorption sites [32]. Then the adsorption capacity increases slowly up to about 24 h. The adsorption capacity of TTAB-Mt at the first hour of the adsorption was determined to be 3.06 mg/g, 3.24 mg/g, 3.71 mg/g, and 4.6 mg/g for benzene, toluene, ethylbenzene, and xylene, respectively. But the corresponding adsorption capacity at the equilibrium time was estimated to be 3.98 mg/g, 5.15 mg/g, 6.0 mg/g, and 6.98 mg/g.

The order of the sorption capacity of the modified adsorbent is $B < T < E < X$. This order may be due to the water solubility [2], B (1790 mg/L) > T (530 mg/L) > E (152 mg/L) > X (150.5 mg/L) and the corresponding nature of hydrophobicity (based on $\log k_{ow}$) estimated as $B = 2.13$, $T = 2.69$, $E = 3.15$, and $X = 3.15$ [1]. Many previous studies have confirmed that the sorption of BTEX from aqueous solutions with various adsorbents follows a similar order as above [1, 2, 4, 8]. Removal of BTEX by various adsorbents is presented in Table 2. As seen, the adsorption capacity of BTEX with the modified clay in this study is higher than other clays, especially for benzene. The removal efficiency of BTEX by activated carbon (Table 2) is nearly equal with TTAB-clay.

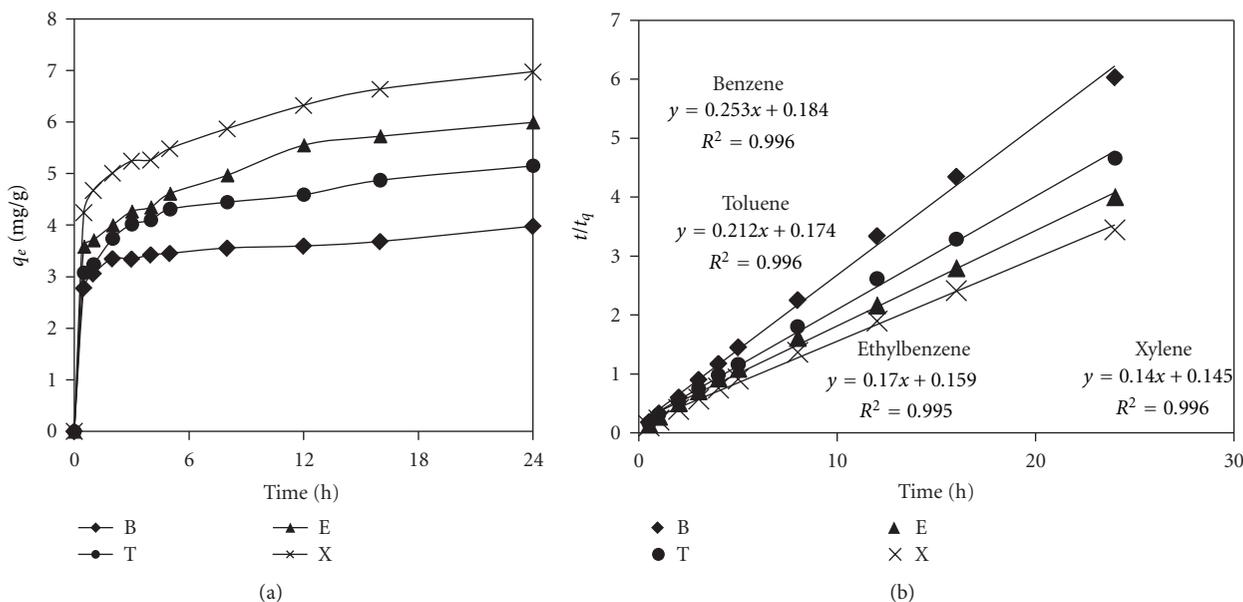


FIGURE 3: (a) Effects of contact time in removal of BTEX by TTAB-Mt (BTEX solution = 150 mg/L, initial pH = 7 ± 0.5 , contact time = 24 h, and organoclay conc. = 5 g/L), (b) pseudo-second-order model.

However the uptake efficiency for carbon nanotube (CNT-NaOCl) is much higher than TTAB clay. The effect of contact time on removing BTEX by the Raw-Mt (data not presented) showed that the adsorption capacity of the raw adsorbent for these compounds was 11 to 13 times less than that for TTAB-Mt. Therefore, TTAB-Mt and contact time of 24 h were used, respectively, as the adsorbent and optimum time for the remaining experiments.

3.3.1. Adsorption Kinetics. Adsorption kinetics is one of the most important parameters for determining the adsorption mechanism and also to investigate the efficacy of adsorbent for the removal of pollutants. In this study, three kinetic models, pseudo-first-order, pseudo-second-order, and intraparticle diffusion models, were used to predict the sorption behavior of the data.

The pseudo-first-order kinetic model [26] is defined as

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (2)$$

where q_e (mg/g) and q_t (mg/g) are the amounts of BTEX adsorbed by TTAB-Mt at equilibrium conditions and at time (t), respectively. k_1 (1/h) is the rate constant of pseudo-first-order kinetic model [26]. k_1 and q_e are determined from the slope and intercept of $\ln(q_e - q_t)$ versus t , respectively. The pseudo-second-order model was also fitted to the adsorption data using the following equation [33]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (3)$$

where q_e and q_t are the same as for the pseudo-first-order parameters. k_2 (g/mg·h) is the rate constant of pseudo-second order. In Figure 3(b), k_2 and q_e values are obtained from the intercept and slope of linear plot of t/q_t against t ,

respectively [33]. At initial stage of the adsorption process ($t \sim 0$), the initial adsorption rate, h (g/mg·h), is obtained from

$$h = k_2 q_e^2. \quad (4)$$

The intraparticle diffusion kinetic model is mathematically described by the following equation [28]:

$$q_t = k_{id} t^{1/2} + C, \quad (5)$$

where k_{id} (g/mg·h) is the rate of the intraparticle diffusion kinetic model [28]. k_{id} and C are obtained from the slope and intercept of q_t versus $t^{1/2}$, respectively.

Figure 3(b) shows a plot of pseudo-second-order kinetic model for the adsorption of BTEX with TTAB-Mt. As can be seen from the correlation coefficient (R^2), the pseudo-second-order kinetic model fits to the experimental data better than the other kinetic models. Moreover, the $q_{e, \text{calculated}}$ (mg/g) achieved using the pseudo-second-order kinetic model is rationally similar to the $q_{e, \text{experimental}}$ (mg/g) obtained from the experimental data. On the other hand, the pseudo-first-order and intraparticle diffusion models, because of the difference between calculated q_e from the models and experimental q_e , do not suitably predict BTEX sorption by the adsorbent. Aivalioti et al. (2010 and 2011) reported that sorption of BTEX with raw and thermally modified diatomite was described well by the pseudo-second-order kinetic model [1, 4]. The parameters for pseudo-second-order kinetic model are listed in Table 3. As seen, the values of the rate constant for pseudo-second-order kinetic models, k_2 (g/mg·h), follow the order of $B > T > E > X$, while the initial adsorption rate constant values of this kinetic model, h (g/mg·h), are shown to have the order of

TABLE 2: Removal of BTEX from aqueous solutions by various adsorbents.

Adsorbent	Benzene (mg/g)	Toluene (mg/g)	Ethylbenzene (mg/g)	Xylene (mg/g)	Reference
TMPA-clay	1.13	8.65	3.18	4.24	[12]
Adam-clay	0.47	4.32	1.59	2.44	[12]
HDTMA-clay	0.47	6.8	4.24	7.21	[12]
CNT(NaOCl)	200	220	250	270	[2]
Diatomite	0.031	0.037	0.042	0.042–0.095	[4]
Activated carbon	4.5	5	6	6.5	[8]
TTAB-Clay	3.98	5.15	6	6.98	This study

TABLE 3: Parameters of pseudo-second order kinetic model obtained from the adsorption data.

Adsorbate	$q_{e,experimental}$ (mg/g)	Pseudo-second order			R^2
		k_2 (g/mg · h)	h (g/mg · h)	$q_{e,calculated}$ (mg/g)	
Benzene	3.98	0.35	5.43	3.95	0.996
Toluene	5.15	0.26	5.75	4.72	0.995
Ethylbenzene	6.00	0.18	6.29	5.88	0.996
Xylene	6.98	0.14	6.90	7.14	0.996

B < T < E < X. The reason for this (the order of h value) may be due to availability of more adsorption sites of the adsorbent at the beginning of the sorption process [32]. Hence, the lower hydrophilic compounds such as xylene and ethylbenzene have a higher tendency to the adsorbent, especially at the start of the adsorption process. But as the time elapsed, the order of k_2 value has a reverse relation with the order of h value. This may be attributed to the molecular weight of BTEX. Due to lower molecular weight, benzene and then toluene can better penetrate onto the internal adsorption sites of the adsorbent as in comparison to higher-molecular-weight compounds such as ethylbenzene and xylene.

3.4. Effects of pH and Adsorbate Concentration. The results for the effects of solution pH on the sorption of BTEX with TTAB-Mt are shown in Figure 4(a). It is clear that the amount of adsorbate uptake via the adsorbent slightly depends on the solution pH and increase of pH from 4 to 12 has not significantly affected BTEX adsorption by TTAB-Mt. This can be an indication of on high stability of the adsorbent over a wide range of pH [2]. Figure 4(b) shows the influences of initial BTEX concentrations between 10 and 200 mg/L on the sorption using TTAB-Mt at initial pH for 24 h. Based on the results, the initial concentration of BTEX has substantial role on the adsorption capacity. As seen, the adsorption capacity of the sorbent was increased by increasing BTEX concentration in the solution. This may be due to an increase in driving forces affecting BTEX compounds. One of these forces is van der Waal's force that affects active adsorption sites of the adsorbent, which occurs at higher concentrations [8].

3.4.1. Adsorption Isotherms. Adsorption isotherm is one of the most important parameters to find the adsorption mechanism and necessary for designing any sorption system. Three isotherm models, Langmuir, Freundlich, and Dubinin-Radushkevich ($D-R$), were used to analyze the adsorbed

BTEX onto TTAB-Mt. The Langmuir isotherm model can be applied for the maximum monolayer adsorption capacity of the adsorbent [34]. This isotherm model in liner form is shown by

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m}, \quad (6)$$

where C_e (mg/L) and q_e (mg/g) are the concentration of adsorbate and the adsorption capacity of the adsorbent at the equilibrium time, respectively. b (L/mg) is the Langmuir constant and Q_m (mg/g) is maximum adsorbent capacity [34]. Q_m and b are attained by the slope and intercept of C_e/q_e versus C_e , respectively. The values of the Langmuir isotherm parameters are given in Table 4.

The Freundlich isotherm model is used for multilayer adsorption on a heterogeneous adsorbent surface [18]. The Freundlich isotherm model can be described by

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e, \quad (7)$$

where K_f (L/g) and n are the isotherm constants and indicate the capacity and intensity of the adsorption, respectively. As shown in Figure 4(c), K_f and n are determined from the intercept and slope of $\ln q_e$ versus $\ln C_e$, respectively [18]. The Freundlich isotherm parameters and its correlation coefficient (R^2) are exhibited in Table 4. The results show that Freundlich isotherm model fits well to the experimental data. Many researchers have showed that sorption of BTEX from aqueous solutions with different adsorbents is described well by Freundlich isotherm model [1, 2, 7, 12]. The adsorption bond between adsorbent and adsorbate would be relatively strong if the n value, obtained from Freundlich isotherm model, is greater than one [18]. Therefore, the n values of 1.04 to 1.55 obtained by this isotherm model showed that BTEX is suitably adsorbed by TTAB-Mt. Sharmasarkar et al. (2000) reported that the n values for the removal of BTEX via the

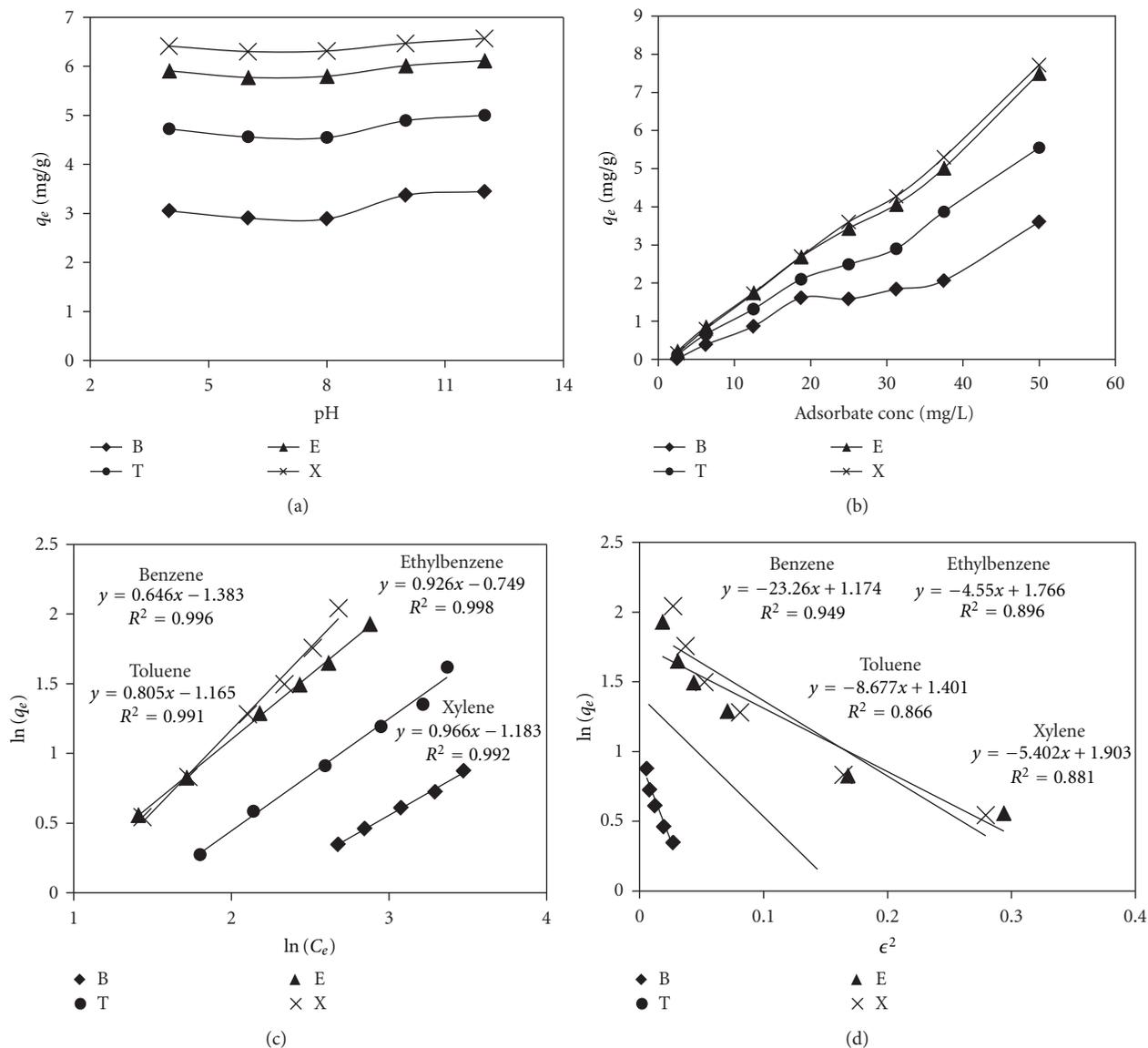


FIGURE 4: (a) Effect of pH on the adsorption of BTEX by the TTAB-Mt (BTEX solution = 150 mg/L, contact time = 24 h and TTAB-Mt conc. = 5 g/L). (b) The effect of BTEX concentration on the adsorption by TTAB-Mt. (initial pH = 7 ± 0.5 , contact time = 24 h and TTAB-Mt conc. = 5 g/L). (c) Freundlich isotherm model and (d) *D-R* isotherm model.

cationic modified clays (TMPA-SW_y and Adam-SW_y) were in range of 1.59 to 1.88 [12].

The Dubinin-Radushkevich isotherm (*D-R*) model has been used to determine the type of adsorption process as physical, chemical adsorption or ion exchange [35]. The linear form of the *D-R* isotherm model can be shown as:

$$\ln q_e = \ln q_m - \beta \varepsilon^2, \quad (8)$$

where, q_m (mg/g) is the theoretical sorption capacity based on the isotherm, β (kJ/mol) is related to mean adsorption energy and ε (Polanyi Potential) is equal to $RT \ln(1 + 1/C_e) \cdot R$ (kJ/mol·K) is the universal gas constant and T (K) is temperature [35].

Figure 4(d), q_m and β are obtained from the intercept and slope $\ln q_e$ versus ε^2 , respectively. E (kJ/mol) is the mean adsorption energy that is illustrated by equation (9):

$$E = \frac{1}{\sqrt{2\beta}}. \quad (9)$$

The type of adsorption process is specified by the E value as follow: The physical and chemical adsorptions are occurred in $E < 8$ kJ/mol and $E > 16$ kJ/mol, respectively. But the chemical ion exchange occurs for E in the 8–16 kJ/mol [36]. The values of parameters for *D-R* isotherm model are presented in Table 4. As seen, the adsorption of BTEX through TTAB-Mt has occurred for E values in the range

TABLE 4: Parameters for Langmuir, Freundlich, and *D-R* isotherm models for adsorption of BTEX by TTAB-Mt.

Adsorbate	Langmuir isotherm			Freundlich isotherm			<i>D-R</i> isotherm		
	Q_m (mg/g)	b (L/mg)	R^2	K_f	n	R^2	q_m (mg/g)	E (kJ/mol)	R^2
Benzene	3.61	0.049	0.971	0.041	1.55	0.996	3.22	0.147	0.949
Toluene	5.52	0.083	0.940	0.068	1.24	0.991	4.04	0.240	0.866
Ethylbenzene	6.90	0.201	0.986	0.160	1.08	0.998	5.82	0.331	0.896
Xylene	8.26	0.126	0.847	0.066	1.04	0.992	6.67	0.304	0.881

TABLE 5: Thermodynamic parameters for removal of BTEX by TTAB-Mt.

Adsorbate	q_e (mg/g)				ΔG (kJ/mol)				ΔH	ΔS
	283 K	293 K	303 K	313 K	283 K	293 K	303 K	313 K	(kJ/mol)	(J/mol · K)
Benzene	2.98	3.85	4.46	5.55	-0.35	-1.75	-3.14	-4.53	39.10	139.34
Toluene	4.52	4.88	5.93	6.87	-1.09	-2.21	-3.33	-4.45	30.70	112.24
Ethylbenzene	4.46	5.48	6.36	7.33	-1.42	-2.40	-3.39	-4.37	26.46	98.44
Xylene	5.55	6.28	6.80	7.75	-1.63	-2.63	-3.62	-4.62	26.50	99.35

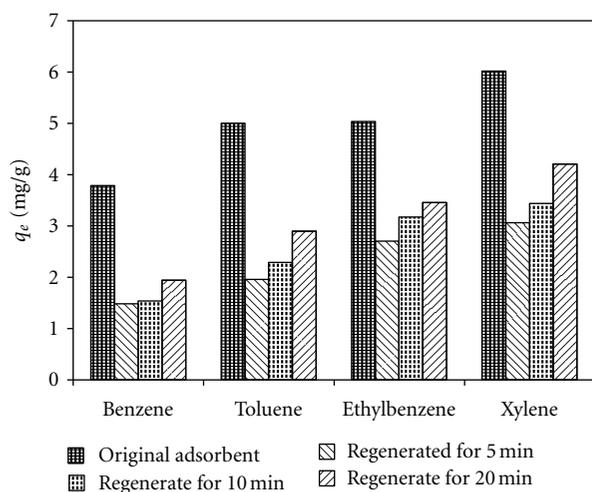


FIGURE 5: Effect of temperature of 150°C at various times (5, 10 and 20 min) on the regeneration of the TTAB-Mt. (BTEX solution = 150 mg/L, initial pH = 7 ± 0.5, contact time = 24 h and adsorbent conc. = 5 g/L).

of 0.147–0.331 kJ/mol. Hence, the removal of BTEX in the solution by TTAB-Mt is governed by the physical adsorption.

3.5. Effect of temperature. The influence of temperature on the adsorption of BTEX via TTAB-MT was assessed for temperatures vary between 10 to 40°C. Thermodynamic equations and their parameters such as enthalpy (ΔH), Gibbs free energy (ΔG) and entropy (ΔS) are presented by equations 10 to 12 [29].

$$\Delta G = \Delta H - T\Delta S, \quad (10)$$

$$K = \frac{q_e}{C_e}, \quad (11)$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}. \quad (12)$$

K (L/g), C_e (mg/L) and R (8.314 J/mol · K) are distribution coefficient, equilibrium concentration and universal gas constant, respectively. The sorption thermodynamic parameters including entropy (J/k · mol) and enthalpy (kJ/mol) were obtained from the intercept and slope of plotting $\ln K$ versus $1/T$, respectively [29]. The Gibbs free energy (kJ/mol) was also calculated from (10). The temperature effect on the adsorption is given in Table 5. The negative values of the free energy change (–1.75 to –4.62 kJ/mol) for the removal of BTEX with TTAB-Mt indicate that the adsorption process is thermodynamically feasible and spontaneous [35]. The decrease in the values of ΔG at lower temperature showed that the sorption of BTEX by the adsorbent is favorable at higher temperature. As seen from Table 5, the sorption capacities of TTAB-Mt for BTEX at various temperatures also confirmed this fact. Typically, physical adsorption occurs for the value of Gibbs free energy (ΔG) in the range of –20 to 0 kJ/mol but the values of ΔG for chemical adsorption is between –400 and –80 kJ/mol [29]. Therefore, this indicates that the sorption of BTEX by TTAB-Mt is physical in nature. As mentioned previously, the *D-R* isotherm model also showed that the adsorption of BTEX by TTAB-Mt is physical. A positive value for ΔH value also showed that the sorption of BTEX by the adsorbent is endothermic. The positive values of ΔS may describe an increase in degree of freedom of the adsorbed species.

3.6. Regeneration on TTAB-Mt Saturated by BTEX. In this study, temperature of 150°C at different times (5, 10 and 20 min) was used to regenerate the BTEX saturated adsorbent. As seen from Figure 5, the adsorption capacity of the regenerated TTAB-Mt was increased by increasing the regeneration time. The ratio of the sorption capacity of the regenerated adsorbent to the original adsorbent was increased from 39–54% for regeneration time of 5 min and to 51–70% for regeneration time of 20 min. The order of adsorption capacity of the regenerated TTAB-Mt, similar to that for the original adsorbent, was found to be B < T < E < X.

4. Conclusion

Montmorillonite as a type of clay was modified by tetradecyl trimethyl ammonium bromide (TTAB-Mt) to remove BTEX from aqueous media. It was found that the optimum adsorption condition takes place for the surfactant loading rate of 200% CEC at contact time of 24 h. The pseudo-second-order kinetic and Freundlich isotherm models, respectively, fitted to the experimental data better than other kinetic and isotherm models. Thermodynamic study also showed that the sorption of BTEX by TTAB-Mt was endothermic, spontaneous, and physical.

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