

original article

Comparison of the efficiencies of modified clay with polyethylene glycol and tetradecyl trimethyl ammonium bromide for BTEX removal

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ABSTRACT

Aims: In this study, the effectiveness of modified clay [montmorillonite (Mt)] with polyethylene glycol (PWG) and tetradecyl trimethyl ammonium bromide (TTAB) on the benzene, toluene, ethylbenzene and xylene (BTEX) removal from aqueous solution was investigated.

Materials and Methods: The batch adsorption experiments including surfactant loading rates (0.2–4 cation exchange capacity [CEC] of the clay), contact time (0–24 h), pH (4–12) and adsorbate concentration (10–200 mg/L) were conducted at room temperature (25°C) with 100 mL of BTEX solution into a 200-mL conical flask and mixed by an orbital shaker (250 rpm for 24 h).

Results: It was found that the optimum adsorption condition obtains for the surfactant loading rate of 200% clay CEC for both the adsorbents at the contact time of 24 h. The sorption capacity of BTEX by both the adsorbents was in order of benzene toluene ethylbenzene xylene. The results of both the adsorbents also showed that the pseudo-second-order kinetic model and Freundlich isotherm model fitted the experimental data better than of other kinetic and isotherm models, respectively.

Conclusion: The adsorption capacity of TTAB-Mt (22.11 mg/g) was slightly higher than PEG-Mt (18.77 mg/g). With regard to lower toxic effects and lower cost of nonionic surfactants than the cationic type, using the nonionic modified Mt is preferred than cationic modified Mt for the removal of BTEX from aqueous solution.

Key words: Adsorption, clay, monoaromatic hydrocarbons, polyethylene glycol, tetradecyl trimethyl ammonium bromide

INTRODUCTION

Environmental pollution with hydrocarbons is one of the main global problems in recent years, especially for soil and water.^[1] Benzene, toluene, ethylbenzene and xylene (BTEX) are volatile and mono-aromatic hydrocarbons that have been used in many industrial solvents and are found in fuels such as petroleum

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and gasoline.^[2,3] Petrochemical wastewaters, fuel leakage from reservoirs, transportation, pipelines and road accidents lead to irregular discharge of these pollutants into the environment.^[4] Human contact with these hazardous contaminants can result in adverse health effects including cancer, irritation of eyes, hematological changes, weakened central nervous system and respiratory problems.^[5,6] The US Environmental Protection Agency (US-EPA) has considered these compounds as priority pollutants and that their concentrations must be decreased to a very low amount in water and wastewater.^[7] Based on the guidelines of the World Health Organization (WHO), the maximum allowable levels of benzene, toluene, ethylbenzene and xylene in drinking water are 0.01, 0.7, 0.3 and 0.5 mg/L, respectively.^[8] Thus, it is necessary to specify and use effective removal methods for these compounds. Chemical oxidation, biological treatment, air stripping, membrane techniques and adsorption have been successfully applied for the removal of BTEX from aqueous solutions.^[5] Adsorption is an effective and authoritative procedure for pollutants removal from water and wastewater.^[9] In many studies, several adsorbents including activated carbon,^[10,11] carbon nanotube,^[3,12] diatomite^[4,13] and organoclay^[1,14-16] have been used for the adsorption of BTEX from aqueous solutions. Activated carbon is the most common material used extensively as an adsorbent for the purpose^[11] but it is expensive and has high regeneration cost.^[10,17] Montmorillonite (Mt), a type of clay, has been widely applied for the removal of various pollutants including organics and inorganics from water and wastewater.^[18] Because of its high surface area,^[19] low cost,^[20] eco-friendly and high adsorption tendency,^[21] Mt is considered as an attractive adsorbent for the removal of pollutants, especially organics.^[22-24] Natural clay, due to hydrophilic nature on its surface, is an ineffective sorbent for nonpolar, nonionic organic compounds such as BTEX in aqueous solution.^[15] The modification of clay with surfactants can shift its hydrophilic property to hydrophobic.^[25] Therefore, in this study, Mt has been modified by polyethylene glycol (PEG) and tetradecyl trimethyl ammonium bromide (TTAB) as nonionic and cationic surfactants, respectively. The performance of them in the removal of BTEX was compared as a function of various conditions including loading rate of surfactant, contact time, pH and pollutant content.

MATERIALS AND METHODS

Materials

The Mt was provided by Laviosa Co (Italy). The surfactants, tetradecyl trimethyl ammonium bromide (TTAB with $\geq 99\%$ purity) and polyethylene glycol (PEG-600 with 99% purity) were supplied 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) was prepared on the base of the even concentration ratio (100 mg/L) of each component (benzene, toluene, ethylbenzene and xylene) in distilled water and kept in a refrigerator. The working solutions were provided through dilution of the stock solution by distilled water.

Analysis

The adsorbent cation exchange capacity was measured by ammonium acetate procedure.^[26] The Fourier transform infrared spectroscopy (FTIR) spectra and the composition of the raw and modified adsorbents were characterized using a FTIR spectrophotometer (JASCO, FT/IR-6300, Japan) Any more information was not provided along its manual in the range of 400–4000 cm^{-1} and X-ray diffractometer (Bruker, D8ADVANCE, Germany) Any more information was not provided along its manual using Ni filtered Cu K radiation (1.5406 Å), respectively. The BTEX concentration in the solutions was measured by a gas chromatography (Agilent GC, 7890A) Any more information was not provided along its manual equipped with flame ionization detector (GC-FID). The GC-FID method for the determination of BTEX was optimized as follows: The amount of 250 μL of sample was injected into the instrument by head space sampling method. Helium (with flow rate of 1.11 mL/min) and H_2 (with flow rate of 30 mL/min) were used as carrier gas and fuel gas, respectively. The characteristic of GC column was Agilent 19091S-433: 30 m \times 250 μm \times 0.25 μm . The detector temperature was 250°C and the temperature of the oven was 36°C for 1 min and increased at a rate of 10°C/min to 90°C and then increased up to 150°C with rate of 25°C/min for 6 min (total run time: 14.8 min).

Purification and modification of the adsorbent

In order to purify the clay, 30 g of the raw Mt was mixed with 1 L distilled water in a glass flask and mixed with a mechanical stirrer (600 rpm for 24 h) at room temperature (25°C). The solid was then separated by centrifugation (6000 rpm for 15 min) that as a result of it, the Mt impurities such as iron oxide and quartz, because of higher density, precipitated at the bottom of the tube. The impurities were removed and the high purity Mt was then dried (110°C for 24 h), milled and sieved to 125 μm . The Na-montmorillonite (Na-Mt) was prepared by mixing the high purity clay with 1N NaCl using mechanical stirrer at room temperature (25°C). The Na-Mt was then separated by centrifugation, washed four times with distilled water. The Na-Mt was dried, pulverized (such as the above) and modified with the each of the cationic and nonionic surfactants as follows: the amounts of each surfactants, equal to 0.2, 0.5, 0.7, 1, 1.2, 1.5, 2, 3 and 4 cation exchange capacity (CEC) of the clay, were dissolved in 100 mL distilled water and 5 g Na-Mt was added to it. The suspensions were mixed by a mechanical stirrer (600 rpm for 24 h) at 60°C. The modified Mt was then centrifuged, washed by distilled water, dried (60°C for 24 h) and ground to 125 μm for subsequent use.

Adsorption experiments

The adsorption experiments including surfactant loading rates (0.2–4 CEC of the clay), contact time (0–24 h), pH (4–12) and adsorbate concentration (10–200 mg/L) were conducted at room temperature (25°C) with 100 mL of BTEX solution into a 200-mL conical flask (with air-tight cape) and mixed

by an orbital shaker (250 rpm for 24 h). After agitation, the suspensions were centrifuged (6000 rpm for 15 min) and the clear supernatant was analyzed for BTEX by GC-FID. Blank samples (BTEX solution in the absence of the adsorbent) were also applied to measure the amount of BTEX loss. The blank recoveries ranged from 92 to 98% and the data were adjusted for these recoveries. The adsorbent capacity of the modified Mt for BTEX was measured by equation (1):

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

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

including FT-IR and XRD analyses are presented in Figures 1a and b. FT-IR results showed that the surfactants were best intercalated into the layers of the adsorbents. XRD patterns also show that the modification of the clay have increased the inter-layer spacing of the modified adsorbent vs unmodified clay. The effects of different loading rates of surfactants onto the adsorbents are illustrated in Figure 2. The effects of contact time and adsorption kinetics in the removal of BTEX are shown in Figure 3 and Table 1, respectively. The results of the contact time effect on the adsorption of BTEX by both the modified clays also showed that at the contact time of 24 h, the adsorption process reached equilibrium. The influences of pH and adsorbate concentration on the sorption are also shown in Figures 4 and 5, respectively.

RESULTS

The characteristics of the raw and modified adsorbents

DISCUSSION

Characterization

The chemical composition of raw adsorbent was determined on the base of percent (%) as follows: SiO₂: 60, Al₂O₃: 20.03, Fe₂O₃: 2.31, Na₂O: 3.02, MgO: 4.02, P₂O₅: 0.05, K₂O: 0.13, CaO: 1.46,

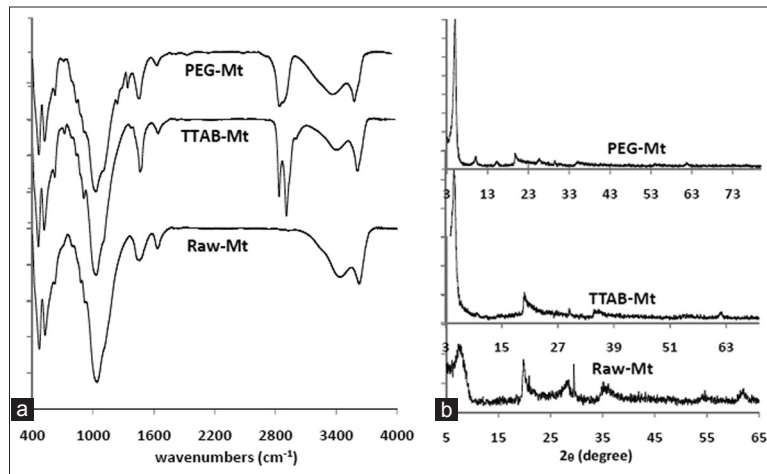


Figure 1: (a) FT-IR and (b) XRD of the raw and modified montmorillonite

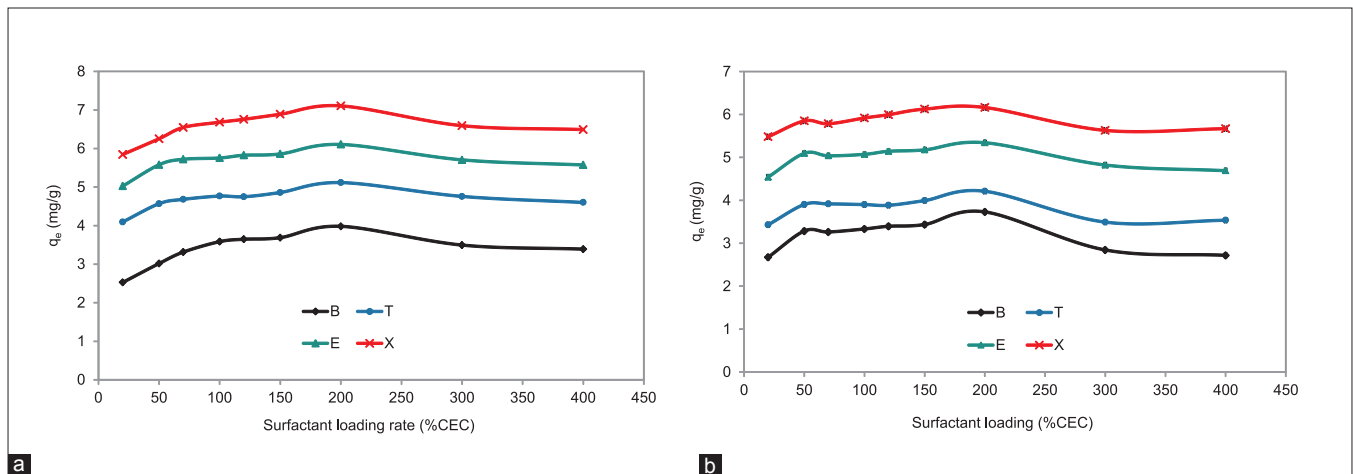


Figure 2: The effect of different loading rates of surfactant on the adsorption of BTEX by (a) TTAB-Mt and (b) PEG-Mt (BTEX solution = 150 mg/L, initial pH = 7 ± 0.5, contact time = 24 h and adsorbent Dose = 5 g/L)

Table 1: Studies for the removal of BTEX from aqueous solutions

Adsorbent	Benzene (mg/g)	Toluene (mg/g)	Ethylbenzene (mg/g)	Xylene (mg/g)	Reference
TMPA-clay	1.13	8.65	3.18	4.24	1
Adam-clay	0.47	4.32	1.59	2.44	1
HDTMA-clay	0.47	6.8	4.24	7.21	1
CNT (NaOCl)	200	220	250	270	3
Diatomite	0.031	0.037	0.042	0.042–0.095	4
Activated carbon	4.5	5	6	6.5	10

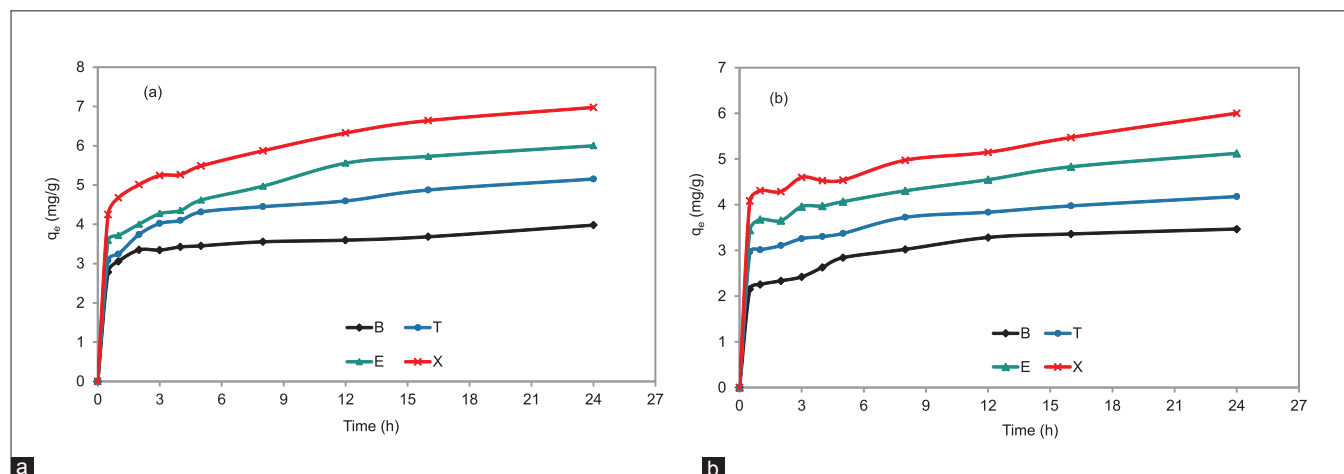


Figure 3: The effects of contact time on BTEX adsorption by (a) TTAB-Mt and (b) PEG-Mt (BTEX concentration: 150 mg/L, solution pH: 7 ± 0.5 and adsorbent dose: 5 g/L)

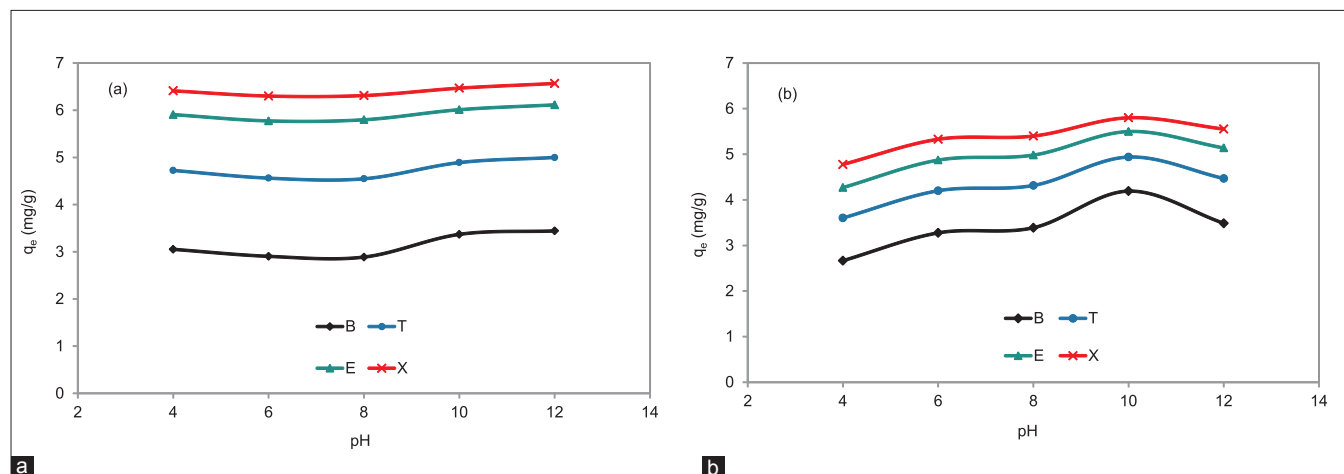


Figure 4: The effect of pH on the adsorption of BTEX by (a) TTAB-Mt and (b) PEG-Mt (BTEX concentration: 150 mg/L, adsorbent dose: 5 g/L and contact time: 24 h)

TiO₂: 0.23, MnO: 0.03 and H₂O: 8.71. The results showed that the major components of Mt are silica and alumina along with trace elements such as iron, manganese, potassium, calcium, sodium, magnesium and titanium. Because of the purification process, the adsorbent impurities were decreased from 8% to 1–2% and that as a result of it, the CEC of the Mt was increased from 86 to 108 mEq/100 g clay. Figure 1a presents the FT-IR analysis of the Na-Mt and TTAB-Mt and PEG-Mt. The results of infrared spectrum showed that the absorption bands are corresponding to the Mt. As seen, the absorption band at 3627 cm⁻¹ is attributed to stretching vibration of -OH groups, which may be due to the isomorphous substitution in

the Raw-Mt tetra- and octa-hedral layers.^[22] The wide band at 3436 cm⁻¹ is attributed to water stretching vibration.^[17] The IR band of 1635 cm⁻¹ is also assigned to aluminum and magnesium-bound water molecules.^[27] A 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 Si-O-Si vibrations, respectively.^[28] The bands at 2851 cm⁻¹ and 2922 cm⁻¹ in the modified adsorbent, because of the surfactants loading, are due to C-H stretching vibrations. These adsorption bands showed that the surfactants are effectively situated into the layers of the clay. The XRD analysis of Na-Mt and TTAB-Mt and PEG-Mt are presented in Figure

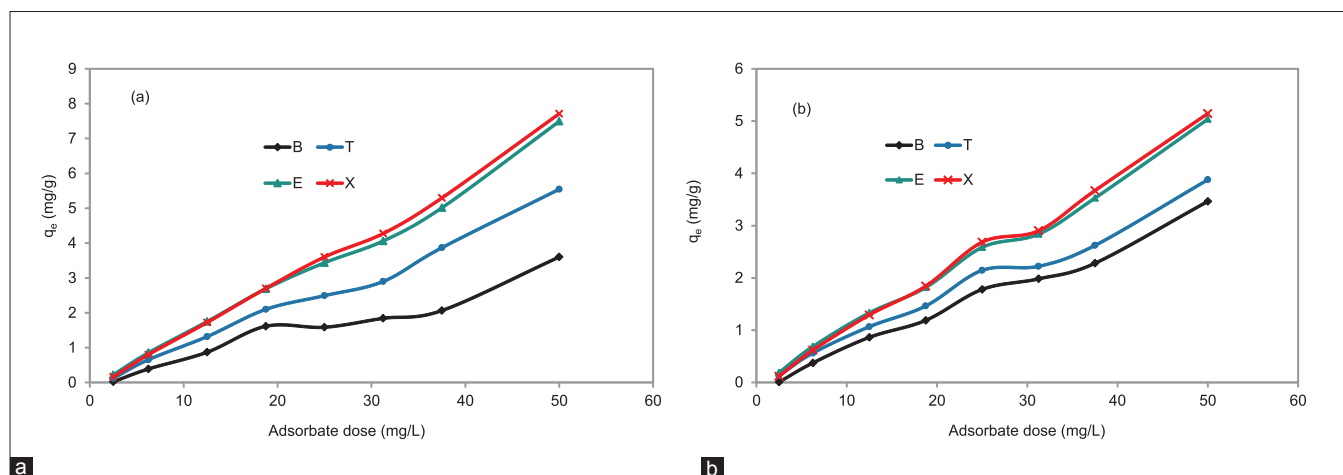


Figure 5: The effect of BTEX concentration on the adsorption by (a) TTAB-Mt and (b) PEG-Mt (Solution pH: 7 ± 0.5 , adsorbent dose: 5 g/L and contact time: 24 h)

1b. The XRD basal spacing of the Raw-Mt was 12.10 Å. The interlayer spacing of the Mt was increased by PEG surfactant modification to 17.48 Å. Koyuncu *et al.* (2011) reported that bentonite modification by nonionic surfactant has increased the bentonite interlayer spacing from 14.97 Å to 15.17 Å for the raw and modified bentonite, respectively.^[17] The XRD basal spacing of TTAB-Mt was also found to be 18.59 Å. The increase of the basal spacing for the both Mt indicates that the both surfactants intercalate into the interlayer space of the adsorbent. The interlayer space value in TTAB-Mt is higher than of PEG-Mt that it may be affected on the amount adsorption through the increased penetration of the adsorbate into the layers of the adsorbent.

Effect of the surfactant loading rate

The adsorption of BTEX by PEG-Mt and TTAB-Mt with different loading rates of the surfactant is shown in Figure 2. As seen, the adsorption capacity (q_e) was increased by increasing the surfactant loading up to 200% CEC for the both sorbents. Ma *et al.* (2011) reported that the adsorption capacity for the anionic dyes (Orange II and Orange G) on the hexadecyl trimethyl ammonium bromide (HDTMA)-bentonite was increased by increasing HDTMA loading up to 200% CEC.^[29] The sorption capacity was then decreased by increasing both surfactants' loading rate exceeding 200% CEC to 400% CEC. The higher surfactant loading rates, beyond 200% CEC, may lead to complete occupancy of the interior pores of the both modified adsorbents that causes penetration of BTEX to these regions to be reduced. The modified Mt with the surfactants loading rate of 200% CEC for both the adsorbents was chosen for the subsequent experiments in this study.

Effect of contact time

The adsorption data for uptake of BTEX by the modified adsorbents are presented in Figure 3. As shown in Figures 3a and b, the adsorption capacity of BTEX with both

modified adsorbents was quickly increased at the beginning of contact time, due to the availability of more adsorption sites,^[30] and then slowly increased as time goes forward until 24 h. The adsorption capacity of TTAB-Mt at first hour of the adsorption was determined as 3.06, 3.24, 3.71 and 4.6 mg/g for benzene, toluene, ethylbenzene and xylene, respectively. But the adsorption capacity at the equilibrium time was obtained as 3.98, 5.15, 6.0 and 6.98 mg/g for benzene, toluene, ethylbenzene and xylene, respectively. The adsorption capacity (q_e) of BTEX by PEG-Mt during the first hour and at the equilibrium time was also as benzene (2.25 and 3.47 mg/g), toluene (3.01 and 4.18 mg/g), ethylbenzene (3.67 and 5.12 mg/g) and xylene (4.29 and 6.00 mg/g), respectively. The sorption capacity for both modified adsorbents was in the order of BTEX. It can be related to their water solubility,^[3] benzene (1790 mg/L), toluene (530 mg/L), ethylbenzene (152 mg/L) and xylene (150.5 mg/L), and their hydrophobicity (based on $\log K_{ow}$) as benzene (2.13), toluene (2.69), ethylbenzene (3.15) and xylene (3.15).^[13] Many studies have reported that the sorption of BTEX from aqueous solutions with various adsorbents follow as the mentioned order.^[1-4,10,13] The adsorption capacity (mg/g) of the similar studies^[1-4,10] is presented in Table 1. The removal efficiency of BTEX in this study is higher than some adsorbent such as diatomite^[10] and less than carbon nanotube.^[3] The adsorption capacity of the carbon nanotube is approximately 50 times higher than that of clay in this study, but the cost of carbon nanotube is more expensive than that clay (50000 times). The obtained results in this study also showed that the adsorption capacity of TTAB-Mt is slightly higher than that PEG-Mt. The results of contact time effect on the removal of BTEX by the Raw-Mt (data not presented) showed that the adsorption capacity of the raw adsorbent for these compounds was 9 to 13 times less than that of the modified type. Therefore, the modified adsorbents with contact time of 24 h were used for rest of the experiments.

Adsorption kinetics

In this study, the adsorption data of BTEX by the modified clays were analyzed via two kinetic models including pseudo-first-order and pseudo-second-order models. The pseudo-first order kinetic^[31] is shown by equation (2):

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

Where, q_e (mg/g) and q_t (mg/g) are the amounts of adsorbate uptake on the adsorbent at equilibrium and at time (t), respectively. K_1 (1/h) is the pseudo-first-order rate constant. K_1 and q_e were specified from the slope and intercept of the plotting $\ln(q_e - q_t)$ against t , respectively.^[31]

The experiment data were also analyzed by pseudo-second-order model. This adsorption kinetic is shown by the following equation:^[26]

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

At the beginning the adsorption, because $t \sim 0$, the initial adsorption rate, h (g/mg.h), is calculated via equation (4):

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

Where, q_e and q_t are defined as the pseudo-first-order model parameters. K_2 (g/mg.h) is the pseudo-second-order rate constant. k_2 and q_e can be determined from the intercept and slope of t/q_t versus t in equation (3), respectively.^[26]

Table 2 presents pseudo-second order kinetic model parameters for the adsorption of BTEX from aqueous solutions by the both adsorbents. The higher linear correlation coefficient (R^2) of the pseudo-second-order model reveals that this kinetic model fitted the data better than other kinetic model described earlier. Moreover, the q_e calculated (mg/g) using this kinetic model is reasonably similar to q_e experimental (mg/g) obtained from experimental data. As seen, the pseudo-second-order rate constant values, K_2 (g/mg.h), are observed in the order of BTEX, while the initial adsorption rate constant values of the pseudo-second-order kinetic, h (g/mg.h), are shown in the order

of BTEX. The reason for this (h value for xylene is higher than that ethylbenzene, toluene and then benzene) can be due to more available adsorption external sites of the clay at the start of the adsorption process. Therefore, the lower hydrophilic compounds have a higher tendency to the adsorbent, especially at the start of the adsorption. But over the adsorption time, the K_2 value for benzene is higher than for toluene, ethylbenzene and then xylene. This may be related to the molecular weight of BTEX. It may be because of lower molecular weight, benzene can better penetrate onto the internal adsorption sites than toluene, ethylbenzene and then xylene.

Effects of pH and adsorbate concentration

The effects of solution pH in the sorption of BTEX with the modified adsorbents are shown in Figures 4a and b. It is obvious that the amount of BTEX sorption through the both adsorbents slightly depends on the solution pH and the increment of pH from 4 to 12 has insignificant influence on BTEX adsorption by the both adsorbents. This can show a high stability of the adsorbent over a wide range of the solution pH.^[3]

Figures 5a and b also show the effects of initial BTEX concentrations in range of 10–200 mg/L on the sorption by TTAB-Mt and PEG-Mt at initial pH for 24 h. Based on the results, the initial concentration of BTEX has great role on the adsorption capacity. As seen, the adsorption capacity of the sorbents was increased by the increasing BTEX concentration in the solution. This may be due to an increase in driving force of BTEX compounds including van der Waal's to the active adsorption sites of the adsorbent, which occurs at the higher concentrations.^[10]

Adsorption isotherms

Three isotherm models including Langmuir, Freundlich and Dubinin-Radushkevich (D-R) were used to fit the experimental data. The Langmuir isotherm model is applied as the maximum monolayer adsorption of the adsorbent.^[32] This isotherm model is shown by equation (5):

$$\frac{c_e}{q_e} = \frac{c_e}{Q_m} + \frac{1}{bQ_m} \quad (5)$$

Where, C_e (mg/L) and q_e (mg/g) are the concentration

Table 2: Parameters of pseudo-second-order kinetic model obtained for the removal of BTEX by (a) TTAB-Mt and (b) PEG-Mt

Adsorbate	q_e , experimental (mg/g)	Pseudo-second-order kinetic parameters			
		K_2 (g/mg.h)	h (g/mg.h)	q_e , calculated (mg/g)	R^2
Benzene	a 3.98	0.35	5.43	3.95	0.996
	b 3.46	0.26	3.40	3.58	0.997
Toluene	a 5.15	0.26	5.75	4.72	0.995
	b 4.17	0.24	4.32	4.23	0.997
Ethylbenzene	a 6.00	0.18	6.29	5.88	0.996
	b 5.12	0.19	5.34	5.18	0.995
Xylene	a 6.98	0.14	6.90	7.14	0.996
	b 6.00	0.15	5.49	5.98	0.992

a: TTAB-Mt, b: PEG-Mt

Table 3: Langmuir, Freundlich and D-R isotherm parameters for the adsorption of BTEX by (a) TTAB-Mt and (b) PEG-Mt

Adsorbate	Langmuir isotherm			Freundlich isotherm			D-R 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	a 3.61	0.049	0.971	0.041	1.55	0.996	3.22	0.147	0.949
	b 5.92	0.028	0.876	0.024	1.31	0.992	3.01	0.155	0.871
Toluene	a 5.52	0.083	0.940	0.068	1.24	0.991	4.04	0.240	0.866
	b 6.71	0.026	0.939	0.043	1.38	0.992	2.86	0.214	0.832
Ethylbenzene	a 6.90	0.201	0.986	0.160	1.08	0.998	5.82	0.331	0.896
	b 7.35	0.057	0.932	0.027	1.57	0.995	3.44	0.425	0.746
Xylene	a 8.26	0.126	0.847	0.066	1.04	0.992	6.67	0.304	0.881
	b 8.19	0.047	0.779	0.016	1.39	0.992	3.85	0.327	0.836

a: TTAB-Mt, b: PEG-Mt

of adsorbate and adsorption capacity of the adsorbent at equilibrium time, respectively. b (L/mg) is the Langmuir constant and Q_m (mg/g) is the maximum adsorbent capacity.^[32] Q_m and b are attained by the intercept and slope of straight plotting C_e/q_e versus C_e , respectively. The Langmuir isotherm parameters are given in Table 3.

The Freundlich isotherm model is used for multilayer adsorption on a heterogeneous adsorbent surface.^[17] The Freundlich isotherm model can be described by equation (6):

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (6)$$

Where, K_f (L/g) and n are the isotherm constants and indicate the capacity and intensity of the adsorption, respectively. K_f and n are determined from the intercept and slope of straight plot of $\ln q_e$ against $\ln C_e$, respectively.^[17]

The results showed that the experimental data were best fitted by the Freundlich isotherm. The Freundlich isotherm parameters are presented in Table 3. Many researchers have shown that the sorption of BTEX from aqueous solutions with different adsorbents described well by the Freundlich isotherm.^[3,5,25] The adsorption bond between adsorbent and adsorbate is relatively strong as the n values, originated from the Freundlich isotherm, is more than one.^[17] Therefore, the n values of 1.04–1.55 obtained by this isotherm model showed that BTEX is suitably adsorbed by the modified Mt. Sharmasarkar *et al.* (2000) reported that n values for removal of BTEX via the cationic modified clays (TMPA-SWy and Adam-SWy) were in range of 1.59 to 1.88.^[25]

The Dubinin–Radushkevich isotherm (D–R) is used to explain the type of pollutants removal process as physical, chemical adsorption or ion exchange.^[32] The linear form of D-R isotherm can be shown as equation (7):

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (7)$$

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 $RT \ln(1 + 1/C_e)$. R (kJ/mol.K) is the universal gas constant and T (K) is temperature.

^[32] As given in Table 3, the values of q_m and β are obtained from the intercept and the slope of linear plotting $\ln q_e$ versus ϵ^2 , respectively. E (kJ/mol) is the mean adsorption energy that illustrated by equation (8).

$$E = \frac{1}{\sqrt{2\beta}} \quad (8)$$

The type of adsorption process is determined by the E value as follow: The physical and chemical adsorptions are occurred by $E < 8$ kJ/mol and $E > 16$ kJ/mol, respectively. But the chemical ion exchange is defined as E value range from 8–16 kJ/mol.^[33] The D–R isotherm parameters are presented in Table 3. As seen, the adsorption of BTEX compounds through TTAB-Mt and PEG-Mt has the E values in range of 0.147–0.331 and 0.155–0.425 kJ/mol, respectively. Hence, the removal of BTEX in the solution with both the modified clays is followed by physical adsorption.

CONCLUSION

This study was conducted to determine the effects of modified Mt with two surfactants, cationic and nonionic, for the removal of BTEX from solutions. The results showed that the optimum contact time for the adsorption by both adsorbents was 24 h. The BTEX adsorption capacity for PEG-Mt and TTAB-Mt was in order of BTEX. The adsorption capacity of TTAB-Mt (22.11 mg/g) was slightly higher than PEG-Mt (18.77 mg/g). Because of the cytotoxicity tests determined that nonionic surfactants have a lower toxic influence than other ones and can be shown as cationic > anionic = amphoteric > nonionic.^[34] Moreover, the nonionic surfactant has lower cost than the cationic type. Therefore, using the nonionic modified Mt because of lower adverse health effect and cost is preferred than cationic modified Mt for the removal of BTEX from aqueous solution.

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