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Application of soils for removal of methyl tertiary butyl ether (MTBE) from aqueous solution: adsorption kinetics and equilibrium study

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ABSTRACT

Methyl tertiary butyl ether (MTBE) is widely used as a gasoline additive. The contamination of surface water and groundwater with MTBE has attracted further attention due to the relatively high potential MTBE related health risks. In the current research, the adsorption capability of MTBE by kaolinite, bentonite, sandy loam and clay loam was studied through series of batch sorption procedures. The results were investigated with respect to the linear, Freundlich, Langmuir, Toth and Langmuir-Freundlich sorption isotherms. In the equilibrium condition, the MTBE concentration (C_{eq}) was 0.68–6.88 mg/L for clay loam, 0.89–8.94 mg/L for sandy loam, 1.3–11.26 mg/L for bentonite and 1.56–13.5 mg/L for kaolinite. The obtained modeling results revealed that the sorption affinity of the studied soils for MTBE increases in the order of kaolinite < bentonite < sandy loam clay loam. Moreover, the effects of contact time, pH, and temperature on the sorption affinity of MTBE into the soil samples were investigated and the thermodynamic parameters (ΔG, ΔH and ΔS) were calculated. Approximately 80% of the total MTBE removal was occurred within the first 80 min of experiments. Moreover, the maximum MTBE removal (57.4%) was obtained at pH of 3 while the least efficiency (23.1%) at pH of 11. A decrease in sorption distribution coefficient (K_d) was observed with increasing the temperature and its maximum value was found at 298.15°K. According to our findings, different types of soils due to their acceptable efficiency and low cost could be applicable for the MTBE removal from the aqueous solutions.

Keywords: Sorption; MTBE; Isotherms; Soil

1. Introduction

Methyl tertiary butyl ether (MTBE) is a gasoline additive widely used to increase the octane rating and consequently the efficiency of gasoline combustion [1,2]. Another advantage of the MTBE addition into gasoline is decreasing the percentage of aromatic compounds in gasoline, which is required for obtaining an assigned octane number [3]. On the other hand, the U.S Environmental Protection Agency (USEPA) has classified the MTBE as a possible human carcinogen substance because of several adverse effects on the human health and environment [4].

Moreover, the MTBE can cause an unpleasant odour even at very low concentrations [5,6]. Due to MTBE's low Henry's constant, relatively high water solubility, and also resistance to biodegradation, the MTBE is a relatively stable compound with major concerns when it comes to its disposal and remediation [7–10].

Different technologies have been proposed in the literature for the MTBE removal from the aqueous systems, such as biological treatment (including aerobic and anaerobic), chemical treatment, and absorbent technologies [11–14]. Among these technologies, it should be mentioned that the application of soils as sorbents for the MTBE removal is considered as an effective method, which is economically competitive with other well established remediation and removal technologies, as well as other sorbents for the MTBE removal [15,16].

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The mechanism responsible for the MTBE removal from the aqueous solution cannot be understood without comprehensive understanding the sorption processes of the MTBE by sorbents because the sorption process can significantly affect the efficiency of the MTBE removal and consequently design procedure and implementation of an effective scheme for removal of MTBE from aqueous system [17,18]. The partition coefficient (K_d) is an important parameter widely applied in the sorption studies and can be directly obtained from batch sorption experiments [19].

Table 1 shows previous excessively investigated reports on the MTBE removal by various sorbents from the aqueous solution [20–26]. Some of natural and artificial sorbents demonstrated relatively high efficiency in the MTBE removal from the aqueous solution. However, their application, especially in large scale, is limited due to high cost [16]. Therefore, it is necessary to develop easily available, cost effective, and an efficient sorbent for removing the MTBE from the aqueous [27].

However, there is limited information in the literature on the MTBE removal from the aqueous solution by the soils as inexpensive and also easily available material in a batch system. The objective of the current study is to assess the MTBE removal from the aqueous solution using different types of the soils and the sorption behaviour including sorption affinity and mechanism of MTBE on selected soil samples. Furthermore, our efforts were continued to study the effects of temperature, pH, and contact time on the sorption process. The clay loam, sandy loam, kaolinite and bentonite are selected as natural sorbents in the current study since these types of soil have already been used for solving various environmental problems; as well, a systematic MTBE sorption data comparison on these soil samples has not been conducted so far.

As well, this study examined kinetic and equilibrium sorption experiments and applied Linear, Freundlich, Langmuir, Toth and Langmuir-Freundlich isotherm models to obtain related isotherm data. Finally, the sorption affinities of studied soils for MTBE are compared, and the observed sorption mechanisms are discussed in details.

Table 1
Sorption of MTBE on various sorbents

Sorbent	Maximum reported adsorption capacity (mg/g)	Water used	Reference
All-silica β Zeolite	87.0[a]	n.r.	[46]
Modified granulated nanozeolite Y	220[b]	DIS	[20]
GCN 830	45[b]	PW	[21]
SYK	25[b]	PW	[21]
F300	10[b]	PW	[21]
SYC	6[b]	PW	[21]
BAC A	0.8[b]	PW	[21]
Mordenite (SiO_2/Al_2O_3 = 200)	80.1[a]	MW	[22]
Ambersorb 563 (untreated)	22.4	MW	[23]
Ambersorb 563	5.6	SG	[24]
Ambersorb 572	8.9	SG	[24]
Ambersorb 563	12.6	MW	[23]
Fisher-activated carbon	3.07	MW	[22]
Filtrasorb400	3.1	SG	[24]
Optipore L493	3.8	MW	[23]
XAD4	3.16	n.r.	[25]
XAD4	1.97	MW	[23]
XAD7	0.11	MW	[23]

SG: synthetic groundwater; MW: Millipore water; DW: deionized water; DIS: distilled water; PW: pure water; OFW: organic-free water, buffered (pH = 7); n.r.: not reported.
[a]Values reported by the author.
[b]Values estimated from the figures.

2. Materials and methods

2.1. Materials

Milli pore water was used in the current study for all the sorption experiments. The main chemical and physical properties of the MTBE used ($(CH_3)_3COCH_3$, and CAS No.1634-04-4) are presented in Table 2. The MTBE with purity over 99% was used in sorption experiments. All of the used chemicals were Merck (Germany).

The investigated clay soil samples(including kaolinite and bentonite)were purchased from Iran Barite Inc. Based on the product technical data sheet, the cation exchange capacities (CEC) of kaolinite and bentonite were 9.91 mmol charge/100 g and 9.91 mmol charge/100 g, respectively. The elemental composition of studied absorbents was determined by recruiting the X-ray fluorescence (XRF) analytical technique (Philips instrument) (Table 3).

The prepared samples were also characterized using Brunauer–Emmet–Teller (BET) analysis. Based on derived results, BET surface area (SBET) of kaolinite, bentonite, sandy loam, clay loam was, 25, 84, 75, 93 m^2/g, respectively.

Table 2
Environmentally relevant physical and chemical parameters of MTBE [47]

Compound	MTBE
Compound class	Ethers
Physical state (at NTP)	colorless liquid
Molecular weight (g/mol)	88.15
Boiling point in (°C)	55
Blending RON	116–118
Log K_{ow}	0.94
Density (kg/L)	0.744
Vapor pressure (mm Hg)	333
Henry's law Constant (atm·m$^{3)}$/(g·mol)	5.87 × 10^{-4}
Water solubility (mg/L)	51000

All values are reported at 25°C.

Table 3
Chemical composition of kaolinite and bentonite used in this study

Constituents	Contents (%)	
	Kaolinite	Bentonite
SiO_2	52–58	68–72
Al_2O_3	14–18	13.5–16.5
Fe_2O_3	6–9	<1.9
Na_2O	2.5–3.5	0.3–0.5
MgO	2.5–3.2	2.3–2.5
CaO	2–2.5	2.4–2.6
K_2O	0.2–0.3	0.9–1.1
TiO_2	1–1.4	<0.1

Table 4
Some basic properties of the soils used in this study

Properties	Clay loam	Sandy loam	Bentonite	Kaolinite
Specific gravity (g/cm^3)	2.88	2.72	2.82	2.67
Natural moisture content (%)	3.44	4.1	4.6	1.03
pH	6.8	7.1	8.2	6.7
Organic carbon content (%)	5.03	4.12	0.33	0.97
Percent clay fraction (<2 μm)	27	7	55	29
q'_{max}, (mg/g)	0.14	0.12	0.1	0.08

The kaolinite and bentonite were washed carefully with deionized water in order to remove any soluble inorganic salts. The samples were centrifuged at 8000 rpm for 20 min and then dried at temperature of 105°C for 24 h. Finally, the samples were passed through a No. 40 mesh sieve in order to remove lumps or large particles.

The clay loam and sandy loam samples were obtained from Rey Plain located at southwest of Tehran, Iran. The loam soil samples were taken from the depth of 20–45 cm below the surface by using grab method and were transported in to high-density polyethylene (HDPE) containers. The coolers were used to store the containers that were transported to the laboratory for testing. In the laboratory, the loam soil samples were dried in the air for two weeks and any roots or impurities were separated finally. The main chemical and physical properties of studied soil samples are presented in Table 4.The theoretical maximum sorption capacity of the micro spores in soil samples can be estimated by:

$$q'_{max} = V_m\,\rho \tag{1}$$

q'_{max} and other properties of the soils are presented in Table 4.

2.2. Testing procedures

All sorption experiments were conducted at room temperature (25°C). The solutions contaminated with MTBE in vials were developed through the addition of MTBE into water. The range of MTBE concentrations was opted according to previous experiments listed in Table 1. The head space in the vials was kept less than 0.2 mL and all lids were sealed. Batch sorption tests were performed on the soil suspensions where interaction between soil particles and MTBE contaminated solution is possible. In summary, the procedure included shaking 14 g of soil sample with a series of the MTBE contaminated solutions. The pH of solutions was adjusted to the range of 3–11 by adding 0.1 M NaOH and/or 0.1 M HNO_3 shaken for 8 h to evaluate the pH effect on sorption of MTBE on selected soil samples. Moreover, the mentioned procedure was repeated at five different temperatures (298, 318, and 338°K) in order to assess the effect of temperature the MTBE removal from the aqueous solution by the soil. The prepared solution was left to reach equilibrium at selected temperature within 24 h and finally solid phase micro extraction/gas chromatograph (SPME/GC) procedure applied to measure the concentration of MTBE in the mixture.

In the SPME procedure, a 75-m PDMS/Carboxen commercial fibre (SupelcoInc) was immersed in the mixture for extracting MTBE. The extraction time was 1 h and the temperature during the extraction process was kept constant at 18ºC. The extracted fibre was injected into a GC (6890 Plus, Agilent Technologies Inc) equipped with a flame ionization detector. The sorption amount of MTBE in the sample (q) was calculated by Eq. (2).

$$q = \left(C_0 - C_{eq}\right)\frac{V}{M} \tag{2}$$

where V is the volume, M is the mass, and C_0 and C_{eq} are the initial and equilibrium concentrations, respectively. It should be noted that the head space method was adopted in the current study; therefore, the MTBE mass in the gas phase should be considered in calculating the MTBE mass in the solid phase. Thereby, the solid phase concentration of MTBE can be calculated as:

$$q = \frac{C_0V_w - C_eV_w - C_eH_{25}V_g}{M} \tag{3}$$

where H_{25} is the Henry's law constant at 25°C and can be obtained from Table 2.

2.3.Sorption isotherms

Several sorption isotherms such as Temkin, BET, Hill-de Boer, Volmer, Fowler Frumkin and Gibbs have been used in different studies in order to describe sorption affinity and mechanism of various sorbent, sorbate, and solvent. The mentioned isotherms of sorption can be mainly employed for gases sorbates [28], but not hereby in this study. On the other hand, linear, Freundlich, Langmuir, Toth and Langmuir-Freundlich isotherms are widely used to describe sorption affinity and mechanism of liquid sorbates on soils. Accordingly, the mechanism of MTBE sorption on the selected soil was describe in the current study by these models. Each of sorption models should be evaluated by fitting parameters. The value of fitted q_{max} was considered as the first fitting parameter, which was used in the current study. This value should not be more than maximum sorption capacity (q_{max}) (see Table 3). Because, the q_{max} is sorption capacity when all micros pores are completely filled by the solute and thereby sorption more than q'_{max} is theoretically impossible. The next adopted fitting parameters in the current study are the coefficient of determination (r^2value) and the sum of squares due to error (SSE value).

The used parameters are obtained from results of batch sorption tests. A linear sorption isotherm could be established if the relation between C_{eq} and q is estimated by a straight line. The mathematical equation describing the linear sorption isotherm is as follows:

$$q = K_d\, C_{eq} \tag{4}$$

where K_d is a constant. This sorption isotherm proposes a constant relative affinity of the solute molecules generally occurred at low range sorption [29]. Also, the percentage of MTBE removal from the aqueous solution can be calculated as:

$$\mathrm{Re} = \frac{\left(C_0 - C_{eq}\right)}{C_0} \times 100 \tag{5}$$

The hydrophobic theory can be adopted as another method for obtaining K_d for organic contaminants by the following equation [30]:

$$q = K_{oc} f_{oc} \tag{6}$$

It should be mentioned that K_{oc} can be estimated based on the value of K_{ow} (which is known for several compounds) through different empirical equation [19].

Accordingly, due to the fact that a nonlinear relationship is obtained in sorption experiments, so a linear sorption isotherm is improper in these cases. One of the sorption isotherms fitted to the derived nonlinear data from sorption experiments is Freundlich sorption isotherm expressed as [31].

$$q = KC_{eq}{}^{\eta} \tag{7}$$

It is obvious that the linear sorption isotherm can be considered as a special case of the Freundlich isotherm if is equal to one. Overall, the value of η is more than one when the amount of solute in the solution is less than adsorbed amount, referring to the unfavourable condition. Contrariwise, the value of η is less than one when the amount of solute in the solution is more than adsorbed amount, which refers to the favourable condition.

The Langmuir sorption isotherm is another isotherm fitted to the derived nonlinear data from sorption experiments [32]. Limited sorption sites are available on solid surfaces based on Langmuir sorption isotherm and thereby solid surfaces will no longer be able to absorb the solute from the solution when all the sorption sites are filled. On the other word, Langmuir sorption isotherm puts a threshold on the amount of sorbent in a sorption system and therefore the maximum amount of sorbent in each sorption system can be predicted [33]. Analytically, Langmuir sorption isotherm can be expressed as:

$$q = \frac{KC_{eq}}{1 + KC_{eq}} \tag{8}$$

The next adopted isotherm used to fit data from sorption experiments in the current study is the Toth sorption isotherm written as:

$$q = q_{\max} \frac{C_{eq}}{\left(1 + \alpha C_{eq}^{\eta}\right)^{1/\eta}} \tag{9}$$

Finally, Langmuir–Freundlich isotherm was adopted in this research in order to consider the role of partitioning in a sorption system. This isotherm can be mathematically described as:

$$q = q_{\max} \frac{KC_{eq}^{\eta}}{1 + KC_{eq}^{\eta}} \tag{10}$$

3. Results and discussion

3.1. Sorption isotherms

The isotherm parameters for MTBE sorption, which are derived from sorption experiments, are presented in Table 5. It should be noted that the sorption mechanism cannot be fully understood, except for the sorption isotherms. Several mechanisms of interaction between sorbent and sorbate are possible in a sorption system based on the properties of sorbent, sorbate, and solvent. Sorption generally occurs in the micro spores of the soils mainly by Van der Waals forces for low molecular weight molecules such as MTBE.

There is no electrical distortion in an MTBE molecule to create positive or negative sides, but the electrons are generally mobile that can find themselves towards one end of MTBE molecule at any one instant. Therefore, the mentioned end of MTBE molecule gets slightly positive and the other end gets slightly negative because of the absence of electrons. The MTBE molecule electrons will be attracted by slightly positive end of the soil particles when an MTBE molecule, which has a temporary polarity, approaches a non-polar particle of soil, resulting in induced dipole in the soil particle, which the slightly negative end of one is attracted by the slightly positive end of another. The electrons of MTBE molecule can move to the other end of MTBE molecule at one instant later and the electrons in the soil particle will be repelled. Thus, the polarity of molecules reverses and there is still an attraction between the slightly positive and slightly negative ends. It should be noted that polarities and consequently the attraction between the slightly positive and slightly negative ends is maintained as long as the molecules stay close to each other.

The results from sorption experiments in this research can be approximated by a linear sorption isotherm as shown in Fig. 1. The slope of the drawn line is that is respectively 0.0088 L/g (0.958), 0.0054 L/g (0.914), 0.0033 L/g (0.962) and 0.0013 L/g (0.945) for the interaction of MTBE on the clay loam, sandy loam, bentonite and kaolinite. The obtained results imply that the MTBE has the greatest affinity to the clay loam in comparison to the other studied soils in low concentration. This can be attributed to the higher

Table 5
Isotherms parameter values for MTBE sorption

Models	Parameters and coefficient of determination	Clay loam	Sandy loam	Bentonite	Kaolinite
Linear		0.0088	0.0054	0.0033	0.0013
	(–)	0.958	0.914	0.962	0.945
	SSE[a]	1.37×10^{-4}	1.84×10^{-4}	4.49×10^{-5}	2.58×10^{-5}
Freundlich	[(mg/g)·(mg/L)$^{-\eta}$]	0.0118	0.0076	0.0042	0.0006
	(–)	0.822	0.818	0.0885	1.337
	(–)	0.981	0.938	0.971	0.981
	SSE	5.69×10^{-5}	1.31×10^{-4}	3.78×10^{-5}	9.028×10^{-6}
Langmuir	[(mg/L)$^{-1}$]	0.0599	0.0464	0.0266	0.0117
	(mg/g)	0.1944	0.1532	0.153	0.1279
	(–)	0.986	0.941	0.922	0.919
	SSE	4.54×10^{-5}	1.27×10^{-4}	3.70×10^{-5}	3.82×10^{-5}
Toth	(–)	0.06164	0.01607	0.05399	0.1171
	(–)	0.5636	1.62	0.03621	0.01951
	(mg/g)	0.01147	0.006571	0.01589	0.5037
	(–)	0.9812	0.9408	0.9689	0.9147
	SSE	6.24×10^{-5}	1.27×10^{-4}	4.10×10^{-5}	4.02×10^{-5}
Langmuir-Freundlich	[(mg/L)$^{-\eta}$]	0.009597	0.008918	0.01105	0.01849
	(–)	0.3204	0.295	0.3748	0.154
	(mg/g)	2.58	2.095	1.069	0.4238
	(–)	0.6723	0.609	0.698	0.2624
	SSE	1.086×10^{-3}	8.38×10^{-4}	3.98×10^{-4}	3.48×10^{-4}

[a]SSE=measured-fitted)^2, *n* is number of data points

fines content of the clay loam compared to the rest of investigated soils that created more available sorption sites for the MTBE sorption.

The test results in the high concentration range significantly (more than 5 mg/L) deviate from the linear relationship. Several studies have indicated derived from linear isotherm is valid for all the concentration range in different sorption experiments while derived K_d from linear isotherm in the current study is valid only at low concentration of MTBE.

Using Eq. (5), K_{oc} for MTBE is 0.0112 L/g [14], and with f_{oc} of 5.03%, 4.12%, 0.57% and 0.33% for the clay loam, sandy loam, bentonite and kaolinite, K_d is 0.0563 L/g, 0.0461 L/g, 0.0036 L/g and 0.0063 L/g, respectively. The difference between the results of sorption experiments and the mentioned estimation can be attributed to relatively high solubility of MTBE because this estimation is based on hydrophobic theory developed mainly for low solubility compounds [34].

The derived data from sorption experiments has been plotted in Fig. 2 in order to evaluate the sorption parameters of the Freundlich sorption isotherm. The obtained curves can be approximated with reasonable correlation coefficients, as $r^2 = 0.981$, 0.938, 0.971 and 0.981 respectively for clay loam, sandy loam, bentonite and kaolinite.

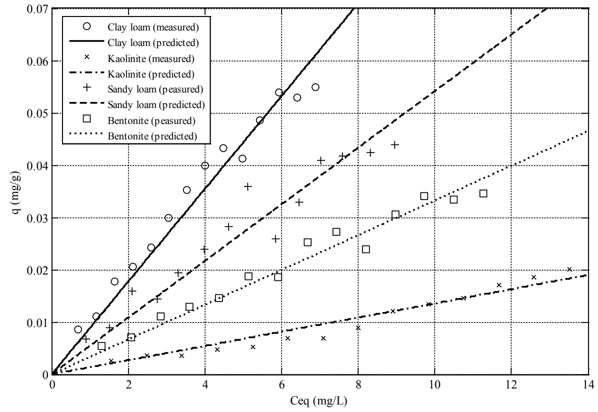

Fig. 1. Modeling results of the linear sorption isotherms for MTBE.

As shown in Fig. 2, the *K* and η of the Freundlich sorption isotherm are 0.0118 [(mg/g)·(mg/L)$^{-\eta}$] and 0.822 for clay loam, 0.0076 [(mg/g)·(mg/L)$^{-\eta}$] and 0.818 for sandy loam, 0.0042 [(mg/g)·(mg/L)$^{-\eta}$] and 0.885 for bentonite and

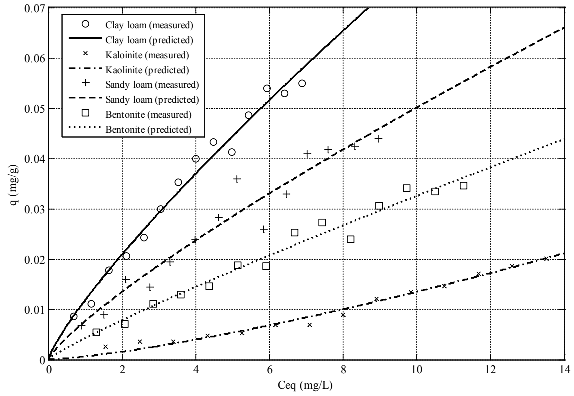

Fig. 2. Modeling results of the Freundlich sorption isotherms for MTBE.

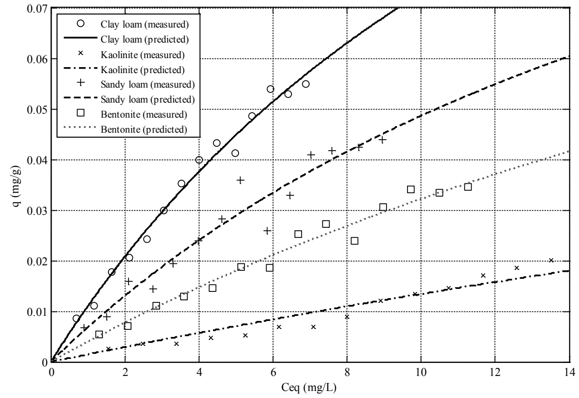

Fig. 3. Modeling results of the Langmuir sorption isotherms for MTBE.

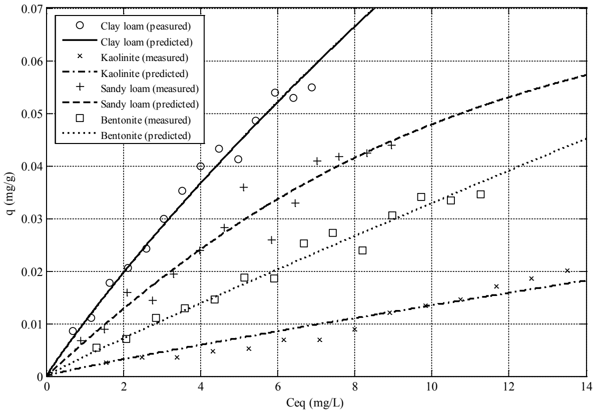

Fig. 4. Modeling results of the Toth sorption isotherms for MTBE.

0.0006 [(mg/g)·(mg/L)$^{-\eta}$] and 1.337 for kaolinite. Therefore, a favourable sorption of MTBE on clay loam, bentonite, sandy loam ($\eta < 1$) and unfavorable sorption of the MTBE on kaolinite ($\eta > 1$) can be seen. Moreover, based on *K* values of the Freundlich sorption isotherm in the investigated concentration range, the MTBE has the highest sorption affinity to clay loam and the lowest sorption affinity to kaolinite among studied soil samples.

The modelling results based on Langmuir isotherm is presented in Fig. 3. The *K* value is 0.0599 L/mg for the clay loam, 0.0464 L/mg for sandy loam, 0.0266 L/mg for bentonite and 0.0117 L/mg for kaolinite. This parameter reflects that the MTBE has a higher affinity to loam soils than bentonite and kaolinite.

In addition, experimental results demonstrated that sorption is enhanced by increasing the equilibrium concentration until a certain threshold. The maximum sorption is observed at this threshold. According to the Langmuir's theory, the derived q_{max} value is the maximum sorption. The obtained values are 0.1944 mg/g, 0.1532 mg/g, 0.153 mg/g, 0.1279 mg/g for clay loam, sandy loam, bentonite and kaolinite, respectively. According to the q_{max} values, clay loam has more capacity for MTBE sorption in comparison to the other studied soils.

Based on the coefficient of determination (r^2= 0.986, 0.941, 0.922 and 0.919 respectively for clay loam, bentonite, sandy loam and kaolinite), the Langmuir isotherm can be considered as an appropriate isotherm to describe the experimental sorption data on whole experimental concentration ranges, but the fitted q_{max} of the Langmuir isotherm is more than the theoretical maximum sorption capacity (q'_{max}), implying that the mentioned isotherm is unable to describe the sorption process in a physically meaningful sense.

As shown in Fig. 4, the Toth isotherm fits the experimental data well in the studied concentration range. However, this isotherm predicts a solid phase concentration less than the measured values at the high concentration range (more than 5 mg/L). Furthermore, the fitted q_{max} values of the Toth isotherm are lower than the experimental data (similar to those of Langmuir isotherm).

The Langmuir-Freundlich isotherm is improper to describe the sorption data since this isotherm shows a curvature on the studied concentration range (as shown in Fig. 5). Also, the coefficient of determination (r^2) for modelled data by Langmuir-Freundlich isotherm is less than 0.7 for all studied soils.

In addition, the shape of sorption isotherms is an important characteristic in sorption studies, because they provide information about the sorption mechanisms.

Giles et al. [35] proposed classification according to the qualitative criteria to describe the experimental data instead of using empirical equations. In order to apply the mentioned classification to isotherm equations, mathematical criteria including slope at low concentration ($\lim\limits_{C_{eq}\to 0}\frac{dq}{dC_{eq}}$) and also curvature (concave or convex given by $\frac{d^2q}{d\,C_{eq}^2}$) and require further studies.

The slope of clay loam and sandy loam isotherms are relatively constant when the concentration approaches zero and no plateau was observed. Therefore, the sorption isotherm of MTBE for the mentioned soils belongs to the L1-class isotherm. The sorption isotherm of MTBE on bentonite is a C1-class isotherm because the sorption of MTBE on bentonite has a constant sorption affinity and can be described as a straight line in plot of *q* vs. C_{eq} without any significant plateau [36].

The sorption isotherm of MTBE on kaolinite has a concave shape without a plateau and can be classified as an

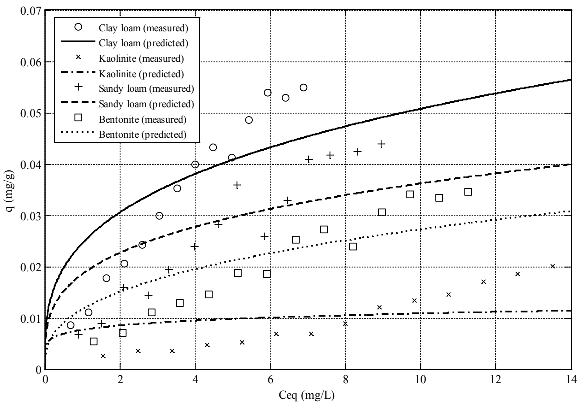

Fig. 5. Modeling results of the Langmuir-Freundlich sorption isotherms for MTBE.

S-class isotherm, which implies that sorption becomes easier by increasing the concentration in the liquid phase [37]. This type of sorption mainly will happen if solute molecule is mono-functional nature and also has a moderate intermolecular attraction leading to a vertical packing in the adsorbed layer. Moreover, there is strong competition for sorption sites in this case among adsorbed molecules and molecules of other solvents or other species.

The leading reasons for various sorption behaviours in the soils are the complexity of the soils and the properties of constitution compounds. If the clay/OC (organic carbon content) ratio is more than 62, then 50% of MTBE sorption will be due to the clay [38].

In the current research, the clay/OC ratio is 5.36 for clay loam, 1.69 for sandy loam, 63.15 for kaolinite and 166.3 for bentonite. Thus, sorption on clay should be considered significant in kaolinite and bentonite. The OC content is the primary and clay content of soils is the secondary critical parameters that correlate with the sorption of MTBE in soils.

3.2. *Effects of contact time, pH, and temperature*

The contact time can be considered as one of important parameters affecting the efficiency of a sorbent [39]. In the current study, kinetic feature of MTBE sorption onto the selected soil samples was studied by contact time of 180 min. The effect of contact time on the MTBE removal from aqueous solution at temperature of 298°K is shown in Fig. 6.

It can be seen that the MTBE removal efficiencies after 80 min for kaolinite, bentonite, sandy loam, clay loam is 53, 36, 23, and 14.8, respectively. It is obvious that the MTBE removal rate for all studied sorbents was initially rapid and about 80% of the total MTBE removal occurred within the first 80 min. Since the MTBE removal is influenced by availability sorption sites, so the observed trend can be attributed to the high availability of the sorption sites of studied sorbents at the baseline [40]. It can be seen that MTBE removal curves become almost flat by the time, and no significant change in MTBE removal was observed with time after 110 min. The final MTBE removal efficiencies of the studied sorbents reached to the 18.3, 28.3, 39.3, and 58.8% for kaolinite, bentonite, sandy loam, and clay loam, respectively.

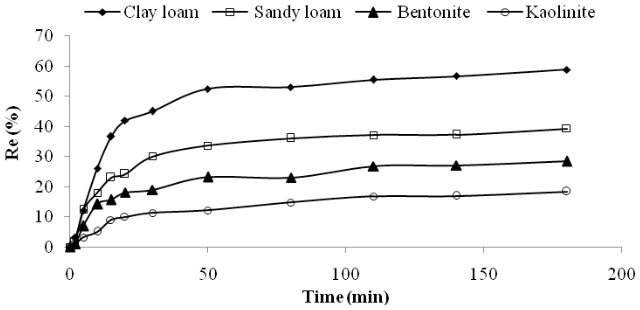

Fig. 6. Effect of contact time on the MTBE removal from aqueous solution.

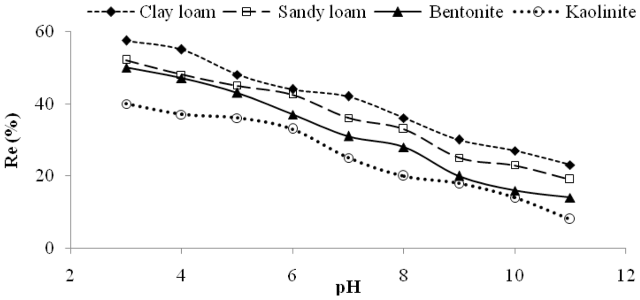

Fig. 7. Effect of pH on MTBE removal from aqueous solution.

Fig. 7 exhibits the pH effect on MTBE removal from the aqueous solution. As can be seen, the MTBE removal decreases by increasing the aqueous solution pH from 3 to 11. It should be mentioned that the MTBE is a non-polar compound. The maximum positive charge of MTBE (as non-polar compound) is obtained at low pH value. The surface charge was rapidly decreases by increasing the pH value [41]. Therefore, the maximum MTBE removal efficacy (57.4%) was occurred at acidic range (pH = 3) and decreased gradually as a straight line to reach minimum value of 23.1% at pH of 11. The similar trend was also reported by Ghadiri et al. [42] in a study on the mechanism of MTBE sorption regarding natural sorbents.

Furthermore, the temperature effect was investigated on the MTBE sorption on the soil samples (Fig. 8), as the K_d was decreased generally by increasing temperature.

The temperature effect can be described by the water solubility of MTBE (40 g/l at 20°C), which is function of temperature to be increased at higher temperatures resulting in reduced MTBE sorption affinity into selected soil samples. Several studies also reported sorption reduction of organic pollutants on natural sorbents by increasing temperature [43–45].

A better insight can be provided by assessing the thermodynamic parameters concerning MTBE sorption onto select soil samples. Therefore, the further study was conducted on the temperature effects on MTBE removal from the aqueous solution through calculating thermodynamic factors of ΔG, ΔH and ΔS respectively indicating Gibb's free energy, enthalpy, and entropy using Van 't Hoff equation as follow:

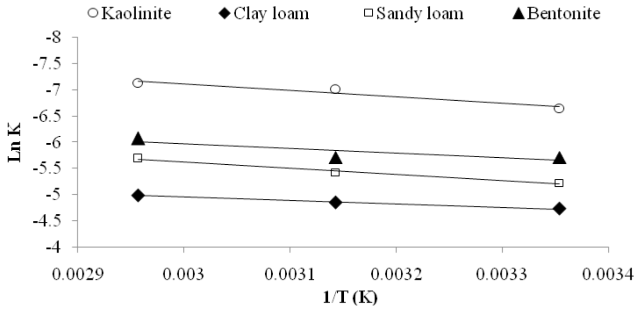

Fig. 8. Effect of temperature on MTBE removal from aqueous solution.

Table 6
Thermodynamic parametersfor MTBE sorption

Soil Sample	ΔH (kJ/mol)	ΔS (J/mol/K)	ΔG (kJ/mol)		
			298 K	318 K	338 K
Clay loam	–5.39	57.38	–22.50	–23.64	–24.79
Sandy loam	–9.66	75.70	–32.23	–33.74	–35.26
Bentonite	–7.40	71.82	–28.81	–30.25	–31.68
Kaolinite	–10.27	89.98	–37.10	–38.90	–40.70

$$LnK_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{11}$$

As well, ΔG can be calculated as:

$$\Delta G = \Delta H - T\Delta S \tag{12}$$

Table 6 shows the thermodynamic parameters calculated. The negative values of ΔH imply exothermic nature of the sorption process, verifying the earlier finding of decreasing K_d with increasing the temperature. The ΔH of all sorption was over –60 kJ/mol, confirming the absence of covalent bonding that mainly causes ΔH to be between –60 and –80 kJ/mol [46]).

The positive values of ΔS show higher entropy due to the loss of structured water molecules close to the sorbate that is more than the loss of entropy through transition of sorbate molecules from the aqueous solution.

The ΔG value for studied soil samples was different from –22.5 to –40.7 kJ/mol that is decreased with temperature, indicating spontaneous sorption MTBE into the selected soil samples. Higher negative ΔG values by increasing temperature demonstrate increased spontaneity of sorption by rising temperature.

3.3. Comparison study

Four different clay particles of perlite, dolomite, diatomite, and perlite/ diatomite/dolomite composites have been studied by Sheykhaoleslami et al. [48] for the MTBE removal from the aqueous solution. The Langmuir isotherm described well the MTBE equilibrium data. The order of diatomite (143.19 mg/g) > perlite/ diatomite/ dolomite (133.12 mg/g) > dolomite (103.18 mg/g) > perlite (93.13 mg/g) was achieved for the highest sorption capacity of clays for the MTBE sorption at equilibrium time of 120 min.

[49] et al. Evaluated the potential of hyporheic zone soils with organic carbon content of 1 to 7% for MTBE removal and other organic pollutants. The linear isotherm accurately was used to model the sorption mechanism of MTBE onto the studied soil samples ($0.937< r^2< 0.999$). The values obtained for K_d (based on linear isotherms) ranged from 0.0015 to 0.0087 L/kg for MTBE were highly related with the organic carbon content of the target sorbents.

According to Sim et al. [50], the MTBE removal from the aqueous solution was carried out through clays, including bentonite, vermiculite, and bentonite enhanced by a cationic surfactant (CTAB). The results modelled by Freundlich and Langmuir isotherms and sorption of MTBE was fitted properly with the Freundlich model ($0.977< r^2< 0.994$). The adsorbed amount of MTBE was in the order of vermiculite (K = 0.1568) > bentonite (K = 0.1326) > CTAB (K = 0.0998). They also found highly correlation of the MTBE removal from the aqueous solution with the organic acid and pH.

The MTBE uptake by Cohansey sand, an acid washed sand, and Neshaminy clay showed that the results modelled by linear isotherms and the K_d (based on linear isotherms) were 0.0925 L/kg with r^2 of 0.936 [51].

According to the present findings for the MTBE removal from the aqueous solution are comparable and moderately higher than those of reported in the literature in some cases.

4. Conclusion

The MTBE sorption was investigated on selected soil samples, including clay loam, sandy loam, bentonite and kaolinite, through a comprehensive batch sorption experiments. The linear, Freundlich, Langmuir, Toth and Langmuir-Freundlich sorption isotherms were employed to analyse the obtained results. Overall, an increase in the sorption affinity of the studied soils for MTBE was based on the order of kaolinite < bentonite < sandy loam < clay loam in the determined concentration ranges. Among the applied MTBE sorption isotherms, the Freundlich model fits best the data for MTBE sorption by all the studied sorbents. Furthermore, evaluating the effects of contact time, pH, and temperature on sorption affinity of MTBE into the soil samples indicated relatively 80% of the total MTBE removal within the first 80 min. A decrease in the MTEB removal efficiency was observed by increasing pH values and the maximum MTBE removal efficiency (57.4%) was achieved at pH of 3. The temperature effects on the sorption process indicated that its significant role in the sorption of MTBE to soils. Based on the results obtained to calculate thermodynamic parameters of ΔG, ΔH and ΔS, the negative values of ΔH were indicative of the exothermic nature of the sorption process. The ΔG value for studied soil samples varied from –22.5 to –40.7 kJ/mol, exhibiting spontaneous sorption.

Our results provided valuable in sight in understanding the sorption characteristics of studied soil samples, highlighting that the studied loam soils could be used for the MTBE removal from the aqueous solutions as low cost adsorbents. Finally, it should be mentioned that further researches are required for achieving more efficient field application of the soils for the MTBE removal.

Symbols

C_0 — Initial aqueous concentration (mg/L)
C_{eq} — Equilibrium aqueous concentration (mg/L)
f_{oc} — Fraction of organic carbon available for partitioning (w/w, dimensionless)
K — Affinity coefficient (dimension depend on equation)
K_d — Sorption distribution coefficient (L/kg)
K_{oc} — Organic carbon normalized partitioning coefficient (L/kg)
K_{ow} — Octanol/water partition coefficient (dimensionless)
M — Sorbent mass (g)
q — Solid phase concentration (mg/g)
q_{max} — Maximum sorption capacity (mg/g)
q'_{max} — Theoretical maximum sorption capacity (mg/g)
V — Volume of solution
V_g — Volume of gas phase (L)
V_m — Micro pore volume per mass of the sorbent (cm^3/g)
V_w — Solution volume added into the nominal vial
α — Heterogeneity or shape parameter (dimensionless)
ΔG — Gibb's free energy (kJ/mol)
ΔH — Enthalpy (kJ/mol)
ΔS — Entropy (J/mol/K)
η — Exponent (dimensionless)
ρ — Density of the solute

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