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Activated Carbon Adsorption of Fuel Oxygenates MTBE and ETBE from Water

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Abstract The aqueous phase adsorption of fuel oxygenates methyl tertiary butyl ether (MTBE) and ethyl tertiary butyl ether (ETBE) onto commercially available granular activated carbon (GAC; Norit GAC 1240) was investigated in a batch system at 27°C. The oxygenate concentrations were determined by headspace gas chromatography/mass spectrometry analyses. The experimental data were used with four two-parameter isotherm models (Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich) and two kinetic models (pseudo first-order and pseudo second-order) to determine equilibrium and kinetic parameters. Considering the correlation coefficient and root mean square error, Dubinin–Radushkevich isotherm showed better fit with the equilibrium data for MTBE. However, the performances of Langmuir and Dubinin–Radushkevich models were comparable for ETBE. The adsorption capacities were calculated as 5.50 and 6.92 mg/g for MTBE and ETBE, respectively, at an equilibrium solution concentration of 1 mg/L using Dubinin–Radushkevich isotherm. The differences between the model predictions and experimental data were similar for the pseudo first-order and pseudo second-order kinetic models. Gibbs free-energy changes of adsorption were found to be −22.59 and −28.55 kJ/mol for MTBE–GAC and ETBE–GAC systems, respectively, under the experimental conditions studied.

Keywords Adsorption · Fuel oxygenate · MTBE · ETBE

1 Introduction

Oxygen-containing compounds (i.e., oxygenates) were first used as octane enhancer in gasoline in late 1970s. The phase-out of lead-including additives due to their toxic properties increased the consumption of oxygenates in gasoline. The addition of oxygenate into gasoline also reduced the toxic emissions from motor vehicles. Therefore, in the USA, oxygenated fuel and reformulated gasoline were required in CO and ozone non-attainment areas, respectively in Clean Air Act Amendments of 1990. There are two main groups of compounds that can be considered as fuel oxygenates: alcohols (e.g., methanol and ethanol) and ethers (e.g., methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), and tertiary amyl methyl ether (TAME)). Ethers have low heat of vaporization and can be blended at the refinery. They are not as sensitive to water as the alcohols and can be transported efficiently to the marketplace using the current gasoline distribution systems. Therefore, ether oxygenates have been preferred by the refiners. MTBE is the most common fuel oxygenate used worldwide.

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ETBE is mostly used in Europe (e.g., France, Italy, and Spain). The consumption of ETBE is expected to increase due to tax incentives for the use of ethanol in its production since ethanol can be obtained from renewable sources.

The widespread introduction of oxygenates, especially MTBE, into fuel systems has increased the incidence of surface water and groundwater contaminations. Water contamination can occur mainly from leaking aboveground and underground fuel storage tanks, pipelines, and refueling spills. Additionally, watercraft activities can also cause contaminations in harbors, lakes, and open water reservoirs. With respect to other gasoline constituents (e.g., benzene, toluene, ethylbenzene, and xylenes (BTEX)) MTBE has a relatively high solubility in water (43–54 g/L) and little affinity for soil (log K_{oc}=1.0–1.1 (log L/kg); API, 2000). Consequently, it moves rapidly from leaking fuel storage tanks or point of spill through the soil to an aquifer. ETBE has lower water solubility (26 g/L) and higher partition coefficient (log K_{oc}= 1.0–2.2 (log L/kg)) compared to MTBE.

Ethers affect the esthetic quality of drinking water since they have unpleasant taste and odor. MTBE can be detected at 2.5 μg/L for odor and 2.0 μg/L for taste (US EPA 2000). For that reason, public water systems are required to monitor MTBE contamination by the local or federal authorities in many regions. The US Environmental Protection Agency (EPA) classified MTBE as a possible human carcinogen on the basis of inhalation cancer tests (US EPA 2000). Recently, Finish Environment Institute has also prepared risk-assessment report for MTBE on behalf of the European Commission (EC 2002).

Trihalomethanes, solvents, and gasoline oxygenates were the most commonly detected volatile organic compounds in ambient groundwater sampled by the National Water-Quality Assessment Program of the US Geological Survey (USGS; USGS 2001). MTBE was detected in about 5% of groundwater samples collected across the USA with concentrations typically well below the EPA drinking water consumer advisory concentrations of 20 to 40 μg/L (US EPA 1997). Only less than 1% of samples exceeded 20 μg/L. The USGS study also indicated that MTBE was most frequently detected in groundwater underlying urban areas in comparison to agricultural and mixed land-use settings. In a joint study of USGS and EPA, data on finished drinking water from selected communities in 12 states in the USA were examined (USGS 2001). MTBE was detected in 9% of the community water systems. The concentrations were low, and less than 1% exceeded the EPA consumer advisory concentration, a finding which is consistent with the USGS study of ambient groundwater. MTBE concentrations measured in river water and drinking water in Germany have been reported to be approximately two to three orders of magnitude lower than the US drinking water standard of 20–40 μg/L (Achten et al. 2002). In Spain, a monitoring program was carried out to determine MTBE, its main degradation products, and other gasoline additives in 21 groundwater wells that were located near different gasoline point sources (Rosell et al. 2003). All samples contained MTBE at levels ranging from 0.3 to 70 μg/L (with a maximum concentration of 670 μg/L in one site). ETBE was detected below 1 μg/L.

The removal of ether contaminants from water has been studied extensively in the literature. The most of these studies focused on MTBE remediation since it is the main fuel oxygenate used. The effectiveness of several water treatment processes has been considered such as catalytic conversion (Centi et al. 2002), membrane separation (Urkiaga et al. 2002), biodegradation (Steffan et al. 1997), air stripping (Wilhelm et al. 2002; Sutherland et al. 2004; Sutherland et al. 2005), advanced oxidation (O_3/H_2O_2 and UV/H_2O_2; Sutherland et al. 2004; Sutherland et al. 2005), and adsorption (Wilhelm et al. 2002; Sutherland et al. 2004; Sutherland et al. 2005). Adsorption is one of the most utilized and effective processes for the removal of volatile organic compounds from water. Different adsorbents have been tested for the ether oxygenates: zeolites (Anderson 2000; Li et al. 2003; Erdem-Senatalar et al. 2004), resins (Annesini et al. 2000; Davis and Powers 2000; Lin et al. 2002; Bi et al. 2005; Hung and Lin 2006), and activated carbon (granular, powdered, or activated carbon fiber; Sutherland et al. 2004; Sutherland et al. 2005; Davis and Powers 2000; Li et al. 2002; Shih et al. 2003; Yu et al. 2005; Quinlivan et al. 2005).

Batch adsorption experiments were carried out to screen the alternative sorbents (synthetic carbonaceous resins, porous graphitic carbon, acrylic resins, octadecyl (C18) silicas, and bituminous coal granular activated carbon (GAC; Calgon F400)) for treating groundwater contaminated with MTBE (Davis and Powers 2000). The results showed that porous graphitic carbon and two synthetic carbonaceous resins had a greater capacity for MTBE than activated carbon.

Yu et al. (2005) have obtained isotherms for the adsorption of MTBE and other fuel oxygenates (ETBE, TAME, diisopropyl ether (DIPE), tert-butyl alcohol (TBA), and ethanol (EtOH)) on two bituminous coal activated carbons (Calgon F400 and F600). The relative capacities of adsorbents were DIPE > TAME > ETBE > MTBE > TBA, EtOH.

The performances of two coconut shell GACs in removing MTBE in the presence of competitors (natural organic matter, TBA, and BTX) have been evaluated using rapid small-scale column tests (Shih et al. 2003).

The majority of the adsorption studies in the literature are on the removal of MTBE from water. However, the consumption of ETBE as a fuel oxygenate is expected to increase due to the phase-out of MTBE in some countries. There are few studies on equilibrium and kinetics of ether oxygenate adsorption. Our objective in this study was to investigate equilibrium and kinetics of MTBE and ETBE adsorption onto GAC and calculate Gibbs free-energy change of adsorption. The adsorbent selected (i.e., NORIT GAC 1240) was steam-activated coal GAC. It was recommended for the superior adsorption properties for compounds causing taste and odor problems in water.

2 Materials and Methods

MTBE (99.8%) and ETBE (99%) were obtained from LabScan and Aldrich, respectively. Sodium chloride (99.5%, Panreac) was used to increase the extraction efficiency in headspace analysis. The adsorbent (NORIT GAC 1240) was purchased from Fluka. Some of the manufacturer-provided properties of GAC are given in Table 1. Adsorbent was dried at 110°C for 4 h and stored in a desiccator before being used in the experiments.

Table 1 Properties of adsorbent (Norit GAC 1240)

	GAC	Units
Iodine number	1075	–
Methylene blue adsorption	22	g/100 g
Total surface area (BET)	1,175	m^2/g
Apparent density	480	kg/m^3
Effective size	0.6–0.7	mm
Ash content	7	mass%

All the solutions were prepared with deionized water obtained from Milli-Q Ultrapure Water Purification system. The concentrations of MTBE and ETBE in stock solutions were 2,000 mg/L. Standard oxygenate solutions were made from these stock solutions. Batch equilibrium and kinetic experiments were carried out in headspace-free 40 ml vials with polytetrafluorethylene (PTFE)-faced silicon septum (EPA Vial, Cole-Parmer). The solid/liquid ratio was constant for all the samples at 8 g/L, which was decided after preliminary tests. Since MTBE concentrations up to 80 mg/L have been reported in groundwater in the vicinity of gasoline-contaminated sites (Schirmer et al. 2002), initial oxygenate concentrations (C_0) were in the range of 1–50 mg/L in adsorption isotherm experiments. Samples were equilibrated in a shaking water-bath (GFL 1086) with microprocessor-controlled temperature regulation (temperature constancy: ±0.1°C) at 27°C and shaking frequency of 100 rpm for 48 h. Preliminary tests have also indicated that the time to reach the equilibrium was less than 48 h for both MTBE and ETBE. In kinetic experiments, samples were taken periodically for the determination of aqueous-phase oxygenate concentrations. Three different initial oxygenate concentrations (i.e., C_0=2, 5, and 15 mg/L) were studied in these tests. Ten milliliters of supernatant in the vial was transferred with a gas-tight syringe equipped with PTFE filter (PTFE Membrane 25/45, Agilent) to 20 ml headspace vial containing 2 g NaCl for the sample quantification. Blank vials (containing only deionized water) and control vials (containing standard oxygenate solutions of known concentration) were also used for each set of isotherm and kinetic experiments. The analyses of control vials confirmed that there were no significant losses of oxygenates due to volatilization during the experiments.

Gas chromatography (GC) has been used mainly with different detectors (e.g., photoionization detector, flame ionization detector, mass selective detector) for the analyses of ether oxygenates in water. GC/MS is a more reliable and sensitive technique. A variety of sample preparation or enrichment methods can be coupled to GC/MS such as direct aqueous injection (Church et al. 1997; Hong et al. 1999; Zwank et al.

2002), headspace (Lin et al. 2003), solid phase microextraction (Piazza et al. 2001; Dewsbury et al. 2003), and purge and trap (Rosell et al. 2003). The selection of the analysis technique depends on the desired selectivity, sensitivity, and matrix to be analyzed.

Quantitative analyses were performed using a static headspace-gas chromatography/mass spectrometry system (HS-GC/MS; HS: Agilent 7694 Headspace Sampler, GC: Agilent 6890, MS: Agilent 5973) equipped with a capillary column (HP-5MS, 30 m× 0.25 mm×0.25 µm). Samples were heated in the headspace oven at 80°C for 20 min. Headspace vial was then pressurized with helium for 1.0 min. Sample was transferred to the injection port of GC through the heated transfer line kept at 180°C. The GC injection port temperature was 200°C. The split ratio was 1:13. Carrier gas was helium with a flow rate of 1.0 ml/min. The column head pressure was maintained at 6.78 psi. The oven temperatures were 35°C initial for 1 min and 20°C/min ramp to 250°C. Selected ion monitoring mode was used for the detection and quantification of MTBE and ETBE with the following selected ions; MTBE: 73, 57 ETBE: 59, 87. MS source and quadruple temperatures were 230°C and 150°C, respectively. Five-point calibrations were performed for the determination of concentrations of oxygenates. The correlation coefficients (R^2) for the calibration curves were 0.989 and 0.987 for MTBE and ETBE, respectively. Instrumental MTBE and ETBE detection limits were 0.1 µg/L (based on the signal/noise=3). Some of the isotherm experiments were completed twice to check the repeatability. It was found that data were repeatable (mean ± standard deviation= 9.8±6.4 %).

3 Results and Discussion

The experimental data were analyzed by equilibrium and kinetic models. Four two-parameter isotherm models (Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R)) and two kinetic models (pseudo first-order and pseudo second-order) were tested.

The amount of oxygenate adsorbed per unit adsorbent mass was calculated by a simple mass balance:

$$q = (C_0 - C_t)\frac{V}{m}$$

where q is the amount adsorbed (mg/g), C_0 is the initial oxygenate concentration (mg/L), C_t is the concentration at time t (mg/L), V is the solution volume (L), and m is the mass of the adsorbent (g).

Batch equilibrium and kinetic parameters were obtained using nonlinear regression analysis (POLYMATH 5.1). Two indicators were used to compare various models representing the same dependent variable (i.e., q_e for the isotherm models and q for the kinetic models): correlation coefficient (R^2) and root mean square error (RMSE; or root mean square deviation). The correlation coefficient is frequently used to decide whether the model represents correctly the experimental data. RMSE is defined as;

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{1}^{N}\left(q_{\mathrm{exp}} - q_{\mathrm{model}}\right)^2}{N}}$$

where q_{exp} and q_{model} are the experimentally measured and model prediction for the amount of oxygenate adsorbed, respectively. A model with smaller RMSE represents the data more accurately than a model with larger values of this indicator.

The single-solute equilibrium data and isotherm model predictions are given in Fig. 1 for MTBE and Fig. 2 for ETBE. In figures, symbols represent experimental data, and lines represent model predictions. The isotherm parameters obtained by nonlinear regression analysis are provided in Table 2. Brief information about the isotherm model equations used is given below.

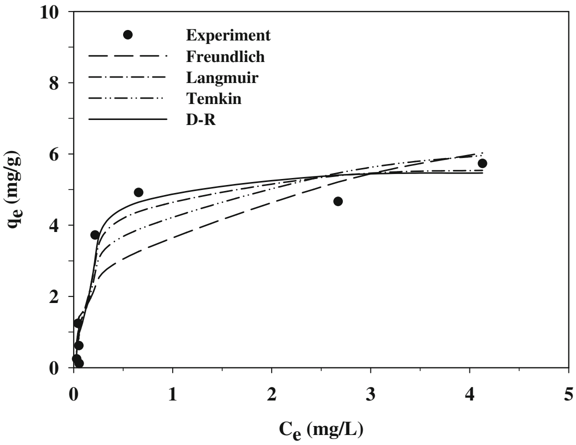

Fig. 1 Experimental equilibrium data and adsorption isotherms for MTBE

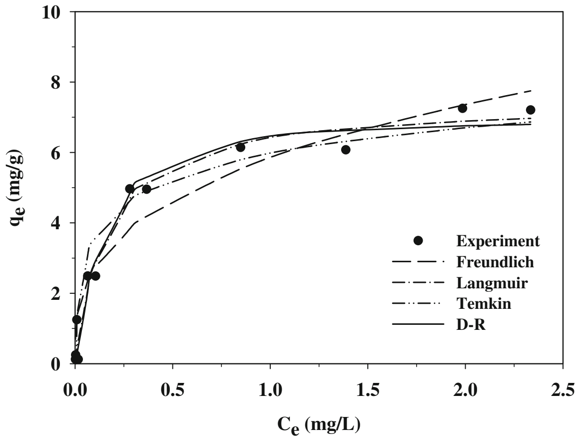

Fig. 2 Experimental equilibrium data and adsorption isotherms for ETBE

3.1 Freundlich Isotherm

$$q_e = K_f C_e^{1/n}$$

where K_f and n are Freundlich constants and related to the adsorption capacity and adsorption intensity, respectively. Since $1<n<10$ for both oxygenates ($n=2.994$ for MTBE and $n=3.005$ for ETBE), adsorption onto GAC is favorable (Gunay et al. 2007). However, for MTBE, low correlation coefficient ($R^2=0.778$) and high RMSE (RMSE=1.029) were obtained with this model. Yu et al. (2005) have also reported n values for two GACs as 1.479 and 1.608 (GAC: Calgon F400) and 1.414 and 2.028 (GAC: Calgon F600) for MTBE and ETBE, respectively.

3.2 Langmuir Isotherm

$$q_e = \frac{K_L a_L C_e}{1 + a_L C_e}$$

where K_L and a_L are Langmuir parameters related to the adsorption capacity and energy of adsorption, respectively. The ratio of K_L/a_L is the maximum amount of oxygenate adsorbed per unit mass of adsorbent (q_{max}) to form a complete monolayer. The maximum monolayer adsorption capacities were found to be similar for both oxygenates (1.266 mg/g for MTBE and 1.252 mg/g for ETBE). These q_{max} values are comparable with those reported in the literature for different GACs. Yu et al. (2005) have reported q_{max} for the adsorption of MTBE and ETBE onto Calgon F400 and F600. q_{max} was 0.686 and 1.799 mg/g when the adsorbent was F400 and 1.434 and 1.849 mg/g when the adsorbent was F600 for MTBE and ETBE, respectively.

The separation factor (R_L) is used for Langmuir isotherm to decide whether the adsorption process is favorable or unfavorable (Gunay et al. 2007). It is a dimensionless constant and defined as:

$$R_L = \frac{1}{(1 + a_L C_0)}$$

Depending on the initial oxygenate concentrations, R_L values were found to be in the range of 0.004–0.178 and 0.003–0.144 for MTBE and ETBE, respectively, which indicate favorable adsorption.

3.3 Temkin Isotherm

$$q_e = \frac{RT}{b} \ln(K_{Te} C_e)$$

where K_{Te} is Temkin isotherm constant (L/g), b is related to heat of adsorption (J/mol), R is the gas constant (8.314×10^{-3} kJ/K mol), and T is the absolute temperature (K). Temkin model constants K_{Te} and b

Table 2 Adsorption isotherm parameters

		MTBE	ETBE
Freundlich	K_f	3.753	5.844
	n	2.994	3.005
	R^2	0.778	0.937
	RMSE	1.029	0.668
Langmuir	K_L	5.829	7.468
	a_L	4.605	5.962
	R^2	0.916	0.977
	RMSE	0.634	0.410
Temkin	b	221.299	235.122
	K_{Te}	47.750	276.934
	R^2	0.887	0.936
	RMSE	0.733	0.651
Dubinin–Radushkevich	q_m	5.516	6.933
	E	24.980	28.316
	R^2	0.940	0.971
	RMSE	0.536	0.457

were determined as 47.750 L/g and 221.299 J/mol for MTBE, and 276.934 L/g and 235.122 J/mol for ETBE, respectively. High RMSE (RMSE=0.733) and low correlation coefficient (R^2=0.887) were obtained for MTBE when Temkin isotherm was tested.

3.4 Dubinin–Radushkevich Isotherm

$$q_e = q_\mathrm{m} \exp\left(\frac{(RT\ln(1+1/C_e))^2}{-2E^2}\right)$$

where q_m is the maximum adsorption capacity (mg/g), and E is the energy of adsorption (kJ/mol). The constants q_m and E were found to be 5.516 mg/g and 24.980 kJ/mol for MTBE and 6.933 mg/g and 28.316 kJ/mol for ETBE, respectively. The q_m values were higher than those obtained from the Langmuir equation. It has been reported that E values lower than 83 kJ/mol confirms the physical nature of the adsorption (Gimeno et al. 2003).

R^2 and RMSE values were similar for the Langmuir and D–R models for ETBE (Table 2). However, relatively higher correlation coefficient (R^2 of 0.940) and lower error (RMSE of 0.536) were obtained with D–R model compared to other isotherms used for MTBE. Therefore, the amount of oxygenate adsorbed at C_e=1 mg/L was calculated using D–R model and found to be 5.50 and 6.92 mg/g for MTBE and ETBE, respectively. GAC used in the experiments showed greater affinity to ETBE than MTBE since ETBE has lower solubility in water. Similar result was also obtained with different GACs (Yu et al. 2005). Davis and Powers (2000) have reported sorption capacity of Calgon F400 as 3.1 mg/g at C_e=1 mg/L for MTBE. The sorption capacities higher than those reported here were stated for carbonaceous resins (Ambersorb 563, Ambersorb 572; Davis and Powers 2000; Bi et al. 2005), mordenite (Anderson 2000), and all-silica β zeolite (Li et al. 2003).

3.5 Adsorption Kinetics

To investigate adsorption kinetics, pseudo first-order and pseudo second-order models were tested with experimental adsorption capacity (q) versus time (t) data. In pseudo first-order kinetic equation, adsorption capacity is given as:

$$q_t = q_\mathrm{e}(1-\exp(-k_1 t))$$

where; q_t is the adsorption capacity at time t, q_e is the adsorption capacity at equilibrium, and k_1 (h^{-1}) is the first-order rate constant. q_e and k_1 were determined by nonlinear regression.

The pseudo second-order kinetic model can be expressed as;

$$q_t = \frac{q_\mathrm{e}^2 k_2 t}{1 + q_\mathrm{e} k_2 t}$$

where k_2 (g/mg h) is the pseudo second-order rate constant and was calculated by nonlinear regression analysis.

The experimental adsorption capacity versus time data and model predictions are given in Figs. 3 and 4 for MTBE and ETBE, respectively. The model parameter values are presented in Table 3. The experimental q_e values were also included in Table 3 to compare with those predicted. As can be seen from Figs. 3 and 4, the amount of MTBE and ETBE adsorbed increased with time until the equilibrium was reached. The maximum adsorption capacity was obtained at about 15 h for MTBE and 20 h for ETBE with the exception of C_0=15 mg/L ETBE data. When the initial ETBE concentration was 15 mg/L, it took about 30 h to reach the equilibrium. An increase in initial oxygenate concentration from 2 to 15 mg/L increased the amount of oxygenate adsorbed both for MTBE and ETBE. The performances of kinetic models tested were comparable based on the correlation coefficients and RMSEs for each oxygenate. The highest RMSE (0.174 and 0.178 for pseudo first-order

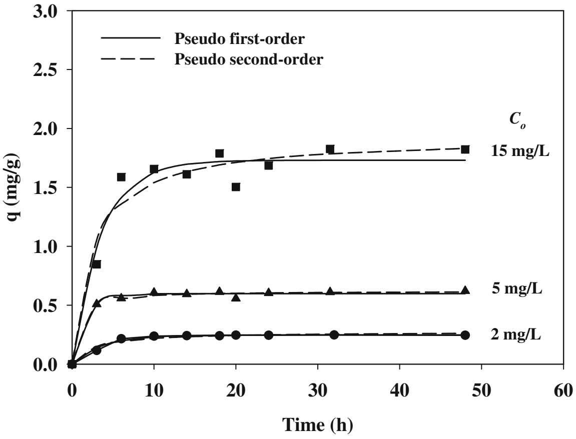

Fig. 3 Comparison of pseudo first-order and pseudo second-order kinetic models with experimental data for MTBE adsorption

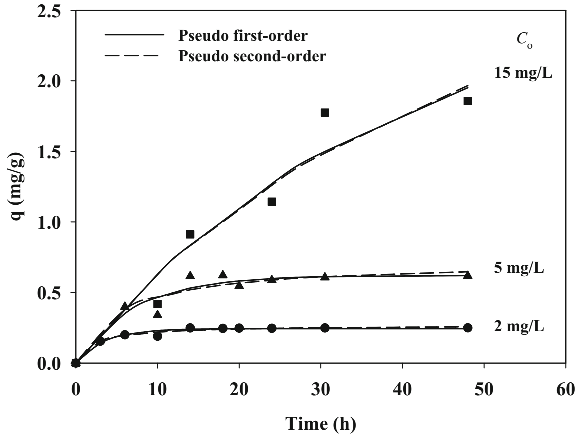

Fig. 4 Comparison of pseudo first-order and pseudo second-order kinetic models with experimental data for ETBE adsorption

and pseudo second-order models, respectively) were obtained for ETBE at C_0=15 mg/L.

3.6 Gibbs Free-Energy Change of Adsorption

The Gibbs free-energy change (ΔG) of adsorption was calculated from the following equation (Milonjic, 2007):

$$\Delta G = -RT \ln 10^3 K$$

where K is the equilibrium constant. Since the value of K obtained from Khan and Singh plot ((ln(q_e/C_e) versus q_e; Fig. 5) has a unit of (l g^{-1}), K was recalculated as dimensionless by multiplying it with 10^3 to have a correct value of ΔG. The Gibbs free-energy changes were determined as −22.59 kJ/mol for MTBE and −28.55 kJ/mol for ETBE at 27°C.

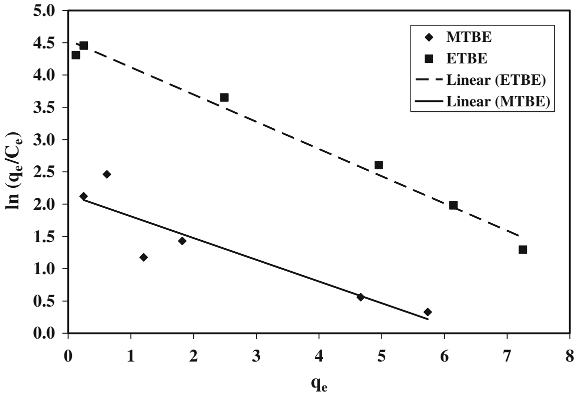

Fig. 5 Khan and Singh plots of ln (q_e/C_e) vs. q_e for the adsorption of MTBE and ETBE onto GAC

4 Conclusions

The equilibrium and kinetic parameters of MTBE and ETBE adsorption onto granular activated carbon were determined using nonlinear regression analysis. While Dubinin–Radushkevich isotherm described the equilibrium data better than the other isotherms tested for MTBE adsorption, similar values of R^2 and RMSE were obtained for Langmuir and Dubinin–Radushkevich isotherms for ETBE. The adsorption capacity of GAC was slightly higher for ETBE than that for MTBE, a result which is in agreement with those reported in the literature for the other GAC adsorbents. There were no significant differences between the performances of pseudo first-order and pseudo second-order kinetic models. Gibbs free-energy changes were negative for both the adsorption of MTBE and ETBE onto GAC. Although promising results were obtained for the single solute (i.e., MTBE

Table 3 Adsorption kinetic parameters

C_0 (mg/L)	q_e (Exp.; mg/g)	Pseudo first-order				Pseudo second-order			
		q_e (mg/g)	k_1 (h^{-1})	R^2	RMSE	q_e (mg/g)	k_2 (g/mg h)	R^2	RMSE
MTBE									
2	0.246	0.248	0.266	0.987	0.009	0.275	1.418	0.962	0.016
5	0.618	0.599	0.604	0.989	0.019	0.620	2.532	0.991	0.018
15	1.820	1.730	0.282	0.956	0.121	1.926	0.207	0.945	0.135
ETBE									
2	0.249	0.244	0.283	0.965	0.015	0.268	1.652	0.977	0.012
5	0.612	0.621	0.138	0.915	0.061	0.720	0.257	0.907	0.063
15	1.859	2.737	0.026	0.944	0.174	4.485	0.004	0.941	0.178

or ETBE) adsorption capacity of NORIT GAC 1240, competitive effects of other gasoline components like BTEX or natural organic matter, and the performance of adsorbent under continuous operation should be investigated before the application of this adsorbent for the remediation of oxygenate-contaminated water.

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