

Equilibrium and kinetic studies of simultaneous adsorption of methyl *tert*-butyl ether (MTBE) and *tert*-butyl alcohol (TBA) by nano-perfluorooctyl alumina (PFOAL_g)

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ABSTRACT

Methyl *tert*-butyl ether (MTBE) has emerged as an important water pollutant because of its high mobility, persistence, and toxicity. Equilibrium and kinetic adsorption of MTBE and its main degradation product *tert*-butyl alcohol (TBA) onto nano-perfluorooctyl alumina prepared by using nano- γ -alumina (nano-PFOAL_g) was investigated in a batch system. The oxygenate concentrations were determined by head space gas chromatography/mass spectrometry analyses. The experimental data were used with three isotherm models (Langmuir, Freundlich and BET) and two common kinetic models (pseudo first-order and pseudo second-order) to determine equilibrium and kinetic parameters. Considering the correlation coefficient, all three isotherm models were obtained good correlation between the experimental and predicted data. The kinetic data proved a closer fit to the pseudo-second order model. Values for the rate constant, k_2 , were obtained for MTBE and TBA adsorption, as 0.00226 and 0.023 ($g\ mg^{-1}\ sec^{-1}$), respectively. Results reveal that PFOAL_g is an effective adsorbent for methyl *tert*-butyl ether and *tert*-butyl alcohol.

NOMENCLATURE

K_s	Equilibrium constant of adsorption for first layer in Langmuir and BET isotherms, (mg/L) ⁻¹
K_L	Equilibrium constant of adsorption for upper layers in BET isotherm, (mg/L) ⁻¹
k_1	pseudo-first-order rate constant (sec^{-1})
k_2	Pseudo-second-order rate constant ($g\ mg^{-1}\ sec^{-1}$).
nano-PFOAL _g	nano-perfluorooctyl alumina prepared by using γ -alumina
C_{eq}	Equilibrium concentration of solution
q	Amount of adsorbate adsorbed on the solid surface, (mg/g)
q_m	Amount of adsorbate corresponding to complete monolayer adsorption, (mg/g)
K_f	Affinity coefficient in Freundlich isotherm (dimensions depend on equation)
m_s	sorbent mass, (g)

INTRODUCTION

Oxygenates like MTBE were developed in the 1970s as octane enhancers to replace toxic additives like tetra ethyl lead (TEL), which have

been phased out of gasoline. On the other hand TBA can be used directly as fuel oxygenate. TBA is also the main degradation product of MTBE and a potential impurity from the MTBE manufacturing process [1]. Due to leaking underground gasoline storage tanks, oxygenates are the third most commonly detected VOC contaminant in ambient ground water [2]. MTBE and TBA tend to partition strongly from the gas phase into the water phase [3]. MTBE is a suspected carcinogenic agent, which poses significant health threat to people. In addition, it gives a very unpleasant taste to drinking water when present even in very low amounts [4]. Health concerns for TBA include eye and skin irritation due to exposure, liver and kidney damage due to ingestion and central nervous effects due to inhalation [5]. Due to MTBE and TBA's high water solubility, low Henry's law constant and resistance to biodegradation complicate its removal from water by conventional treatment techniques [5-7]. The adsorption process is a proven technology for the removal of synthetic organic compounds from water. Adsorption processes, moreover, have the advantage of ease in use and are easy to combine with other treatment technologies. Furthermore Adsorption processes do not add undesirable byproducts to drinking water. Granular activated carbon (GAC) adsorption is a widely used technology for treating water contaminated with many taste- and odor-causing organics [8]. However, GAC performance in removing MTBE was observed to be reduced when other synthetic organic compounds coexist with MTBE or in the presence of natural organic matter (NOM) [4, 9]. The application of alternative adsorption materials (e.g. zeolites or resins) shows high potential, but as long as these new materials are too expensive to be applied in large quantities, their use will not expand into drinking water production [1, 10]. Recent developments in synthesis of new adsorbents such as perfluorooctyl alumina (PFOAL) may be economically competitive with other more established treatment technologies (air stripping, advanced oxidation processes, and granular activated carbon) for MTBE and TBA removal. On the surface of surface-modified alumina, i.e.

PFOAL, perfluorinated organic groups are bonded to the surface from one end of the chain, Fig. 1. These groups have nonpolar characteristics. Consequently, the surface of the alumina modified by these nonpolar groups has a high tendency for adsorption of organic pollutants such as MTBE and TBA [11].

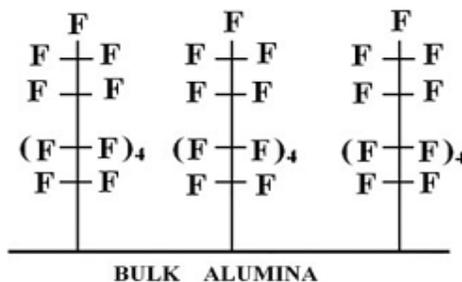


Fig 1. Schematic representation of perfluorooctyl groups the surface of alumina [12].

Because of their larger surface areas, nano forms of PFOAL have higher adsorption capacities compared with conventional forms of PFOAL [13]. Consequently nano forms of PFOAL could have a higher potential for removal of organic pollutants. To evaluate the effectiveness of nano-PFOAL for adsorption and removal of MTBE and TBA from contaminated water, kinetic and equilibrium adsorption of MTBE and TBA onto nano-PFOAL_g in relatively low concentration range (20-180 mg MTBE /L) and (4-36 mg TBA /L) were conducted in this study.

MATERIALS AND METHODS

MTBE (purity > 99%) and TBA (purity > 99%) were obtained from Merck. Sodium chloride (99.5%) was used to increase the extraction efficiency in headspace analysis. nano-PFOAL_g was prepared by using γ -alumina by Dehghani et al [13]. The characteristics of nano-PFOAL_g are presented in Table 1. Prior to experiments, adsorbent samples were dried in an atmospheric oven at 100°C for 12 h. To obtain adsorption equilibrium isotherm data with the powdered sorbents, aqueous phase adsorption experiments were performed in 10 mL glass vials using a fixed sorbent/liquid ratio (0.1 g sorbent/10mL aqueous solution) and varied concentrations of MTBE initial solutions. In all experiments, the vials were agitated on a fixed speed rotator at room temperature (22±2 °C) for a minimum of 3

h at 160 rpm, for adsorption equilibrium to be achieved. Preliminary tests have also indicated that the time to reach the equilibrium was less than 30 min for both MTBE and TBA. The adsorption amount of MTBE in the sample was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m_s}$$

where q_e is the equilibrium adsorption amount (mg/g), C_0 is the initial concentration of MTBE and TBA solutions (mg/L), C_e is the equilibrium concentration of MTBE and TBA (mg/L), V is the volume of solution (L), and m_s is the mass of adsorbent (g).

Table 1
Structural properties of the adsorbent

BET surface area	204.85 (m ² /g)		
Compositions of surface element	C(wt.%)	H(wt.%)	N(wt.%)
	6.18	1.07	0.06
Perfluorinated content	604 (μmol/g)		
Average crystalline size	2.5 nm		

For the measurement of the time-dependent uptake of MTBE onto PFOAL_g, 3 g adsorbent was introduced to a 300-ml headspace-free flask. The flask was placed in room temperature (22±2°C) incubating shaker. Aqueous samples were withdrawn from the flask at different time intervals. Adsorbents were separated from water by filtration through 0.22-μm membrane filters. Then samples were heated in the oven at 80°C for 20 min and some salt added to the sample vials to enhance partitioning of compounds especially TBA into the headspace. The concentration of residual MTBE was determined and the adsorption amount was calculated according to the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m_s}$$

where q_t is the adsorption amount at time t (mg/g) and C_t (mg/L) is MTBE and TBA concentration at time t . Quantitative analyses

were performed using a static headspace-gas chromatography/mass spectrometry system (ThermoFinnigan, Italy) equipped with a capillary column (60 m × 0.25 mm × 0.5 μm, J&W Scientific, USA). The split ratio was 1:10. Carrier gas was helium with a flow rate of 1.1 ml/min. The oven temperatures were 40°C initial for 14 min and 20 °C/min ramp to 100°C.

RESULTS AND DISCUSSION

The Freundlich, Langmuir and BET isotherm models and pseudo first-order and pseudo second-order models were used to model the equilibrium and kinetics of the adsorption process of MTBE and TBA on the surface of nano-PFOAL_g.

Freundlich Isotherm:

$$q_e = K_f C_e^{\frac{1}{n}}$$

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 ($n=1.3497$ for MTBE and $n=1.1817$ for TBA), adsorption onto nano-PFOAL_g is favorable. A good correlation was obtained for adsorption of the both oxygenates by Freundlich model, as reflected by correlation coefficients (R^2) in the value of 0.995 and 0.996 for MTBE and TBA respectively. The bi-solute equilibrium data and Freundlich isotherm model predictions for both MTBE and TBA are given in Fig 2.

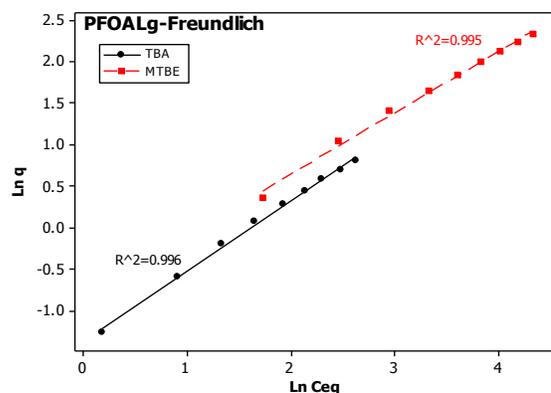


Fig 2. Equilibrium adsorption data and predicted Freundlich isotherm of MTBE and TBA



To describe the equilibrium of adsorption of MTBE and TBA on nano-PFOAL_g, Langmuir isotherm model also was applied.

Langmuir Isotherm:

$$q = q_m \frac{K_S C_{eq}}{1 + K_S C_{eq}}$$

where q_m and K_S are monolayer adsorption capacity and equilibrium constant of adsorption, respectively. It is clear from Fig. 3 that the Langmuir model provided a good fit throughout the concentration range. Correlation coefficients (R^2) are 0.981 and 0.989 for MTBE and TBA respectively. Values of the complete monolayer adsorption, q_m , were obtained from Langmuir isotherm for MTBE and TBA adsorption, as 19.9 and 6.5 mg/g, respectively. The constants obtained are listed in Table 2 for MTBE and Table 3 for TBA.

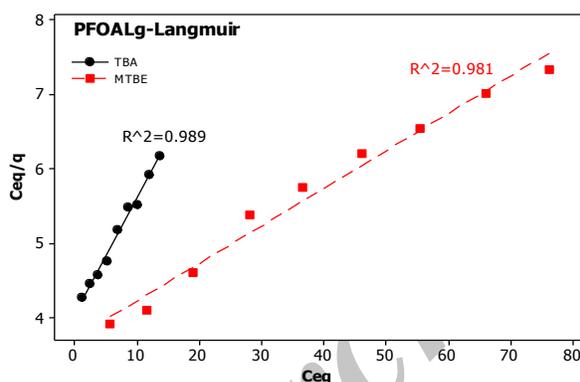


Fig 3. Experimental data and predicted Langmuir isotherm of MTBE and TBA

BET Isotherm for liquid phase adsorption:

$$\frac{C_{eq}}{q} = \frac{1}{q_m K_S} + \frac{K_S - 2K_L}{q_m K_S} C_{eq} + \frac{K_L(K_L - K_S)}{q_m K_S} C_{eq}^2$$

Where K_S is equilibrium constant of adsorption for first layer, $(mg/L)^{-1}$. q_m is the amount adsorbed corresponding to complete monolayer adsorption, (mg/g) and C_{eq} is equilibrium concentration of solution.

BET isotherm is one of the most successful isotherm models to express adsorption

phenomena. This equation has a sound theoretical basis and provides a good understanding about the nature of adsorption phenomena. Multilayer adsorption behavior, monolayer adsorption capacity and heat of adsorption at various adsorption layers are among the parameters of adsorption that can be determined using this isotherm model [14]. For nano-PFOAL_g adsorbent, the plot of C_{eq}/q versus C_{eq} based on a quadratic line for BET isotherm and experimental data for both MTBE and TBA are illustrated in Fig. 4. Monolayer adsorption amount, q_m , obtained from BET isotherm for MTBE was 10.1 mg/g which is lower than that obtained from Langmuir isotherm. This is because the Langmuir isotherm just considers the entire observed adsorption amount as monolayer adsorption. On the other hand the values of q_m from Langmuir and BET isotherm for TBA adsorption were similar. This is because TBA concentration range was low in this study and the fact that BET isotherm reduces to Langmuir isotherm at low concentration ranges [14]. Parameters for all models are summarized in Table 2 and 3 for MTBE and TBA respectively.

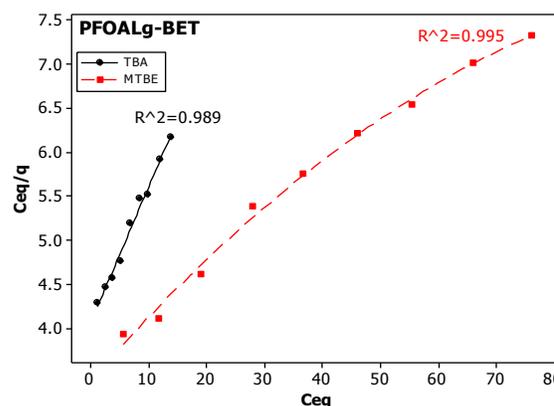


Fig 4. Experimental data and predicted BET isotherm of MTBE and TBA

Kinetic study

Among the kinetic models, pseudo-first-order or pseudo-second-order kinetics is the most widely used model to describe the adsorption process [15, 16].



Table 2.
Isotherm parameters for MTBE adsorption

Freundlich		Langmuir		BET	
K_f	0.4341	q_m	19.9	q_m	10.1
n	1.3497	K_S	0.0134	K_S	0.02901
R^2	0.995	R^2	0.981	K_L	0.003524
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Table 3.
Isotherm parameters for TBA adsorption

Freundlich		Langmuir		BET	
K_f	0.2548	q_m	6.5	q_m	6.4
n	1.1817	K_S	0.0380		0.0386
R^2	0.996	R^2	0.989	K_L	0.00024
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The pseudo-first-order kinetics:

$$\text{Log}(q_s - q_t) = \text{Log} q_s - \frac{k_1}{2.303} t$$

The pseudo-second-order kinetics:

$$\frac{t}{q_t} = \frac{1}{k_2 q_s^2} + \frac{t}{q_s}$$

where q_e is the equilibrium adsorption amount (mg/g), q_t is the adsorption amount at time t (mg/g), k_1 is the pseudo-first-order rate constant (s^{-1}) and k_2 is the pseudo-second-order rate constant ($g.mg^{-1}.s^{-1}$).

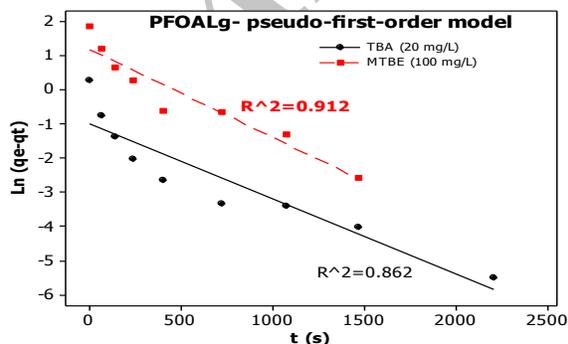


Fig 5. Pseudo-first-order plot for MTBE and TBA sorption onto nano-PFOAL_g

For nano-PFOAL_g the plot of $\log(q_s - q_t)$ versus t based on pseudo-first-order kinetics and the plot of t/q_t versus t based on pseudo-second-order kinetics are shown in Fig. 5 and Fig. 6 respectively. The correlation of pseudo-first-order kinetics did not give a good regression. On the contrary, the good linear plot of t/q_t versus t , with correlation coefficient (R^2) suggests that MTBE and TBA adsorption onto the nano-PFOAL_g adsorbents follows the pseudo-second-order kinetic model. Parameters for both kinetic models are summarized in table 4. Values for the pseudo-second-order kinetic model's rate constant, k_2 , were obtained for MTBE and TBA adsorption, as 0.00226 and 0.023 ($g.mg^{-1}.s^{-1}$), respectively.

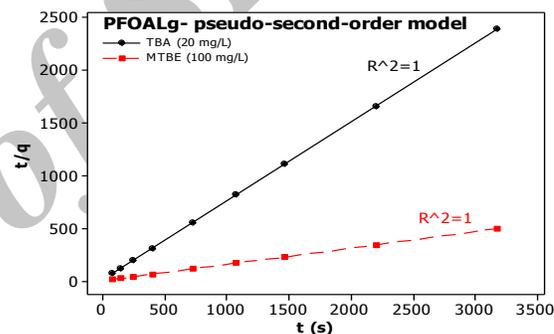


Fig 6. Pseudo-second-order plot for MTBE and TBA sorption onto nano-PFOAL_g

Table 4.
Kinetic parameters for TBA adsorption

pseudo-first-order (s^{-1})		pseudo-second-order ($g.mg^{-1}.s^{-1}$)	
MTBE	TBA	MTBE	TBA
$k_1 = 0.00597$	$k_1 = 0.00507$	$k_2 = 0.00226$	$k_2 = 0.023$
$R^2 = 0.912$	$R^2 = 0.862$	$R^2 = 1$	$R^2 = 1$

Conclusions

The adsorption equilibrium and kinetics of MTBE and TBA onto nano-PFOAL_g in relatively low concentration range have been studied in the present work. For evaluating the adsorption capacities of adsorbent, one of the most important criteria in selecting a suitable adsorbent, the experimental data were analyzed



using the Langmuir, Freundlich and BET isotherm equations. There were no significant differences between the performances of the three isotherm models. The adsorption kinetic data have been analyzed by the pseudo-first-order and pseudo-second-order kinetic models. The results indicate that the adsorption of MTBE and TBA onto nano-PFOAL_g can be well described by pseudo-second-order kinetics. Results reveal that nano-PFOAL_g is an effective adsorbent for methyl *tert*-butyl ether and *tert*-butyl alcohol.

KEYWORDS

Adsorption equilibrium, Adsorption kinetics, MTBE, TBA, nano-perfluorooctyl alumina, BET isotherm

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