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Kinetic and equilibrium modeling of single and binary adsorption of methyl *tert*-butyl ether (MTBE) and *tert*-butyl alcohol (TBA) onto nano-perfluorooctyl alumina

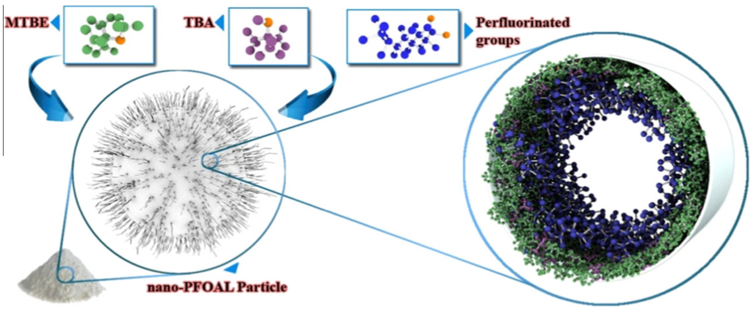
Amir Mirzaei, Amanollah Ebadi *, Peyman Khajavi

Chemical Engineering Department, Sahand University of Technology, P.O. Box 51335-1996, Tabriz, Iran

HIGHLIGHTS

- Two novel adsorbents: nano-PFOAL$_G$ and nano-PFOAL$_B$ were used as sorbents.
- Experimental and modeling analysis of MTBE/TBA adsorption in single and binary systems.
- Effect of the single-component isotherm equation on the binary isotherm predictions.
- Binary adsorption kinetics of the MTBE and TBA were comprehensively studied.
- The adsorbents exhibited good adsorption behavior for MTBE and TBA.

GRAPHICAL ABSTRACT



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ABSTRACT

Wide spread use of methyl *tert*-butyl ether (MTBE) has led to pollution of drinking water sources and has received great attention. In this study, single-component and binary competitive adsorptions of MTBE and *tert*-butyl alcohol (TBA) onto two novel adsorbents, i.e., nano-perfluorooctyl alumina prepared by using nano-γ-alumina (nano-PFOAL$_G$) and nano-boehemite (nano-PFOAL$_B$) as the supports were investigated. In single-component experiments, experimental data were modeled with five isotherm equations (Langmuir, Freundlich, modified BET for liquid phase, Sips and Dubinin–Radushkevich). Results revealed that the adsorption isotherms of both components on two adsorbents were best described by the modified BET isotherm. The multicomponent data were fitted to seven different predictive models, especially an extended form of modified BET, has been used in the present work. For the binary adsorption system, it is found that the quality of respective single-component isotherms for each component has significant effect onto the predicting multicomponent adsorption via Ideal Adsorbed Solution Theory (IAST). Accordingly, IAST-BET provided an accurate description of MTBE/TBA binary adsorption experimental data, hence being a reliable isotherm for the design of industrial adsorption equipment for wastewater treatment especially in high concentration ranges. The kinetic study was also conducted and two common kinetic models (pseudo first-order and pseudo second-order) were used to determine kinetics parameters. The mechanism of the adsorption process was described from the intraparticle diffusion model. The kinetic data showed a closer fitness to the pseudo-second order model. Maximum values for the rate constant, k_2, were obtained for MTBE and TBA adsorption, as 0.252 and 1.494 (g mg^{-1} min^{-1}), respectively.

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* Corresponding author. Tel.: +98 4123459144; fax: +98 4123444355.
E-mail address: ebadi@sut.ac.ir (A. Ebadi).

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1. Introduction

Oxygenate materials such as methyl *tert*-butyl ether (MTBE) used to raise fuel combustion efficiency within the engine, boost fuel octane and reduce vehicle air emissions [1,2]. The high volume use as well as the chemical features of this gasoline additive have resulted in contaminated water supplies around the world where MTBE is used as a gasoline additive [1,3]. MTBE has already been listed as a possible human carcinogen [4,5]. In addition to the potential health risk, this oxygenate also produces an unpleasant odor and taste even at low concentrations [5]. Contaminated water with MTBE is also frequently contaminated with *tert*-butyl alcohol (TBA) [6]. Moreover, TBA is a contaminant in some fuel grade MTBE and a major intermediate in MTBE degradation [7]. In most cases, TBA concentration is strongly correlated to MTBE degradation. Accordingly, distinct TBA values most frequently with concentrations of 10–50% of the MTBE concentrations can be observed [8]. It should be noted that, MTBE is highly soluble in water, however TBA is completely miscible. Therefore, TBA removal from water is even more difficult because it is more polar and has a lower Henry's law constant than MTBE [7,9]. Due to the physicochemical properties of MTBE and TBA, their treatment with conventional water treatment processes, such as advanced oxidation processes (AOP) and air stripping, is ineffective [10–13]. The byproducts of advanced oxidation processes have prevented this technique from general application [14]. Due to the small molecular weight and size, MTBE removal by membrane separation is considered too expensive in general water treatment applications [15]. Adsorption is a water treatment process, which has reliable efficiency in producing high quality effluents especially in low concentrations of pollutants [16,17]. Also, it has the advantages of ease in use and is easy to combine with other treatment techniques [18]. Furthermore, adsorption processes do not add undesirable byproducts to drinking water. Adsorption treatment uses porous materials such as activated carbon [19,20], zeolites [18,21–24] and synthetic resins [9,22,25,26] for removal of organic materials from water. Activated carbon is perhaps the most widely used adsorbent for organic compounds, due to its high adsorption capacity. However, poor removal efficiency may be observed in applying activated carbon as adsorbent, especially when other synthetic organic compounds co-exist with MTBE. Consequently, the adsorption with activated carbon may not be cost-effective for MTBE removal in natural water [15,22,27–29]. Zeolite was deemed as one of the most competitive adsorbents for adsorbing MTBE from the aqueous phase. Nevertheless, there are some problems for zeolites in practical environmental application, as a result of inconvenient operation of nano-sized crystals and the practical application of zeolites have been greatly limited due to relative slow mass transport through the small micropores (<1 nm) [18,24]. Synthetic resins have considerable ability for MTBE adsorption, but they are not yet cost competitive with other adsorbents [30]. The success of the removal of fuel oxygenates by conventional adsorbents, was considered unsatisfactory and, therefore, new and efficient adsorbents are needed to remove MTBE and TBA from contaminated water.

Recent developments in the synthesis of new adsorbents such as perfluorooctyl alumina (PFOAL) may be able to compete with other more established treatment technologies for MTBE removal. Ebadi et al. [31], showed that PFOAL has a considerable adsorption capacity for MTBE, while bare alumina exhibits no tendency for adsorption of organic materials such as MTBE from water. Furthermore, PFOAL can be used as a catalyst for removal of pollutants such as MTBE by catalytic ozonation [32,33]. In order to optimize the design and operation of an adsorption system for water treatment, it is essential to study the adsorption equilibrium and kinetics which could supply the fundamental information of adsorption [34]. Several equilibrium isotherm models have been developed for the purpose of modeling the adsorption behavior. Although, the polluted water rarely contains only one contaminant, most literature data are available for single-component adsorption. Hence, the development of reliable adsorption models for the prediction of adsorption phenomena, especially when several pollutants are co-exist in the polluted water, represents an essential challenge in the study of adsorption systems [35]. In particular, poor information can be found about adsorption kinetics, which is an important criterion for adsorption process design.

In this study, single-component and binary adsorption experiments of MTBE and TBA onto two novel adsorbents, namely, nano-PFOAL$_G$ and nano-PFOAL$_B$ with somewhat different characteristics have been tested by varying the initial concentrations of the two contaminants in the moderate concentration range (20–180 mg MTBE L^{-1}) and (4–36 mg TBA L^{-1}). The MTBE concentrations spanned over a wide range (up to 180 mg L^{-1}), which might be detected in a major MTBE spill in drinking water sources. In this study, TBA concentrations were selected as 20 wt% of the MTBE concentrations. All the experimental tests have been conducted at constant pH and temperature. Single-component adsorption data were analyzed using several sorption models: Freundlich, Langmuir, modified BET, Dubinin–Radushkevich and Sips isotherms. Modeling analysis of the extended Langmuir isotherm, extended Sips, and the Ideal Adsorbed Solution Theory (IAST) has been performed in order to evaluate their ability to describe or predict the binary experimental results by using single-component adsorption isotherm parameters. The correct form of BET equation for liquid phase adsorption was shown in a previous work [36]. Also an extended form of BET isotherm was developed and used for multicomponent adsorption in the present work. Moreover, a combination of modified BET isotherm for liquid phase, with IAST (IAST-BET), has been developed for multicomponent adsorption in liquid medium. The experimental data obtained from binary systems have been compared with multicomponent isotherm models, which just use single-component adsorption parameters. In order to evaluate the effectiveness of adsorbents, kinetics of the binary system of MTBE and TBA, which is more similar with natural conditions, were conducted.

2. Materials and methods

2.1. Materials

MTBE (purity > 99%) and TBA (purity > 99%) were obtained from Merck. Sodium chloride (99.5%, Merck) was used to increase the extraction efficiency in the headspace analysis. The nano-PFOAL$_G$ and nano-PFOAL$_B$ prepared using nano-γ-alumina and nano-boehmite, respectively, in a previous work [38].

2.2. Adsorbents

The surface of metal oxides such as aluminum oxide has hydrophilic nature due to covering surface with hydroxyl groups. Therefore, these materials are inefficient for adsorption of organic molecules from liquid phase. The surface can be modified by reacting organic groups such as perfluorooctanoic acid with the OH groups on the surface (Fig. 1). In this way, the surface of the solid gains hydrophobic characteristics and consequently can be used for adsorption of organic molecules in aqueous medium. The adsorption capacity of the modified surface is proportional to the surface coverage by the monomolecular layer of perfluorinated groups [32]. The surface coverage and perfluorinated phase content of the nano-PFOAL samples were calculated using the carbon content of them determined by the elemental analysis [38]. As reported in Table. 1, the perfluorinated phase contents show that