



Batch adsorptive removal of benzoic acid from aqueous solution onto modified natural vermiculite: Kinetic, isotherm and thermodynamic studies



Ehsan Sadeghi Pouya^a, Hossein Abolghasemi^{a,b,*}, Mohamad Esmaili^a,
Hooman Fatoorehchi^a, Seyed Jalaleddin Hashemi^{a,c}, Alireza Salehpour^d

^a Center for Separation Processes Modeling and Nano-Computations, School of Chemical Engineering, College of Engineering, University of Tehran, P.O. Box 11365-4563, Tehran, Iran

^b Oil and Gas Center of Excellence, University of Tehran, Tehran, Iran

^c Pulp and Paper Research Center, Department of Chemical Engineering, McGill University, Montreal, Canada

^d Laboratory for Instrumental Analysis, School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran

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Dedicated to the memory of our dear colleague Prof. Seyed Jalaleddin Hashemi, who passed away before the submission of this article.

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ABSTRACT

The performance of modified vermiculite for the batch adsorption of benzoic acid from aqueous solution was studied. Grinding treatment enhanced the ion exchange ability of natural vermiculite. Cetyltrimethylammonium bromide improved the adsorptive characteristics of ground vermiculite better than cetylpyridinium bromide. The optimum conditions were obtained as the adsorbent dosage of 0.5 g/50 mL, initial pH of 3.5 and contact time of about 140 min. The pseudo-second-order model provided a good correlation of the kinetic data. The equilibrium data were well described by the Langmuir and Temkin equations. Thermodynamically, it was concluded that the process is endothermic and spontaneous.

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Introduction

Industrial wastewater contains a wide variety of many organic and inorganic compounds. Aromatic carboxylic acids, one of the most known organic contaminants, are extensively found in the effluents of food and beverage, pharmaceutical and chemical

industries [1]. Benzoic acid (BA), one of the simplest aromatic carboxylic acids, is not biodegradable due to the electron-withdrawing carboxyl group on its phenyl ring. In accordance with the recommendation of the World Health Organization, the prolonged or repeated exposure to this substance at high concentrations results in irreparable damage to the central nervous system, liver, lung and kidney. However, there is not any reliable evidence corroborating the carcinogenic, mutagenic and tetragenetic effects of BA [2,3].

Up to now, the removal of BA from aqueous solution has been studied by several different methods like photocatalytic degradation [4], electrochemical oxidation [5], microbial filtration [6], electrosorption [7] and adsorption [1,3,8–12]. From the practical point of view, the adsorption is one of the most frequently applied methods to efficiently treat the wastewater effluents including organic pollutants because of its many remarkable advantages like

* Corresponding author at: Center for Separation Processes Modeling and Nano-Computations, School of Chemical Engineering, College of Engineering, University of Tehran, P.O. Box 11365-4563, Tehran, Iran.
Tel.: +98 21 61112186; fax: +98 21 66954051.

E-mail addresses: sadeghipouya@ut.ac.ir (E.S. Pouya), abolghasemi.ha@gmail.com, hoab@ut.ac.ir (H. Abolghasemi), esmaili@ut.ac.ir (M. Esmaili), hfatoorehchi@gmail.com, hfatoorehchi@ut.ac.ir (H. Fatoorehchi), jhashemi@ut.ac.ir, sj.hashemi@mcgill.ca (S.J. Hashemi), asalehpour@ut.ac.ir (A. Salehpour).

Nomenclature

ΔG°	Gibbs free energy change (kJ/mol)
ΔH°	enthalpy change (kJ/mol)
ΔS	entropy change (kJ/mol K)
a_0	Bohr radius (5.297E–11 m)
A_T	Temkin isotherm equilibrium constant (L/mg)
b_T	Temkin isotherm constant (kJ/mol)
C_0	adsorbate initial concentration (mg/L)
C_C	carbon content in the adsorbent (wt.%)
C_e	adsorbate concentration at equilibrium (mg/L)
$C_{\text{organic cations}}$	concentration of surfactant cations on the adsorbent surface (mol/g)
C_t	adsorbate concentration at a given time (mg/L)
h	initial adsorption rate (mg/g min)
k_1	rate constant of the pseudo-first-order kinetic model (min^{-1})
k_2	rate constant of the pseudo-second-order kinetic model (g/mg min)
K_d	distribution factor
K_{D-R}	Dubinin-Radushkevich isotherm constant (mol^2/kJ^2)
K_F	Freundlich isotherm constant ($(\text{mg/g})(\text{L/mg})^{1/n}$)
k_{id}	intraparticle diffusion rate constant ($\text{mg/g min}^{0.5}$)
K_L	Langmuir isotherm constant (L/mg)
K_W	self-ionization constant of water (mol^2/L^2)
M_c	molecular mass of carbon (g/mol)
n	Freundlich adsorption intensity constant
N	number of data points
n_C	number of carbon atoms in the surfactant
Q_0	Langmuir adsorption capacity (mg/g)
q_{D-R}	Dubinin-Radushkevich adsorption capacity (mg/g)
q_e	adsorption capacity at equilibrium (mg/g)
$q_{e, \text{cal}}$	calculated adsorption capacity at equilibrium (mg/g)
$q_{e, \text{exp}}$	experimental adsorption capacity at equilibrium (mg/g)
q_{max}	maximum adsorption capacity (mg/g)
q_t	adsorption capacity at a given time (mg/g)
R	universal gas constant (kJ/mol K)
R_L	separation factor
t	time (min)
T	temperature (K)
V	solution volume (L)
W	adsorbent mass (g)

high selectivity, simplicity of operation and low cost [13,14]. It can be noted that the most important factor in utilizing the adsorption process is to choose an appropriate adsorbent. In recent years, natural minerals have drawn much attention as a sort of inexpensive, plentiful and ecologically harmless adsorbents [15].

Natural vermiculite is usually derived from mica minerals in their hydrothermal metamorphosis to montmorillonite and typically, it has a larger cation exchange capacity (CEC) than other similar minerals [16,17]. Vermiculite is a generic name that refers to the lamellar aluminosilicates in a 2:1 crystalline proportion and it is characterized by a central magnesium octahedral sheet surrounded by two silicon-oxygen tetrahedral sheets. The chemical formula of vermiculite can be generally expressed as $(\text{Mg, Ca})_{0.3-0.45}(\text{H}_2\text{O})_n\{(\text{Mg, Fe, Al})_3(\text{Al, Si})_4\text{O}_{10}(\text{OH})_2\}$

[18]. Vermiculite possesses a net negative structural charge (due to Al^{3+} substitution for Si^{4+} in the tetrahedral layers and Al^{3+} and/or Fe^{2+} substitutions for Mg^{2+} in the octahedral layers), which is balanced by the presence of inorganic exchangeable cations in its interlayer space [19,20]. The surface of vermiculite is surrounded by a thin layer of water film, which makes its adsorption affinity toward the anionic and hydrophobic pollutants overly low [21].

Recently, various procedures, namely polymerization–carbonization [22], wax coating [23] and surface modification by the long-chain or short-chain cationic surfactants (as the most common one) have been employed to change the hydrophilic character of vermiculite into hydrophobic [21,24]. As it has been reported in the literature [25–29], employing cationic surfactants with concentrations higher than the critical micelle concentration (CMC) results in forming a so-called patchy bilayer of the surfactants with outward pointing head groups on the solid surface. As shown schematically in Fig. 1A, the first layer of surfactants is formed due to the ion exchange of positively charged surfactant cations with the interlayer cations of vermiculite, while the formation of the second layer relates to the van der Waals interactions between the tail groups of surfactants.

Over the last years, numerous researches have been conducted to study the effects of mechanical treatment methods, such as grinding and sonication, on the characteristics of minerals. Grinding treatment by a vibratory disk mill improves the porosity and the surface chemical reactivity of natural vermiculite and subsequently increases its capability to be modified by cationic surfactants [19,30,31].

In the present study, the natural vermiculite has been both mechanically and chemically modified to adsorb BA from aqueous solution in batch mode experiments. Natural vermiculite was initially subjected to the grinding operation in a vibratory disk mill and then modified by two widely used cationic surfactants, cetyltrimethylammonium bromide (CTAB) and cetylpyridinium bromide (CPB). A series of experiments were carried out so as to investigate the effects of several parameters, including the adsorbent dosage, initial solution pH, contact time and temperature on the adsorption of BA. The adsorption kinetics was studied by the pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The applicability of the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherms to the equilibrium data was compared based on the statistical parameters. The Gibbs free energy change, enthalpy change and entropy change were calculated in order to gain an insight into the thermodynamic nature of the adsorption process.

Materials and methods

Materials

Natural vermiculite originated from a mineral deposit in Kaleybar County (East Azerbaijan Province, Iran). Its quantitative chemical composition was determined by a Philips PW 1480 spectrometer. The results are given in Table 1. The adsorbate, BA ($\text{C}_7\text{H}_6\text{O}_2$), was purchased from Merck Co. and the cationic surfactants, CTAB ($\text{C}_{19}\text{H}_{42}\text{BrN}$) and CPB ($\text{C}_{21}\text{H}_{38}\text{BrN}$), were obtained from Sigma–Aldrich Co. The chemicals were all of analytical reagent grade and they were used without any additional purification. Fig. 1B shows the 3-dimensional molecular structure of CTAB and CPB.

Preparation of modified vermiculite

The natural vermiculite was crushed by means of a knife mill and sieved to get a particle size less than $125 \mu\text{m}$ (this sample was designated as V (1)). V (1) was ground by a vibratory disk mill in batches of 20 g at 2000 rpm for 10 min (this sample was

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