

PHYSICAL CHEMISTRY
OF WATER TREATMENT PROCESSES

Removal of Bisphenol From Aqueous Solution by Surfactant-Modified Bentonite¹

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Received October 28, 2016

Revised April 20, 2017

Accepted April 23, 2019

Abstract—In this study surfactant-modified natural bentonite was examined for the adsorption of bisphenol A [2,2-bis(4-hydroxyphenyl)propane; BPA] from aqueous solutions. Batch experiments were performed to investigate the adsorption kinetics, equilibrium and thermodynamics between the adsorbent surfaces and BPA. At acidic pH conditions, removal of BPA was increased due to a neutral molecule form of BPA and hydrophobic surface created by the loaded surfactant molecules. The adsorption of BPA on modified bentonite was enhanced when the ionic strength was increased. The adsorption behavior of BPA onto surfactant-modified bentonite followed the pseudo-second order kinetic model. Langmuir isotherm provided the best fit for adsorption. The adsorption of BPA on modified bentonite is more favorable at lower temperature. According to the experimental results, a physical adsorption is responsible mechanisms for adsorption of BPA on modified bentonite.

DOI: 10.3103/S1063455X19040052

Keywords: bisphenol A, adsorption, kinetic models, thermodynamic, modified bentonite.

INTRODUCTION

Endocrine-disrupting chemicals (EDC) can cause abnormalities in the functions of human endocrine system. Such chemicals have been detected in wastewater, surface waters, sediments, groundwater, and even drinking water [1]. They are not removed completely through biological treatment and can still be detected in the discharge of wastewater treatment plants. Therefore, these molecules have been detected in wastewater, groundwater, sediments, and drinking water [2]. Bisphenol A [2,2-bis(4-hydroxyphenyl)propane; BPA], as one of the phenolic EDC, has been widely used in the production of polycarbonate plastics, epoxy resins and flame retardants as an important monomer. The main sources of bisphenol A release to the environment are thought to be due to the discharge of municipal effluents and industrial wastewaters. Bisphenol A had been detected in all kinds of environmental water. The maximum concentrations reached up to 17.2 mg/L in hazardous waste landfill leachates, 12 µg/L in stream water and 0.1 µg/L in drinking water [3]. During past decades, a variety of techniques have been used for the removal of BPA. However, the development of simple and highly efficient methods for the safe restoration of BPA is still urgently required. In BPA removal, several alternative processes such as biological and chemical methods, advanced oxidation technology, membrane filtration, and adsorption have been proposed. However, these methods suffer drawbacks such as requiring large energy input, slow process or consuming chemicals [4]. Among these treatment techniques, physical adsorption is considered to be the most efficient method [5]. Because BPA is naturally hydrophobic, adsorption is one of the suitable processes for the removal of it from waste waters [6].

Bentonite, which belongs to montmorillonite group, is one of natural clays composed of two silica tetrahedral sheets with an octahedral alumina sheet [7]. One of the drawbacks of clay minerals is their hydrophilic properties which make them inefficient for the removal of organic pollutants. The permanent negatively charged clay surface can be modified by cationic surfactant molecules, and through ion exchange hydrophilic clays can be converted to hydrophobic organoclays. These organoclays are efficient adsorbents for the removal of phenolic compounds [2]. In this study, the adsorption potential of BPA on modified bentonite by hexadecyl trimethylammonium chloride (HDTMA) was investigated. The adsorption kinetics, equilibrium and thermodynamics between the adsorbent surfaces and BPA were evaluated through a series of batch experiments under

¹ The text was submitted by the authors in English.

different experimental conditions such as adsorbent dosage, agitation speed, pH, ionic strength and temperature.

EXPERIMENTAL

The bentonite with particle size <0.6 mm obtained from “Cankiri”, Turkey was used as adsorbent. Particle size is. Bentonite was air-dried and passed through a sieve to ensure the material uniformity at the experiments. Bentonite was modified with HDTMA supplied by “Merck”. BPA purchased from “Aldrich”. Solubility of BPA in water is 120–300 ppm (21.5°C). In experiments, stock BPA solution was prepared at concentration of 100 mg/L.

The surface of natural bentonites is negatively charged. Therefore, bentonites can be modified by cationic surfactants such as HDTMA to enhance adsorption of nonionic organic compounds. In this study, bentonite was treated with 1 mol/L NaCl solution to saturate the exchange sites with sodium ions. After 0.03 mol/L of HDTMA solution was poured into a flask, 10 g bentonite was added. The dispersions were shaken at room temperature with a mechanical shaker for 24 h. After 24 h, they were washed with hot distilled water until the foam is eliminated. Surfactant-modified bentonite was dried at 50°C in an oven.

The concentrations of BPA in the residual solutions were analyzed by means of the UV spectrometer (Hach-Lange DR 5000). The concentration of BPA was analyzed at the maximum wavelength. The calibration curve was found with 10 standards between 0 and 100 mg/L with the coefficient of determination ($R^2 = 0.954$). The adsorption capacities were calculated according to a mass balance of BPA and were represented in units of milligrams of BPA per gram of adsorbent. The adsorption capacities at equilibrium were calculated according to the equation

$$q_e = [(C_0 - C_e)V]/m, \quad (1)$$

where q_e is the amount of BPA adsorbed per unit weight of the adsorbent, mg/g; C_0 is the initial concentration of BPA, mg/L; C_e is the equilibrium concentration of BPA in solution, mg/L at equilibrium; V is the volume of BPA solution, L; m is the mass of adsorbent used, g.

Batch experimental adsorption studies. Batch experiments were performed by shaking of modified bentonite with BPA aqueous solutions at different pH values (2–10), different bentonite dosage (3–50 mg/L), different agitation speed (75–200 rpm), different KCl dosage (4–20 mg/L) and different temperatures (20; 30; 50; 60°C) in a water bath shaker. To monitor the adsorption kinetics, the adsorbent which contained 0.25 g bentonite was added to 50 mL solution with concentration 100 mg/L of BPA at room temperature. The samples were then collected at different time intervals from 5 min to 40 min. For the isotherm study, bentonite and BPA solution at initial concentrations ranging from 10 to 100 mg/L were mixed for 30 min. For the thermodynamic analysis, bentonite and BPA solution at concentration of 100 mg/L were mixed at 20; 30; 50; 60°C for 60 min. The samples were collected at different time intervals. The mixture was filtered through 0.45 μm filters, the residual concentration of BPA was measured spectrophotometrically.

RESULTS AND DISCUSSION

Effect of adsorbent dosage, agitation speed, pH and ionic strength on removal of BPA. Effect of adsorbent dosage on removal of BPA was studied with different adsorbent dosage at initial pH and BPA concentration of 100 mg/L.

From Fig. 1a it is seen that the removal of BPA increases with an increase in adsorbent dose due to the availability of more binding sites on adsorbent surface. After that, removal progresses at less significant rate. When adsorbent dosage increased from 25 to 50 mg/L, removal of BPA declined from 59.1 to 58.7%. The effect of agitation speed on adsorption for BPA was investigated in the range of 50–200 rpm (see Fig. 1b). At low agitation speed, the adsorbent precipitates in mixture. The maximum adsorption of BPA occurred at 75 rpm. The boundary layer thickness around the adsorbent particles decreases as a result of increasing the agitation speed and percentage removal decrease. When agitation speed increased from 75 rpm to 100 rpm, removal of BPA decreased from 31.4 to 26.2%. This may be attributed to an increased desorption tendency of adsorbate molecules. Agitation speed should be sufficient to assure that all the surface binding sites are readily available for BPA. The pH value of the initial solution can remarkably influence the species distribution of BPA. BPA remains as a neutral molecule at the pH of the solution < 9.59, and prevailed as phenolate anions at the pH of the solution > 10.2.

Dependence of BPA adsorption on pH is illustrated in Fig. 1c. Under acidic pH conditions the adsorption of BPA remained fairly constant. It can be seen that adsorption of BPA at pH below 9 increased, while it decreased at pH above 9. It may probably be due to the electrostatic repulsion between the BPA anions and the negatively charged sites on modified bentonite [8]. Also, adsorbents prepared with HDTMA were less

influenced by the solution pH and consistently attracted anionic species of BPA even under the alkaline conditions [2, 5].

High ionic strength might affect adsorption capacity of the adsorbents. Effect of different KCl concentrations on the adsorption of BPA by modified bentonite shows that the removal of BPA was increased with the increase of ionic strength (see Fig. 1d). Removal of BPA was increased from 23 to 53% by increasing from 4 to 16 mg/L of ionic strength in solution.

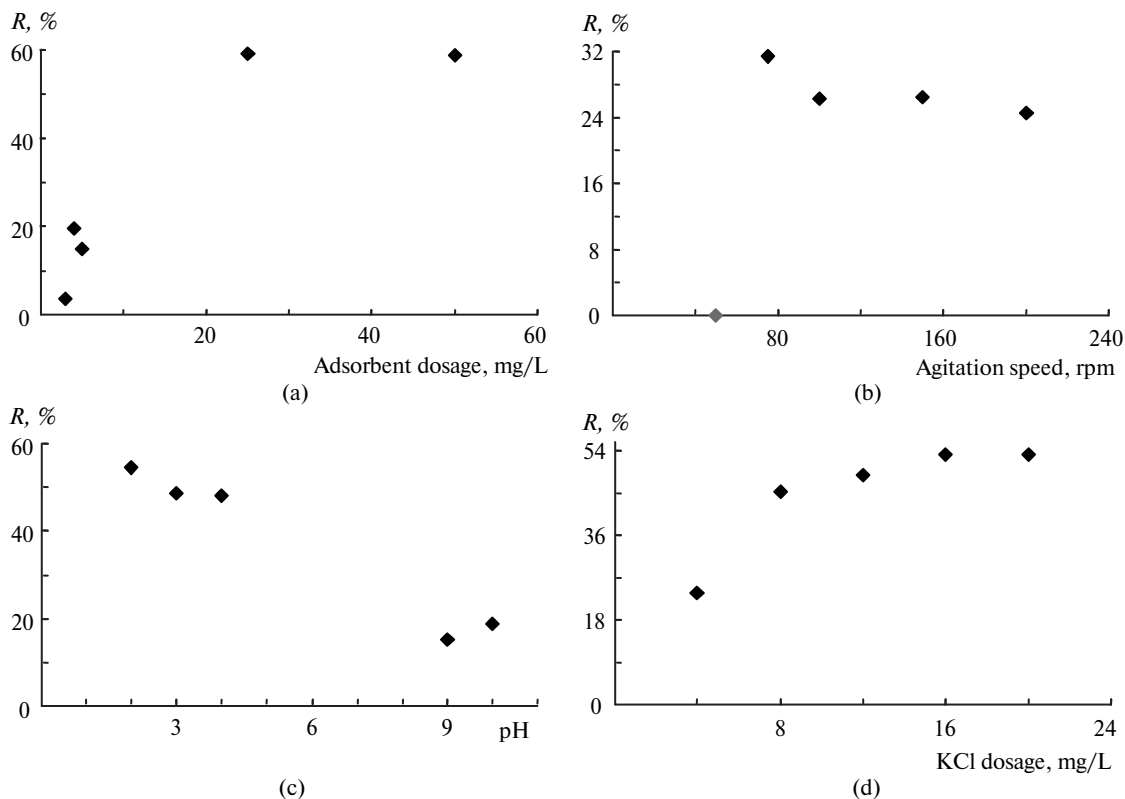


Fig. 1. Effect of adsorbent dosage (a), agitation speed (b), pH(c), ionic strength (d) on the removal of bisphenol A.

Adsorption Isotherms

Adsorption isotherms play important role for understanding adsorption mechanism. In this study, the Langmuir and Freundlich adsorption isotherm models were applied to describe the adsorption of BPA on the modified bentonite.

Langmuir Isotherm

The Langmuir isotherm describes the interaction between the adsorption of the adsorbate and the surface of the adsorbent when the adsorption process reaches equilibrium. It assumes that adsorption process occurs within a monolayer. Once the adsorption occurs at the specific sites in the adsorbent, no further adsorption occurs at these sites. Thus, the adsorption on the surface is strongly related to the driving force such as London-van der Waals force and surface area of the adsorbent [2, 5]. Langmuir isotherm can be described by the equation

$$C_e/q_e = 1/kV_m + C_e/V_m, \quad (2)$$

where V_m is the maximum adsorption capacity of the adsorbent, mg/g; k is the Langmuir constant, L/mg.

The linear form of Langmuir equation for BPA adsorption on bentonite is given by the equation

$$C_e/q_e = 0.064C_e + 0.889, \quad R^2 = 0.775. \quad (3)$$

Freundlich Isotherm

On the other hand, the Freundlich model is based on the use of an empirical expression to describe the adsorption theory, and this model assumes that a multilayer adsorption occurs on the heterogeneous surface

or surface supporting sites of various affinities. The linear form of Freundlich isotherm is written as the following equation:

$$\log q_e = \log K_f + (1/n) \log C_e, \quad (4)$$

where K_f is a relative indicator of adsorption capacity, mg/g; $1/n$ is the adsorption intensity.

The linear form of the Freundlich isotherm from experimental data is given by the equation

$$\log q_e = 1.587 \log C_e - 0.201, \quad R^2 = 0.612. \quad (5)$$

It was concluded that Langmuir isotherm provides better fits for most adsorption data, since the line corresponding to the model fitting is closer to the experimental points than that of Freundlich isotherm. R^2 values are higher in the case of Langmuir isotherm. The adsorption capacities for BPA based on HDTMA-modified other materials previously reported in the literature are summarized in Table 1. The maximum adsorption capacity was 15.63 mg/g, which can be considered to the highest when compared with other adsorbents.

Table 1. Adsorption capacities for bisphenol A by hexadecyl trimethylammonium chloride modified bentonite in comparison to other adsorbents

Adsorbent	V_m , mg/g	References
Bentonite	15.63	Present study
Mesoporous silica	9	[9]
Hydrothermally synthesized zeolite	3.5–1.4	[10]
Andesite, diatomaceous earth, TiO ₂ , activate bleaching earth	<1	[11]
Fe(III)/Cr(III) hydroxide	3.5	[12]

Sorption Kinetics and Effect of Temperature on Kinetic

In order to predict the mechanisms involved in the adsorption process, kinetic models were employed to the experimental data. In this study, several kinetic models are applied.

The pseudo-first order equation reads as follows [13]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (6)$$

where q_t is the concentration of BPA adsorbed in the solid phase at time t (min), mg BPA/g adsorbent; k_1 is the observed rate constant of the pseudo-first order model, 1/min.

The most commonly-applied form of the pseudo-second order equation can be written as

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)t, \quad (7)$$

where k_2 is the rate constant of pseudo-second order adsorption, g/(mg·min).

Moreover, for the pseudo-second order kinetic model, the half adsorption time ($t_{1/2}$) and the initial adsorption rate (h) are given by the following relationships:

$$t_{1/2} = 1/(k_2 q_e); \quad (8)$$

$$h = k_2 q_e^2. \quad (9)$$

The value of $t_{1/2}$ is the time required to uptake half of the maximal adsorbed amount of adsorbate at equilibrium and provides a good characterization of the adsorption rate [3].

The linear forms of kinetic equations for BPA adsorption on modified bentonite at different temperature are given in Table 2. The adsorption behavior of BPA onto bentonite followed the pseudo-second order kinetic model considering higher correlation coefficients, which indicates that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites [14]. The adsorption process did not obey the intra-particle diffusion model, other pathways may also control the adsorption rate. The calculated kinetic constants indicated that higher adsorption rate was observed at the lower temperatures. Maximum k_2 value was obtained at 20°C, thereby confirming that the process was exothermic.

Thermodynamics of BPA Adsorption

The behavior of adsorption can be determined by calculating changes in the free energy of adsorption (ΔG), enthalpy (ΔH), and entropy (ΔS). Changes of temperature can affect sorption nature of BPA on surfactant-modified bentonite, thus sorption of BPA at 20; 30; 50; 60°C was investigated.

Table 2. Thermodynamics results in adsorption of bisphenol A on modified bentonite

Thermodynamics		Parameter
$\ln K_d = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$	$\ln K_d = -\frac{-2.596}{RT} + \frac{0.0509}{R}$	$\Delta H^0 = -2.90 \text{ J/mol}$
		$\Delta S^0 = -0.05 \text{ J/mol K}$
		$\Delta G^0 (20^\circ\text{C}) = 52.52 \text{ J/mol}$
		$\Delta G^0 (30^\circ\text{C}) = 43.50 \text{ J/mol}$
		$\Delta G^0 (50^\circ\text{C}) = 28.83 \text{ J/mol}$
		$\Delta G^0 (60^\circ\text{C}) = 34.50 \text{ J/mol}$
		$R^2 = 0.937$

The relationship between the BPA distribution coefficient K_d and ΔG^0 (J/mol) of adsorption is

$$\Delta G^0 = -RT \ln K_d, \quad (10)$$

where R (8.314 J/(mol·°K)) is the gas constant and T is the reaction temperature (°K). The distribution coefficient for the adsorption process was calculated with equation [15]

$$K_d = q_e / C_e. \quad (11)$$

H^0 (J/mol) and S^0 (J/(mol·°K)) are calculated according to equation [16]

$$\ln K_d = -(H^0)/RT + (S^0)/R, \quad (12)$$

where H^0 and S^0 were obtained from the slope and intercept of the linear plot of $\ln K_d$ against $1/T$ [15].

The thermodynamic parameters are presented in Table 2. The negative enthalpy change (ΔH) and the entropy change (ΔS) suggest that the adsorption of BPA is of an exothermic nature. The adsorption takes place primarily by physical process. The negative values of the change in ΔS suggest an increase in the molecular organization of the adsorption process, and a decrease in degree of freedom at the solid-solution interface [17]. Positive G^0 values were determined for all of the studied temperature conditions.

In order to understand the adsorptive reaction, the activation energy was calculated the following equation [3]:

$$\ln k_2 = \ln A - (E_a/RT), \quad (13)$$

where E_a is the Arrhenius activation energy of adsorption (kJ/mol); A is the Arrhenius factor. The value of E_a can be directly obtained from the intercept of the plot of $\ln k_2$ against $1/T$ (Fig. 2). In this study, the magnitude of E_a was calculated as 20.56 kJ/mol.

The range of 5–40 kJ/mol of activation energy suggests a physical adsorption. Therefore, a physical adsorption is the mechanism responsible for adsorption of BPA on modified bentonite. In Table 3, kinetic models are given in the adsorption of BPA with surfactant modified bentonite.

Table 3. Kinetic models in adsorption of bisphenol A by surfactant-modified bentonite

T, °C	Pseudo-first order model				Pseudo-second order model					
	equation $\ln(q_e - q_t) = at + b$		k_1, min^{-1}	R^2	equation $t/q_t = ct + d$		$k_2, \text{g}(\text{mg}\cdot\text{min})^{-1}$	R^2	$t_{1/2}, \text{min}$	$h, \text{mg}(\text{g}\cdot\text{min})^{-1}$
	a	b			c	d				
20	-0.079	1.580	-0.079	0.557	0.126	0.192	0.1	0.981	1.278	6.1214
30	-0.017	1.847	-0.0173	0.596	0.132	0.507	0.034	0.981	3.891	1.948
50	-0.062	2.161	-0.062	0.822	0.091	0.997	0.0083	0.924	10.97	1.0014
60	-0.015	0.801	-0.015	0.439	0.096	0.356	0.025	0.987	3.84	2.7

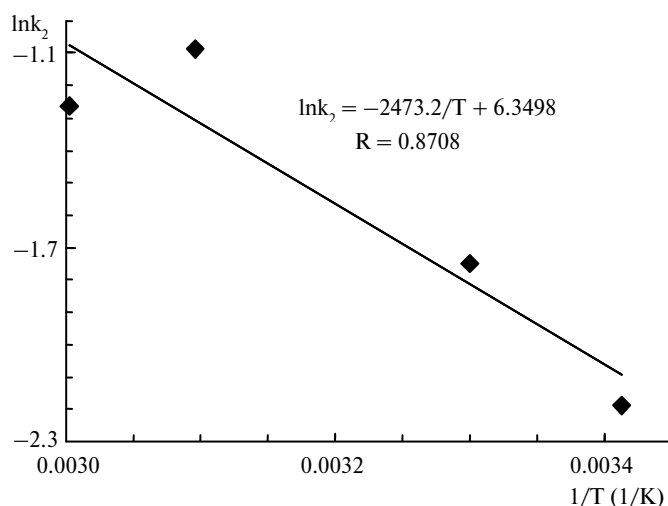


Fig. 2. Arrhenius relationship for adsorption of bisphenol A on modified bentonite.

CONCLUSIONS

In the present study, effects of adsorbate amount, pH, agitation speed, ionic strength and temperature on the adsorption of BPA on surfactant-modified bentonite were investigated. The adsorption kinetics, equilibrium and thermodynamics between the adsorbent surfaces and BPA were also investigated. Following conclusions can be drawn on the basis of results obtained:

- kinetic studies and adsorption isotherms indicated that the adsorption of BPA on modified bentonite could be expressed by a pseudo second order model and the Langmuir isotherm model;
- the adsorption of BPA is an exothermic nature. Higher adsorption rate were observed at the lower temperatures;
- the physical adsorption is responsible mechanisms for adsorption of BPA.

These results indicate that the modified-bentonite could be potentially used as an alternative adsorbent for the removal of BPA.

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