



# Removal of phenol from aqueous solutions by adsorption onto organomodified Tirebolu bentonite: Equilibrium, kinetic and thermodynamic study

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## ABSTRACT

A natural bentonite modified with a cationic surfactant, cetyl trimethylammonium bromide (CTAB), was used as an adsorbent for removal of phenol from aqueous solutions. The natural and modified bentonites (organobentonite) were characterized with some instrumental techniques (FTIR, XRD and SEM). Adsorption studies were performed in a batch system, and the effects of various experimental parameters such as solution pH, contact time, initial phenol concentration, organobentonite concentration, and temperature, etc. were evaluated upon the phenol adsorption onto organobentonite. Maximum phenol removal was observed at pH 9.0. Equilibrium was attained after contact of 1 h only. The adsorption isotherms were described by Langmuir and Freundlich isotherm models, and both model fitted well. The monolayer adsorption capacity of organobentonite was found to be 333 mg g<sup>-1</sup>. Desorption of phenol from the loaded adsorbent was achieved by using 20% acetone solution. The kinetic studies indicated that the adsorption process was best described by the pseudo-second-order kinetics ( $R^2 > 0.99$ ). Thermodynamic parameters including the Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) were also calculated. These parameters indicated that adsorption of phenol onto organobentonite was feasible, spontaneous and exothermic in the temperature range of 0–40 °C.

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## 1. Introduction

As a result of rapid development of chemical and petrochemical industries, the surface and ground waters are polluted by various organic and inorganic chemicals such as phenolic compounds, dyes and heavy metals. Phenol and its derivatives are considered as noxious pollutants, because they are toxic and harmful to living organisms even at low concentrations [1]. Phenols are being discharged into the waters from various industrial processes such as oil refineries, petrochemical plants, ceramic plants, coal conversion processes and phenolic resin industries [2]. The utilization of phenol-contaminated waters causes protein degeneration, tissue erosion, paralysis of the central nervous system and also damages the kidney, liver and pancreas in human bodies [3]. According to the recommendation of World Health Organization (WHO), the permissible concentration of phenolic contents in potable waters is 1 µg L<sup>-1</sup> [4] and the regulations by the Environmental Protection Agency (EPA), call for lowering phenol content in wastewaters less than 1 mg L<sup>-1</sup> [5]. Therefore, removal of phenols from waters and

wastewaters is an important issue in order to protect public health and environment.

The traditional methods such as adsorption, chemical oxidation, precipitation, distillation, solvent extraction, ion exchange, membrane processes, and reverse osmosis, etc. have been widely used for removal of phenols from aqueous solutions [6]. Among them, removal of phenols by adsorption is the most powerful separation and purification method because this technique has significant advantages including high efficiency, easy handling, high selectivity, lower operating cost, easy regeneration of adsorbent, and minimized the production of chemical or biological sludge [7]. Adsorption process is strongly affected by the chemistry and surface morphology of the adsorbent. Therefore, new adsorbents, which are economical, easily available, having strong affinity and high loading capacity have been required. A number of adsorbents such as activated carbon, [8], red mud [9] and rubber seed coat [10], etc. have been used for phenol removal. Adsorption of phenol onto activated carbons is a well-known process because activated carbon has a large surface area and high adsorption capacity. However, its high cost and the difficulties in recovering of activated carbon particles from treated water, limit its use as an adsorbent. In recent years, clay minerals have been widely used as adsorbents for the removal of toxic metals and organic pollutants from aqueous solutions due

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to their low cost, large specific surface area, chemical and mechanical stability, layered structure and high cation exchange capacity [2,11–19].

Bentonite is a member of 2:1 clay minerals (meaning that it has two tetrahedral sheets sandwiching a central octahedral sheet) which consists essentially of clay minerals of montmorillonite group. Bentonite is characterized by an Al octahedral sheet between two Si tetrahedral sheets. It has a negative surface charge created by the isomorphous substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in tetrahedral layer and  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$  in octahedral layer. The bentonite surface is hydrophilic in nature because inorganic cations, such as  $\text{Na}^+$  and  $\text{Ca}^{2+}$ , are strongly hydrated in presence of water. As a result, the adsorption efficiency of natural bentonite for organic molecules is very low [20,21]. The adsorption properties of bentonite can be improved by the modification of clay mineral surface with a cationic surfactant. The cationic surfactants, known as quaternary amine salts, are in the form of  $(\text{CH}_3)_3\text{NR}^+$ , where R is an alkyl hydrocarbon chain. Replacement of inorganic exchangeable cations with cationic surfactants, converts the hydrophilic silicate surface of clay minerals to a hydrophobic surface and the obtained complex is referred as organoclay. It is generally accepted that adsorption of hydrophilic long-chain quaternary ammonium cations onto clays occurs according to the ion-exchange mechanism [22]. As a result organoclay complex is an excellent adsorbent for the removal of phenolic compounds, other organic contaminants and also heavy metals from aqueous solutions.

The objective of this study was to investigate the adsorption potential of bentonite for removal of phenol from aqueous solutions. The natural bentonite was obtained from Tirebolu-Giresun region of Turkey, and modified with a cationic surfactant, cetyl trimethylammonium bromide (CTAB), in order to increase the adsorption capacity. The structures of natural and organobentonite were characterized by using a variety of instrumental techniques including Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). Also the surface area, cation exchange capacity and pH of the bentonite samples were estimated. The effects of experimental parameters such as initial pH of the solution, contact time, initial phenol concentration, organobentonite concentration, etc. were studied. The adsorption mechanisms of phenol onto organobentonite were evaluated in terms of thermodynamics and kinetics. The adsorption isotherms were described by using Langmuir and Freundlich isotherm models.

## 2. Materials and methods

### 2.1. Preparation of organobentonite

The bentonite, which is a type of clay mineral, was used as an adsorbent for removal of phenol from aqueous solutions in the present study. Ca-bentonite samples were sieved to 0.15 mm of particle size before use. A known amount of Ca-bentonite was added to 1 M of  $\text{Na}_2\text{CO}_3$  solution and stirred for 3 h at 800 rpm. In order to dissolve the  $\text{CaCO}_3$ , the concentrated HCl solution was added into the suspension drop-by-drop. The solid particles were separated from the mixture by filtration using Whatmann No. 42 filter paper and washed five times with deionized water until it was chloride free. This was checked by the addition of  $\text{AgNO}_3$  after washing with deionized water to make sure that no precipitate is formed, which is the evidence of chloride existence. And then the obtained solid was dried at  $110^\circ\text{C}$  for one day and designated as Na-bentonite. The Na-bentonite was modified with a cationic surfactant, cetyl trimethylammonium bromide (CTAB),  $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$ . The cationic surfactant can be adsorbed onto negatively charged clay surfaces and is not influenced by the pH of the solution because it is a quaternary ammonium salt

[23]. The CTAB consists of a 16-carbon chain tail group attached to a trimethyl quaternary amine head group with a permanent +1 charge. For modification process: 200 mL of 4% of CTAB solution was contacted with 20 g Na-bentonite by stirring on a mechanical shaker for 24 h. Then the bentonite was separated from the solution by filtration and washed twice with deionized water and then dried at  $70^\circ\text{C}$ . This bentonite is designated as organobentonite ( $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3-\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2\cdot 2\text{H}_2\text{O}$ ) [24].

### 2.2. Characterization

The physical and chemical characteristics of the adsorbents are important in order to estimate the adsorbate binding mechanism of the adsorbent surface. Hence the structures of natural and organobentonite were characterized by using several techniques including FTIR Spectroscopy, XRD and SEM. Also the surface area, cation exchange capacity (CEC) and pH of the bentonite samples were estimated by using several analytical methods.

The IR spectra of the natural bentonite, organobentonite and phenol loaded organobentonite were obtained to determine the surface functional groups by using PerkinElmer 1600 FTIR spectrophotometer in the range of  $4000\text{--}400\text{ cm}^{-1}$ .

The mineralogical compositions of the natural and organobentonite samples were determined from the XRD patterns of the samples taken on a Rigaku D-Max III automated diffractometer using Ni filtered  $\text{Cu K}\alpha$  radiation.

SEM analyses were applied on the natural bentonite, organobentonite and also phenol loaded organobentonite by JSM 6400 Scanning Microscope apparatus in order to disclose the surface texture and morphology of the adsorbent.

The surface areas of the natural and organobentonite were calculated according to Sears' method [25] as follows: 0.5 g of clay sample was mixed with 50 mL of 0.1 M HCl solution and 10.0 g of NaCl salt. The mixture had a pH value of 3.0, and titrated with standard 0.1 M NaOH solution in a thermostatic bath at  $298 \pm 0.5\text{ K}$  from pH 4.0 to 9.0. The surface area was calculated from the following equation:

$$S(\text{m}^2/\text{g}) = 32V - 25 \quad (1)$$

where  $S$  is the surface area, and  $V$  is the volume (mL) of NaOH solution required to raise the pH from 4.0 to 9.0.

The CEC of the natural bentonite was calculated by using bisethylenediamine copper (II)  $[\text{Cu}(\text{en})_2]^{2+}$  complex method [26,27] 50 mL of 1 M copper(II) chloride ( $\text{CuCl}_2$ ) solution was mixed with 102 mL of 1 M ethylenediamine ( $\text{C}_2\text{H}_8\text{N}_2$ ) solution. The slight excess of the amine ensures complete formation of the complex. The solution was diluted with deionized water to 1 L to give a 0.05 M solution of the complex. 0.5 g of a dry clay sample was mixed with 5 mL of the complex solution in a 100 mL flask, diluted with deionized water to 25 mL and the mixture was shaken for 30 min in a thermostatic water bath and then centrifuged. The concentration of the complex remaining in the supernatant was determined by iodometric method. For this, 5 mL of the supernatant was mixed with 5 mL of 0.1 M HCl solution to destroy the  $[\text{Cu}(\text{en})_2]^{2+}$  complex and about 1 g of KI salt was added to this solution. The mixture was titrated with 0.02 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution with starch as indicator. The CEC was calculated from the following formula:

$$\text{CEC}(\text{meg}/100\text{ g}) = \frac{MSV(x-y)}{1000m} \quad (2)$$

where  $M$  is the molar mass of Cu-complex,  $S$  is the concentration of thio solution,  $V$  is the volume (mL) of complex taken for iodometric titration,  $m$  is the mass of adsorbent (g) taken,  $x$  is the volume (mL) of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for blank titration (without adding the adsorbent) and  $y$  is the volume (mL) of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for the titration (with the clay adsorbent).

The pH values of the natural and organobentonite were measured as follows: 0.1 g of samples was mixed with 10 mL of deionized water and shaken for 24 h at 30 °C. After filtration, the pH of solutions was determined by a pH meter.

### 2.3. Adsorption experiments

All chemicals used in this work were of analytical reagent grade and were used without further purification. Deionized water was used for all dilutions. All glassware and plastics were soaked in 10% (v/v) nitric acid solution for one day before use, and then cleaned repeatedly with deionized water. A stock solution of 5000 mg L<sup>-1</sup> phenol was prepared by dissolving 5.00 g of phenol (Merck, Darmstadt, Germany) in 1 L of deionized water. The required concentration of phenol solutions were prepared by diluting the appropriate volumes of the stock solution. The pH of the solutions was adjusted to 9.0 by addition of 0.1 M HCl or 0.1 M NaOH solutions. The adsorption of phenol onto organobentonite was investigated through a batch process. For adsorption experiments, 10 mL of phenol solution in the concentration range of 100–1000 mg L<sup>-1</sup> was transferred into a polyethylene centrifuge tube. Then 100 mg of organobentonite (10 g L<sup>-1</sup> suspension) was added to the solution, and then the mixture was agitated on a mechanical shaker (Edmund Bühler GmbH) at 400 rpm for 1.0 h. After reaching equilibrium, the suspension was filtered through 0.45 μm of nitrocellulose membrane (Sartorius Stedim Biotech. GmbH), and the filtrate was analyzed for residual phenol concentration using a double beam UV–vis spectrophotometer (Unicam UV-2) at 508 nm by the 4-aminoantipyrene method [28]. All experiments were conducted in triplicate, and the averages of the results were submitted for data analysis. The amount of the phenol adsorbed by the organobentonite was calculated as following equation:

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

$$q_e = \frac{C_0 - C_e}{m_s} \quad (4)$$

$C_0$  (mg L<sup>-1</sup>) is the initial concentration of phenol solution,  $C_e$  (mg L<sup>-1</sup>) is the equilibrium concentration of phenol in aqueous solution, and  $m_s$  (g L<sup>-1</sup>) is the organobentonite concentration;  $q_e$  (mg g<sup>-1</sup>) is amount of calculated phenol adsorption onto 1.0 g of organobentonite.

## 3. Results and discussion

### 3.1. Characterization

The chemical composition of bentonite has been defined as: 66.2% SiO<sub>2</sub>, 13.7% Al<sub>2</sub>O<sub>3</sub>, 1.4% Fe<sub>2</sub>O<sub>3</sub>, 3.0% MgO, 1.7% CaO, 0.4% Na<sub>2</sub>O, 0.7% K<sub>2</sub>O, 0.2% TiO<sub>2</sub>, 0.1% MnO, and 12.0% loss of ignition by using Inductively Coupled Plasma Atomic Emission Spectrometric (ICP-AES) method [29].

The FTIR spectra of natural bentonite, organobentonite and phenol loaded organobentonite are depicted in Fig. 1(a), (b) and (c) respectively, in order to compare the differences among three kinds of bentonite. The broad bands observed at 3400–3600 cm<sup>-1</sup> are due to the O–H stretching vibration of the silanol (Si–OH) groups and HO–H vibration of the water adsorbed silica surface [30]. Also the adsorption band near 1640 cm<sup>-1</sup> is due to the H–O–H bending vibration, and the broad band near 1000 cm<sup>-1</sup> is related to the stretch vibrations of Si–O groups. For organobentonite, two peaks appear at 2920–2850 cm<sup>-1</sup> which represent the stretching vibration of –CH<sub>3</sub> and –CH<sub>2</sub>, respectively, and the band near 1460 cm<sup>-1</sup> is related to the –CH<sub>2</sub> deformation peak [31]. These peaks support the

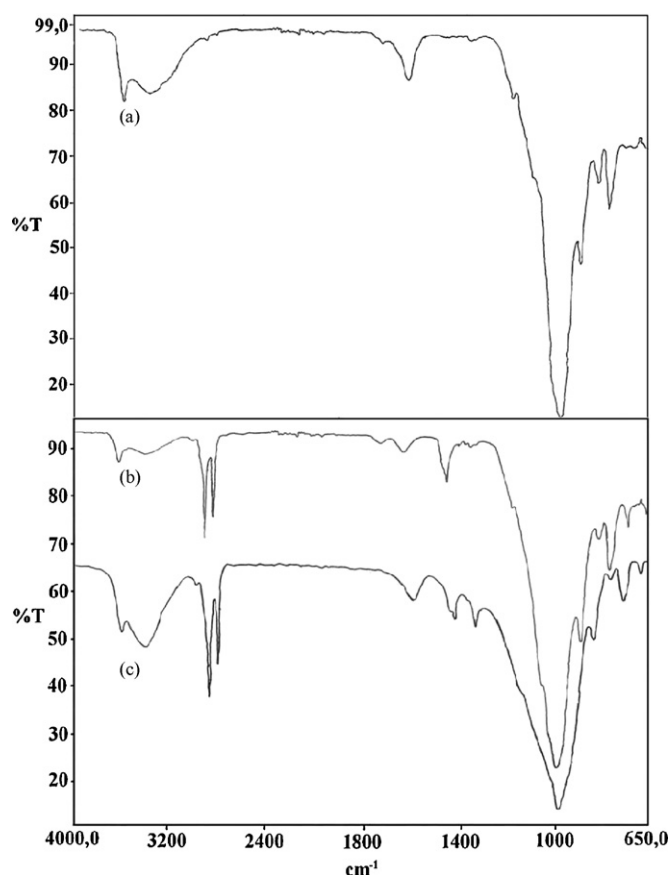


Fig. 1. FTIR spectra of (a) natural bentonite, (b) organobentonite and (c) phenol loaded organobentonite.

modification of bentonite with CTAB. Also it is important to notice that the band intensities decreased in the FTIR spectrum of phenol loaded organobentonite because the functional groups, especially those of CTAB, of the organobentonite surface have been occupied with phenol.

The XRD patterns of organobentonite and natural bentonite are shown in Fig. 2(a) and (b), respectively. XRD measurements have shown that the natural bentonite is mainly composed of saponite, halloysite, palygorskite and muscovite. On the other hand the organobentonite is composed of illite, nacrite and montmorillonite. From the results, modification of bentonite minerals by an organic compound introduces some changes into the crystal structure of bentonite minerals.

The SEM micrographs of natural bentonite, organobentonite and phenol loaded organobentonite are shown in Fig. 3(a)–(c). The surface morphology of bentonite changed slightly by the modification with CTAB. The organobentonite has considerable numbers of heterogeneous pores where there is a good possibility for phenol trapped and adsorbed. The structure of organobentonite changed upon phenol adsorption and exhibited a tendency to form agglomerates.

The surface area of natural bentonite changed from 32.6 to 26.2 m<sup>2</sup> g<sup>-1</sup> after the modification resulting in organobentonite. The CEC of the natural bentonite was found to be 33.0 meq/100 g. The pH of the natural bentonite and organobentonite was determined as 7.10 and 6.45, respectively, indicating that the natural bentonite has negative charge in aqueous solution and the level of surface negative charges decreases by modification.

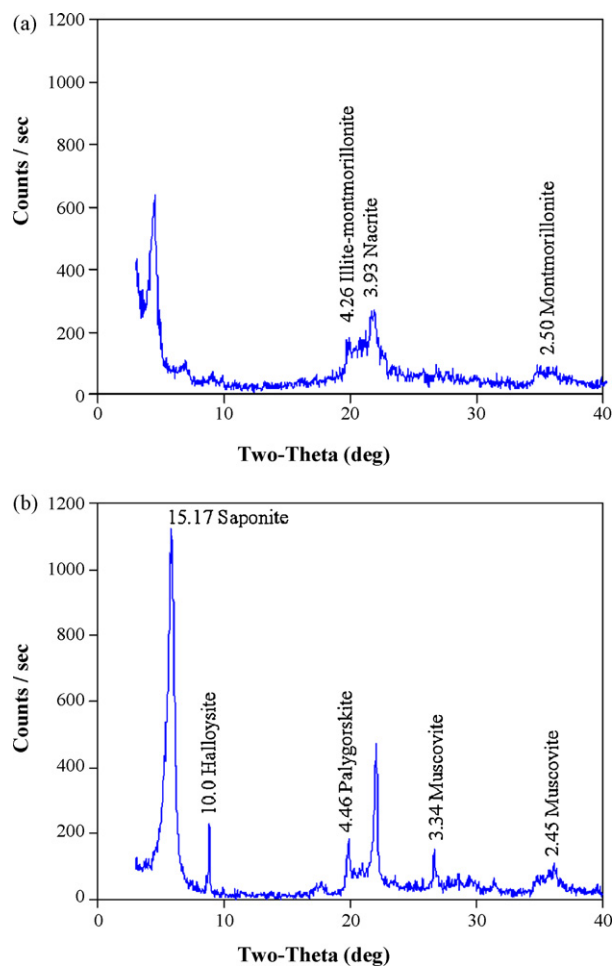


Fig. 2. XRD spectrum of (a) organobentonite and (b) natural bentonite.

### 3.2. Effect of pH

The surface charge of the adsorbent and the ionization degree of the adsorbate are strongly affected by the pH of the aqueous solutions, hence the uptake of phenol by the adsorbent depends on the solution pH. In order to evaluate the effect of pH on the adsorption of phenol onto organobentonite, the adsorption experiments were carried out with initial phenol concentration of  $110 \text{ mg L}^{-1}$  and organobentonite concentration of  $10 \text{ g L}^{-1}$  by varying the pH of the solutions over a range of 1–11 (Fig. 4). The uptake of phenol by the organobentonite is almost constant in the pH range of 1–9. However when the pH value exceeds 9, the adsorption of phenol decreases abruptly. Phenol as a weak acid compound with  $\text{pK}_a$  value of 9.8 is dissociated at  $\text{pH} > \text{pK}_a$  [32]. At higher pH values, the ionization degree of phenol and the quantity of  $\text{OH}^-$  ions increase thereby the diffusion of phenolic ions are hindered, and the electrostatic repulsion between the negatively charged surface sites of the adsorbent and phenolat ions increases. As a result, the removal of phenol is greater at lower pH compared to the higher pH. Similar results were reported by Nayak and Singh [33]. From the experimental results, pH 9.0 was selected as an optimum pH value.

### 3.3. Effect of contact time and adsorption kinetics

The adsorption of phenol onto organobentonite was studied as a function of contact time in order to decide whether the equilibrium was reached. For this,  $100 \text{ mg L}^{-1}$  of phenol solutions at pH 9.0 were contacted with  $10 \text{ g L}^{-1}$  of organobentonite suspensions. The sam-

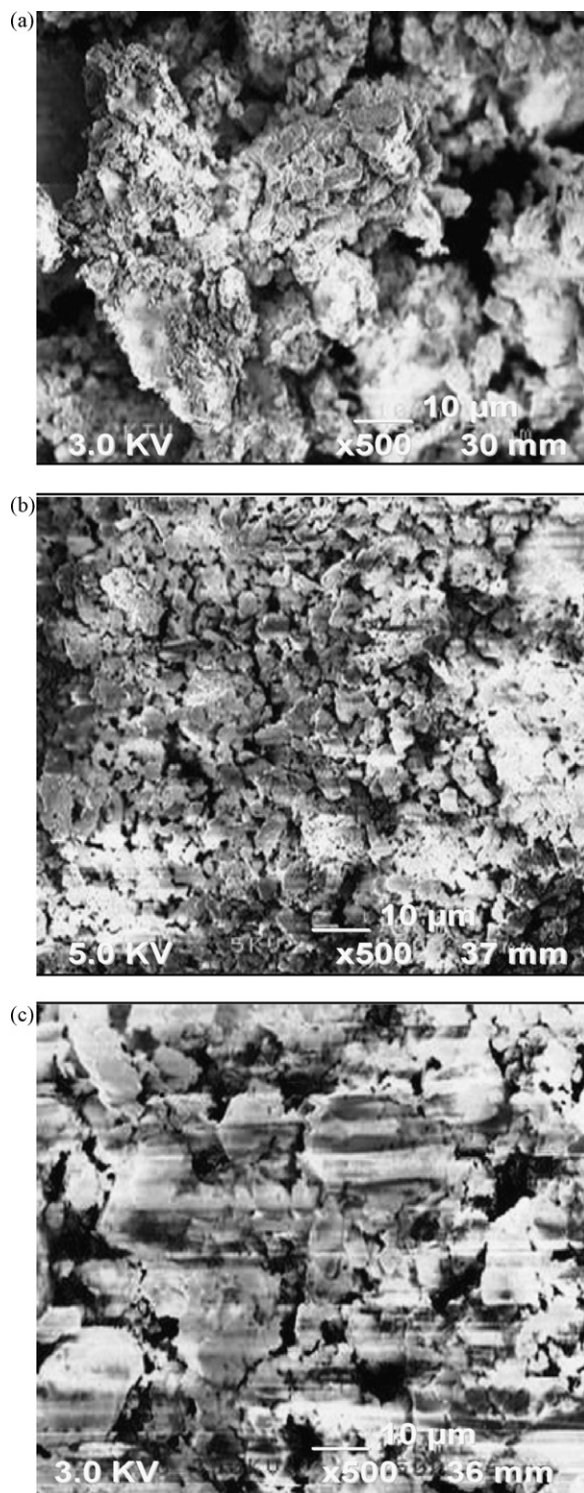


Fig. 3. SEM of (a) natural bentonite, (b) organobentonite and (c) phenol loaded organobentonite (magnification: 500 folds).

ples were taken at different periods of time and analyzed for their phenol concentration (Fig. 5(a)). The phenol adsorption rate is high at the beginning of the experiment because initially the adsorption sites are more available and phenol ions are easily adsorbed on these sites. The equilibrium can be reached within 60 min, and thus, further adsorption experiments were carried out for a contact time of 60 min. The adsorption kinetics is one the most important data in order to understand the mechanism of the adsorption and to

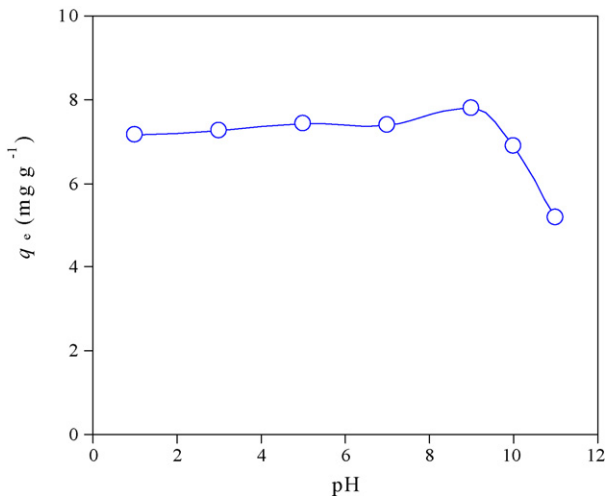


Fig. 4. Effect of pH on phenol uptake by organobentonite (initial phenol conc.: 110 mg L<sup>-1</sup>, organobentonite conc.: 10 g L<sup>-1</sup>, contact time: 60 min).

assess the performance of the adsorbents. Different kinetic models including the pseudo-first-order, pseudo-second-order and intraparticle diffusion models were applied for the experimental data to predict the adsorption kinetics.

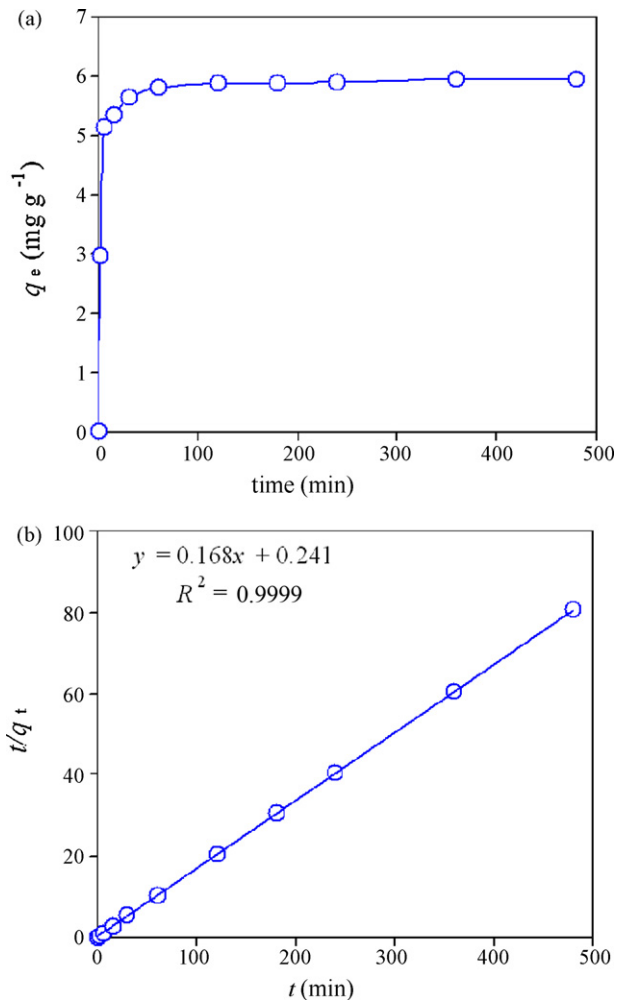


Fig. 5. (a) Effect of contact time on phenol uptake and (b) pseudo-second-order kinetic model (pH: 9.0, initial phenol conc.: 100 mg L<sup>-1</sup>, organobentonite conc.: 10 g L<sup>-1</sup>).

The pseudo-first-order equation can be written as follows [34]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

where  $q_e$  (mg g<sup>-1</sup>) and  $q_t$  (mg g<sup>-1</sup>) are the amounts of phenol adsorbed at equilibrium and at time  $t$ , respectively,  $k_1$  (min<sup>-1</sup>) is the pseudo-first-order rate constant. A straight line of  $\ln(q_e - q_t)$  versus  $t$  suggests the applicability of this kinetic model, and  $q_e$  and  $k_1$  can be determined from the intercept and slope of the plot, respectively.

The pseudo-second-order model is in the following form [35]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the rate constant of the second-order equation. The plot of  $t/q_t$  versus  $t$  should give a straight line if pseudo-second-order kinetic model is applicable and  $q_e$  and  $k_2$  can be determined from slope and intercept of the plot, respectively.

The intraparticle diffusion equation is expressed as [36]:

$$q_t = k_{id} t^{1/2} + c \quad (7)$$

where  $k_{id}$  (mg g<sup>-1</sup> min<sup>-1/2</sup>) is the rate constant of intraparticle diffusion model. The values of  $k_{id}$  and  $c$  can be determined from the slope and intercept of the straight line of  $q_t$  versus  $t^{1/2}$ , respectively.

For evaluating the kinetics of phenol–organobentonite interactions, the pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to fit the experimental data. The pseudo-first-order rate constant  $k_1$  and the value of  $q_{e, cal}$  were calculated from the plot of  $\ln(q_e - q_t)$  versus  $t$ , and the results are given in Table 1. The correlation coefficient ( $R^2$ ) is relatively too low which may be indicative of a bad correlation. In addition,  $q_{e, cal}$  determined from the model is not in a good agreement with the experimental value of  $q_{e, exp}$ . Therefore, the adsorption of phenol onto organobentonite is not suitable for the first-order reaction. From Table 1, the value of  $c$  obtained from intraparticle diffusion model is not zero, and the correlation coefficient is not satisfactory thereby intraparticle diffusion may not be the controlling factor in determining the kinetics of the process. The linear plot of  $t/q_t$  versus  $t$  for the pseudo-second-order kinetic model is shown in Fig. 5(b). The pseudo-second-order rate constant  $k_2$  and the value of  $q_{e, cal}$  were determined from the model and the results are presented in Table 1. The value of correlation coefficient is very high ( $R^2 > 0.999$ ) and the calculated  $q_{e, cal}$  value is closer to the experimental  $q_{e, exp}$  value. In the view of these results, the pseudo-second-order kinetic model provided a good correlation for the adsorption of phenol onto organobentonite in contrast to the pseudo-first-order and intraparticle diffusion model.

### 3.4. Effect of initial phenol concentration and adsorption isotherms

Adsorption isotherms are useful for understanding the mechanism of the adsorption. Although several isotherm equations are available due to their simplicity, two well-known models, Langmuir and Freundlich isotherm models were chosen in this study for evaluating the relationship between the amount of phenol adsorbed onto organobentonite and its equilibrium concentration in aqueous solution.

The Langmuir model assumes that adsorption takes place at specific homogeneous sites on the surface of the adsorbent and also, when a site is occupied by an adsorbate molecule, no further adsorption can take place at this site. The linear form of the Langmuir isotherm model can be presented as [37]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b q_{max}} \quad (8)$$

where  $q_e$  (mg g<sup>-1</sup>) is the amount of the phenol adsorbed per unit mass of adsorbent,  $C_e$  (mg L<sup>-1</sup>) is the equilibrium phenol concentra-

**Table 1**  
Parameters of pseudo-first-order, pseudo-second-order and intraparticle diffusion models.

Exp. $q_e$ (mg g <sup>-1</sup> )	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
	$k_1$ (min <sup>-1</sup> )	$q_e$ (mg g <sup>-1</sup> )	$R^2$	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$q_e$ (mg g <sup>-1</sup> )	$R^2$	$k_{id}$ (mg g <sup>-1</sup> min <sup>-1</sup> )	$C$ (mg g <sup>-1</sup> )	$R^2$
5.96	-0.0128	1.01	0.7426	0.116	5.97	0.9999	0.158	3.505	0.4049

tion in the solution,  $q_{max}$  (mg g<sup>-1</sup>) is the Langmuir constant related to the maximum monolayer adsorption capacity, and  $b$  (L mg<sup>-1</sup>) is the constant related the free energy or net enthalpy of adsorption. The linear plot of  $C_e/q_e$  versus  $C_e$  indicates that adsorption obeys the Langmuir model, and the constants  $q_{max}$  and  $b$  are obtained from the slope and intercept of the linear plot, respectively.

The essential features of the Langmuir isotherm model can be expressed in terms of ' $R_L$ ' a dimensionless constant, separation factor or equilibrium parameter, which is defined by the following equation [38]:

$$R_L = \frac{1}{1 + bC_0} \quad (9)$$

where  $C_0$  (mg L<sup>-1</sup>) is the initial amount of adsorbate and  $b$  (L mg<sup>-1</sup>) is the Langmuir constant described above. The  $R_L$  parameter is considered as more reliable indicator of the adsorption. There are four probabilities for the  $R_L$  value:

- for favorable adsorption  $0 < R_L < 1$ ,
- for unfavorable adsorption  $R_L > 1$ ,
- for linear adsorption  $R_L = 1$  and
- for irreversible adsorption  $R_L = 0$ .

The Freundlich isotherm model is valid for multilayer adsorption on a heterogeneous adsorbent surface with sites that have different energies of adsorption. The Freundlich model in linear form [39]:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (10)$$

where  $K_f$  (mg g<sup>-1</sup>) is the constant related to the adsorption capacity and  $n$  is the empirical parameter related to the intensity of adsorption. The value of  $n$  varies with the heterogeneity of the adsorbent and for favorable adsorption process the value of  $n$  should be less than 10 and higher than unity. The values of  $K_f$  and  $1/n$  are determined from the intercept and slope of linear plot of  $\ln q_e$  versus  $\ln C_e$ , respectively.

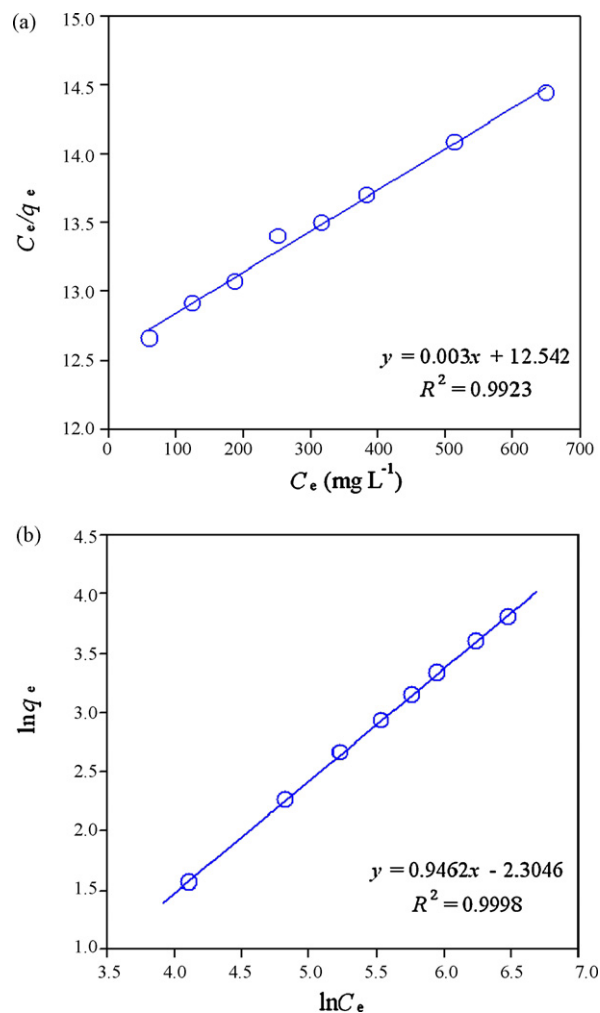
In order to investigate the effect of initial phenol concentration on the adsorption process, the experiments were carried out with initial phenol concentration in the range of 100–1000 mg L<sup>-1</sup> at constant values of pH (9.0), organobentonite concentration (10 g L<sup>-1</sup>) and contact time (60 min). After reaching equilibrium, the phenol concentration in filtrate for each system was measured by UV–vis spectrometry. The equilibrium concentration of phenol increased from 4.8 to 45.0 mg g<sup>-1</sup> in the light of the results whereas adsorption percentage decreased from 48% to 4.5% with increasing the initial phenol concentration from 100 to 1000 mg L<sup>-1</sup>. The initial phenol concentration acts as a driving force to overcome mass transfer resistance for phenol transport between the solution and the surface of the organobentonite. On the other hand, at higher concentrations, phenol present in solution cannot interact with the active binding sites of the organobentonite due to the saturation of these sites [40].

The equilibrium data obtained from the adsorption of phenol onto organobentonite were fitted both the Langmuir and Freundlich isotherm models. The values of Langmuir constants,  $q_{max}$  and  $b$  obtained from the equation of linear plot of  $C_e/q_e$  versus  $C_e$  (Fig. 6(a)) were found to be 333.0 mg g<sup>-1</sup> and  $2.4 \times 10^{-4}$  L mg<sup>-1</sup> respectively, with correlation coefficient ( $R^2$ ) of 0.992. The  $R_L$  values ranged from 0.820 to 0.978 between 100 and 1000 mg L<sup>-1</sup> of initial

phenol concentration and approached zero with increase in the  $C_0$  value, indicated that the organobentonite is a suitable adsorbent for adsorption of phenol from aqueous solutions. The values of Freundlich constants,  $K_f$  and  $1/n$  were obtained from the linear plot of  $\ln q_e$  versus  $\ln C_e$  (Fig. 6(b)) and found to be 0.099 and 0.946 respectively, with correlation coefficient ( $R^2$ ) of 0.999. The Freundlich constant  $1/n$  was smaller than unity indicated that the adsorption process was favorable under studied conditions. From the results, the adsorption pattern of phenol onto organobentonite was well fitted with both Langmuir and Freundlich isotherm model. This may be due to both homogeneous and heterogeneous distribution of active sites on the surface of the organobentonite.

### 3.5. Effect of organobentonite concentration

The effects of organobentonite concentration on the removal of phenol from aqueous solutions were investigated by using seven different organobentonite concentrations in the range of 1–25 g L<sup>-1</sup> and initial phenol concentration of 110 mg L<sup>-1</sup> at pH



**Fig. 6.** (a) Langmuir isotherm model and (b) Freundlich isotherm model.

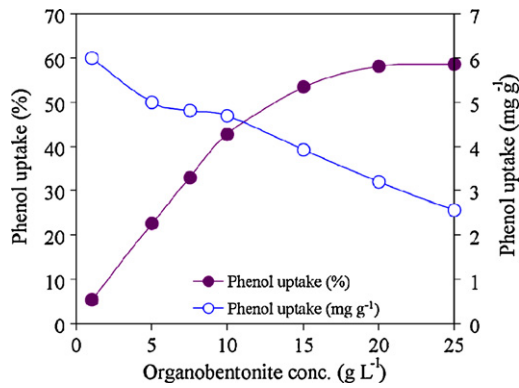


Fig. 7. Effect of organobentonite concentration on phenol uptake (pH: 9.0, initial phenol conc.: 110 mg L<sup>-1</sup>, contact time: 60 min).

9.0. As the organobentonite concentration was increased from 1 to 25 g L<sup>-1</sup>, the equilibrium adsorption capacity of organobentonite ( $q_e$ ), decreased from 6.0 to 2.6 mg g<sup>-1</sup>, whereas, the phenol removal efficiency increased from 5.5% to 58.5% (Fig. 7). The increase in adsorption percentage of phenol was probably due to the increased more availability of active adsorption sites with the increase in organobentonite concentration [40]. The decrease in equilibrium adsorption capacity of organobentonite for phenol uptake could be attributed to two reasons. First, the organobentonite particles aggregated with increasing the adsorbent concentration hence total surface area of the adsorbent decreased and diffusion path length of phenol increased. Secondly, the increase in organobentonite concentration at constant concentration and volume of phenol lead to unsaturation adsorption sites [41], so the equilibrium adsorption capacity of organobentonite decreased.

### 3.6. Effect of temperature and thermodynamic parameters of adsorption

The effect of temperature on the removal efficiency was investigated in the temperature range of 0–40 °C. In order to control the temperature of the solutions, a cryostat (Nüve BD 402, temperature range: –10 to +40 °C) was used for all thermodynamic studies. The experiments were carried out with organobentonite concentration of 10 g L<sup>-1</sup> and initial phenol concentration of 105 mg L<sup>-1</sup> at pH 9.0. The uptake of phenol by organobentonite decreased from 6.2 mg g<sup>-1</sup> (59% removal) to 5.2 mg g<sup>-1</sup> (49.5% removal) when increasing the temperature from 0 to 40 °C, indicating that phenol uptake was favored at lower temperatures (Fig. 8(a)). The decrease in adsorption with the rise of temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbent and adsorbate species and also between the vicinal molecules of the adsorbed phase [42–44]. Similar results were obtained by Hameed [45] with adsorption of 2,4,6-trichlorophenol by activated clay.

The feasibility of the adsorption process was evaluated by the thermodynamic parameters including free energy change ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ).  $\Delta G^\circ$  was calculated from the following equation:

$$\Delta G^\circ = -RT \ln K_d \quad (11)$$

where  $R$  is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>),  $T$  is the temperature (K), and  $K_d$  is the distribution coefficient. The  $K_d$  value was calculated using following equation:

$$K_d = \frac{q_e}{C_e} \quad (12)$$

where  $q_e$  and  $C_e$  are the equilibrium concentration of phenol on adsorbent (mg L<sup>-1</sup>) and in the solution (mg L<sup>-1</sup>), respectively. The

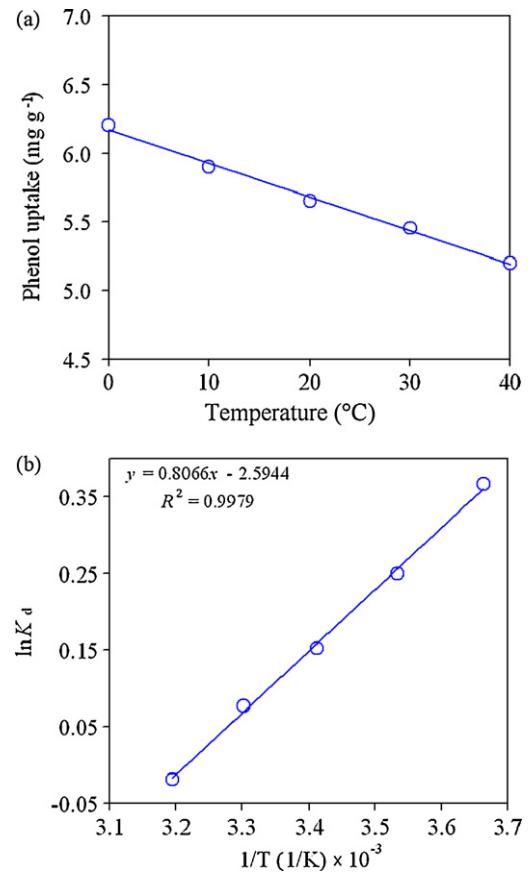


Fig. 8. (a) Effect of temperature on phenol uptake and (b) the plot between  $\ln K_d$  versus  $1/T$  for obtaining the thermodynamic parameters (pH: 9.0, initial phenol conc.: 105 mg L<sup>-1</sup>, organobentonite conc.: 10 g L<sup>-1</sup>, contact time: 60 min).

enthalpy change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ) of adsorption were estimated from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (13)$$

This equation can be written as:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (14)$$

The thermodynamic parameters of  $\Delta H^\circ$  and  $\Delta S^\circ$  were obtained from the slope and intercept of the plot between  $\ln K_d$  versus  $1/T$ , respectively (Fig. 8(b)). The values of  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  for the adsorption of phenol onto organobentonite at different temperatures are given in Table 2. The negative values of  $\Delta G^\circ$  in the temperature range of 0–30 °C indicated that the adsorption process was feasible and spontaneous. In addition, the decrease in the magnitude of  $\Delta G^\circ$  to higher temperatures showed the diminishing of the spontaneous of the process so the adsorption was not favorable at higher temperatures. The negative value of  $\Delta H^\circ$  confirmed the exothermic nature of adsorption which was also supported by the

Table 2

Thermodynamic parameters of the phenol adsorption onto organobentonite at different temperatures.

$T$ (°C)	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> ) <sup>a</sup>	$\Delta H^\circ$ (kJ mol <sup>-1</sup> ) <sup>a</sup>
0	-0.83		
10	-0.59		
20	-0.37	-21.57	-6.70
30	-0.19		
40	0.05		

<sup>a</sup> Measured between 273 and 313 K.

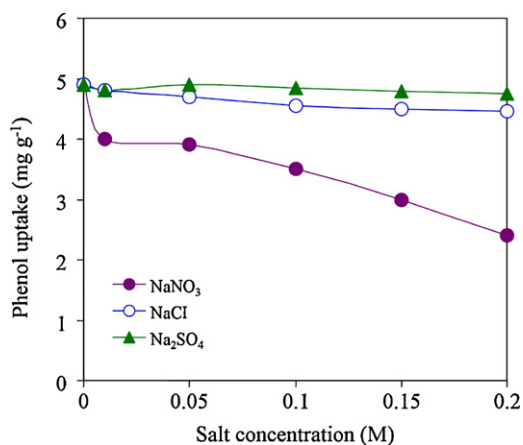


Fig. 9. Effect of ionic strength on the phenol uptake (pH: 9.0, initial phenol conc.: 110 mg L<sup>-1</sup>, organobentonite conc.: 10 g L<sup>-1</sup>, contact time: 60 min).

decrease in value of phenol uptake with the rise in temperature. The negative value of  $\Delta S^\circ$  suggested the decreased randomness at the solid/liquid interface during the adsorption of phenol onto organobentonite.

### 3.7. Effect of ionic strength

Industrial wastewaters and natural waters contain many types of electrolyte that have significant effects on the adsorption process so it is important to evaluate the effects of ionic strength on the removal of phenol from aqueous solutions. In present study, NaCl, NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> were selected as model salts to investigate their influence on the adsorption of phenol onto organobentonite. Adsorption studies were carried out by adding various concentrations (in the range of 0.01–0.20 M) of NaCl, Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub> solutions individually, in 110 mg L<sup>-1</sup> of phenol solutions containing 10 g L<sup>-1</sup> of organobentonite. The present adsorption process was applied to these solutions. The increase in the salt concentration resulted in a decrease of phenol adsorption onto organobentonite (Fig. 9). As the concentration of salts increased from 0 to 0.20 M, the amount of phenol uptake decreased from 4.9 to 4.75, 4.45 and 2.4 mg g<sup>-1</sup> and the percentage removal efficiency decreased from 44.5% to 43.2%, 44.5% and 21.8% for NaCl, Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub> salts, respectively. These results can be explained: the active sites of the adsorbent may be blocked in the presence of these salts so phenol molecules are hindered to bind the surface of the adsorbent. And also the decrease in adsorption with increased ionic strength may be due to the decrease in hydrophobic nature of the dissociated phenol molecules at pH 9.0. From the results, the NaNO<sub>3</sub> salt exhibited a higher inhibition of phenol adsorption compared to the NaCl and Na<sub>2</sub>SO<sub>4</sub> salts.

### 3.8. Applicability of the organobentonite without regeneration

The organobentonite was tested for its reusability without regeneration. The tests were performed by using an initial phenol concentration of 105 mg L<sup>-1</sup> at pH 9.0 with 10 g L<sup>-1</sup> of organobentonite suspension. After shaking for 60 min, the phenol loaded organobentonite was separated, dried in air for one day, and then treated with another 105 mg L<sup>-1</sup> phenol solution. The process was repeated for five times. The largest amount of phenol adsorbed (56.2% removal) was with fresh organobentonite (first cycle), and each its subsequent loading the adsorption capacity of organobentonite was decreased (Fig. 10). After cycles 4 and 5, the newly adsorbed amount of phenols were 2.5 mg g<sup>-1</sup> (23.8% removal) and 1.7 mg g<sup>-1</sup> (16.2% removal), respectively indicated that the quan-

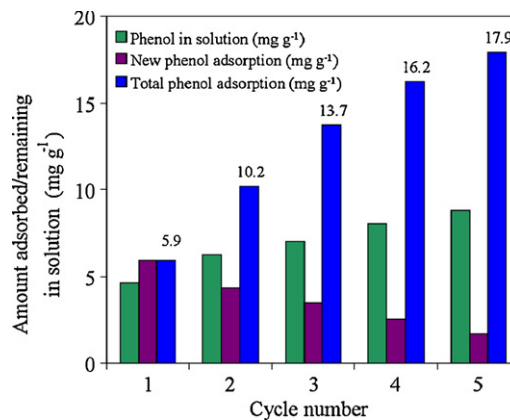


Fig. 10. Reuse of the organobentonite without regeneration (pH: 9.0, initial phenol conc.: 105 mg L<sup>-1</sup>, organobentonite conc.: 10 g L<sup>-1</sup>, contact time: 60 min).

tity of phenol uptake decreased compared to the first three cycles. From the results, already used organobentonite can be applied to fresh phenol solutions and can be used at least five times without regeneration. Similar results were reported in the literatures [46].

### 3.9. Desorption of phenol

It is very important to regenerate the spent adsorbent for keeping the adsorption process costs down [47–49]. Regeneration of organobentonite can be succeeded by washing the phenol loaded organobentonite with a suitable desorbing solution that must be cheap, effective, non-polluting and non-damaging to the adsorbent. For this, desorption of phenol from loaded organobentonite was carried out with deionized water at pH 2.0, 0.1 M of NaOH, 20% acetone, and 20% ethanol solutions, individually. First step: 10 g L<sup>-1</sup> of organobentonite suspension was equilibrated with 10 mL of 100 mg L<sup>-1</sup> initial phenol solution at pH 9.0. After reaching the equilibrium, the organobentonite was separated by filtration then the equilibrium concentration of phenol in the filtrate was determined by UV–vis spectrometry. Second step: phenol loaded organobentonite was washed with deionized water for three times, and then dried in air for one day. The loaded adsorbent was treated 10 mL of deionized water at pH 2.0, 0.1 M of NaOH, 20% acetone and 20% ethanol solutions, individually by agitating at 400 rpm for 60 min.

Among the desorbing solutions used in the present study, 20% acetone solution was identified as the best eluent because of its

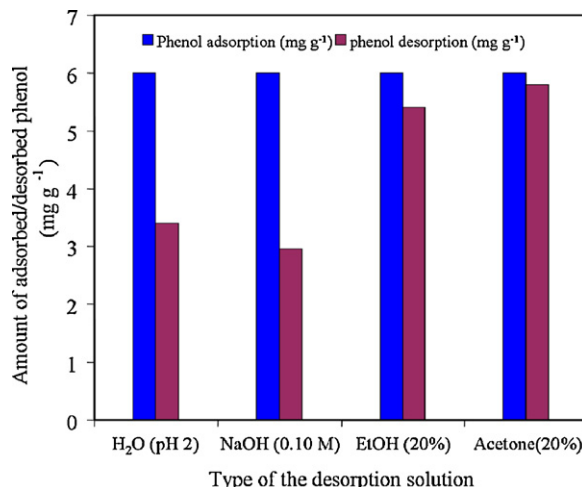


Fig. 11. Desorption of phenols by different desorbing agents.



96.6% desorption efficiency. On the other hand 20% ethanol solution, deionized water at pH 2.0 and 0.1 M of NaOH solution has 90.0%, 56.7%, 49.3% desorption efficiencies, respectively (Fig. 11).

#### 4. Conclusions

The clay minerals are one of the most promising adsorbent due to their low cost, easy availability, high specific surface area, and chemical and mechanical stability. A member of clay minerals, the natural bentonite which was obtained from Tirebolu-Giresun region of Turkey, was modified with CTAB in order to increase its adsorption capacity, and used as an adsorbent for removal of phenol from aqueous solutions.

After the natural bentonite, organobentonite and phenol loaded bentonite were characterized with the FTIR spectroscopy, XRD and SEM, the phenol removal performance of the organobentonite which exhibited higher adsorption capacity was investigated in the light of equilibrium, kinetics and thermodynamics parameters.

The maximum phenol removal was achieved at pH 9.0. The kinetic studies indicated that the adsorption process was extremely fast (equilibrium time is 60 min). The kinetics of phenol adsorption onto organobentonite followed by pseudo-second-order model. When the organobentonite concentration was increased, the equilibrium adsorption capacity ( $\text{mg g}^{-1}$ ) of organobentonite decreased, whereas the percent removal efficiency increased. The straight lines obtained for the Langmuir and Freundlich isotherm models obey to fit to the experimental equilibrium data indicating that disclosing of heterogeneous and homogeneous distribution in the active sites on the surface. The monolayer adsorption capacity of organobentonite was found to be  $333 \text{ mg g}^{-1}$  from Langmuir model equations. The adsorption of phenol onto organobentonite decreased when increasing the temperature. The negative  $\Delta G^\circ$  values indicated that the adsorption of phenol onto organobentonite was feasible and spontaneous. The negative value of  $\Delta H^\circ$  confirmed the exothermic nature of adsorption. The negative value of  $\Delta S^\circ$  suggested the decreased randomness at the solid/liquid interface during the adsorption of phenol onto organobentonite. As the concentration of NaCl,  $\text{Na}_2\text{SO}_4$  and  $\text{NaNO}_3$  salts increased, the amount of phenol uptake decreased. The organobentonite can be used at least five times for further adsorption process without regeneration. For desorption of phenol, 20% acetone solution was considered as the best desorbing solution.

The experimental results indicated that the organobentonite can be successfully used for removal of phenol from aqueous solutions. The present adsorption system using modified bentonite may be considered as a replacement strategy for existing conventional systems.

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