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Removal of phenol and 4-chlorophenol by surfactant-modified natural zeolite

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Abstract

In this study the adsorption characteristics of phenol and 4-chlorophenol by surfactant-modified zeolite was investigated. Batch studies were performed to evaluate the effects of various experimental parameters such as contact time, adsorbent dose, initial concentration, and temperature on the removal of phenol and 4-chlorophenol. The sorption kinetics was tested for intraparticle diffusion, Elovich, and pseudo-second order reaction and rate constants of kinetic models were calculated. Equilibrium isotherms for the adsorption of phenol were analyzed by Freundlich, Langmuir, and Tempkin isotherm models. Freundlich isotherm was found to best represent the data for phenol and 4-chlorophenol adsorption.
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1. Introduction

Organic matter contained by many industrial wastewaters is difficult or impossible to remove by conventional biological treatment processes. Phenols and related compounds are toxic to humans and aquatic life, causing oxygen demand in receiving waters [1,2]. Their presence in water supplies is noticed as bad taste and odor. Coke-oven plants, oil refineries, and petrochemical manufacturing plants are the main sources of phenolic wastewaters [3]. Due to their harmful effects, wastewater containing phenolic compounds must be treated before being discharged to receiving media [4].

There are several methods to remove phenolic compounds from wastewaters. These include physicochemical treatment processes, chemical oxidation, and biological degradation [5–8]. Secondary biological treatment processes cannot treat phenolic wastewaters at high concentrations successfully. The most widely used method is adsorption onto the surface of activated carbon in wastewater treatment. The high cost of activated carbon has stimulated interest in examining the feasibility of using cheaper raw materials [9–13].

Zeolites are hydrated aluminosilicate materials having cage-like structures with internal and external surface areas of up to several hundred square meters per gram and cation exchange capacities of up to several meq./kg. At least 41 types of natural zeolites are known to exist, and many others have been synthesized. Both natural and synthetic zeolites are used in industry as adsorbents, soil modifiers, ion exchangers, and molecular sieves [14].

Natural zeolites possess permanent negative charges in their crystal structures, making them suitable for modification using cationic surfactants. Recent studies on the properties of surfactant-modified zeolite indicate that it is an effective sorbent for multiple types of contaminants [15–21]. Surfactant-modified zeolite can remove organic compounds and oxyanions from water. Partitioning is responsible for organic sorption by surfactant-modified zeolite while transition metal cation sorption is generally unaffected [22]. While the sorption of oxyanions by surfactant-modified zeolite was attributed to anion exchange on the positively charged surfactant bilayer, the sorption of hydrophobic organic contaminants was due to partitioning of the organics into the organic phase created by the surfactant tail groups [23].

The aim of this study was to investigate removal of phenol and 4-chlorophenol from water by surfactant-modified zeolite. The effects of experimental parameters such as adsorbent dose, initial concentration, contact time, and temperature on

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Fig. 1. SEM micrograph of natural zeolite (Ergun, 1977).

Fig. 2. Chemical structures of cationic surfactants used to prepare modified zeolite.

the sorption of phenol and 4-chlorophenol were also investigated.

2. Materials and methods

2.1. Adsorbent

Zeolite samples used in this study were collected from Çankırı-Çorum Basin of Turkey. The mineralogical and geochemical analysis showed that the clinoptilolite is only zeolite mineral in tuff samples and the former volcanic ash shards were altered to the aggregates of clinoptilolite crystallizes up to 97%. SEM micrograph of natural zeolite is shown in Fig. 1. The zeolitized tuffs have drusy texture with very high microporosity. Chemical composition of natural zeolite was given in Table 1 [24]. The total CEC of zeolite was found to be 142–146 meq./100 g [25].

2.2. Adsorbate

Phenol and 4-chlorophenol of analytical reagent grade supplied by Merck GmbH was used for the preparation of the synthetic adsorbate solutions. An aqueous solution with a 1000 mg/L concentration was prepared by mixing an appropriate amount of phenol and 4-chlorophenol with distilled water. Fresh stock solution as required was prepared immediately before use

in the experiments. The initial concentration was ascertained before the start of each experimental run.

2.3. Modification

Prior to use, zeolite samples were sieved to a size of 0.5 mm. Then, the samples were treated with 1 mol/L NaCl solution to saturate the exchange sites with sodium ions. Hexadecyltrimethyl ammonium bromide (HDTMA) and benzyltetradecyl ammonium chloride (BDTDA) supplied by Merck GmbH were used for modification of zeolite (Fig. 2). One hundred milliliters of HDTMA or BDTDA solution with concentration of 0.03 mol/L was placed in a flask and 10 g of zeolite added. The dispersions were shaken at room temperature by a mechanic shaker for 24 h, followed by washing with distilled water. The surfactant-modified zeolite was dried at 50 °C in an oven.

X-ray diffraction (XRD) measurements were taken by Rigaku D-max 1000 model diffractomer. The zeolite samples were modified with related chemical at 60 °C. XRD analysis was performed on the natural and surfactant-modified zeolite samples to confirm the crystal structure and identity. The results showed that the structure was not changed by heat and chemical treatment (Fig. 3).

Table 1
EDXRF results of natural zeolite (Ergun, 1977)

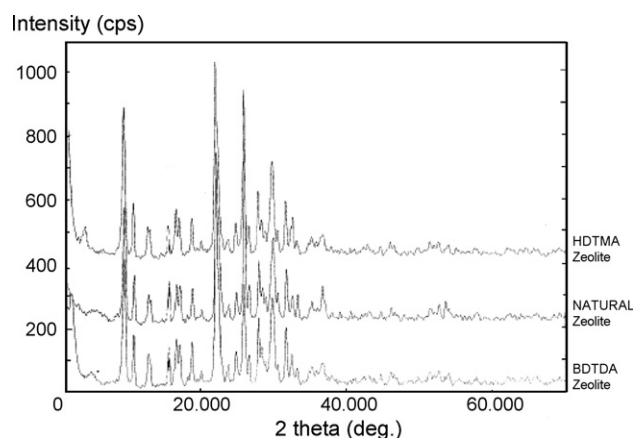| Component	%
Na_2O	5.6
MgO	1.0
Al_2O_5	13.7
SiO_2	65.0
P_2O_5	0.1
CaO	3.1
TiO_2	0.3
MnO	0.03
K_2O	1.0
$FeO + Fe_2O_3$	<0.1

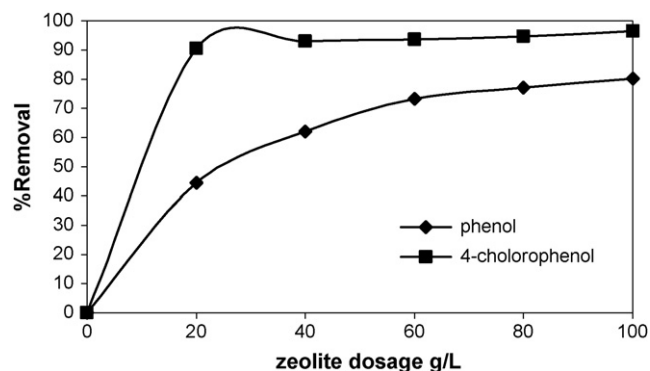Fig. 3. XRD spectrum of zeolite samples used.
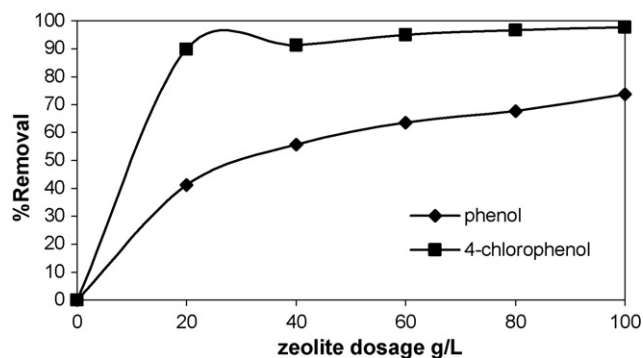
Fig. 4. Effect of HDTMA-zeolite dosage on the removal of phenol and 4-chlorophenol.

2.4. Kinetic and equilibrium experiments

Kinetic and equilibrium experiments were obtained using the batch equilibrium technique obtained by mixing a known amount of surfactant-modified zeolite with 50 ml of phenol or 4-chlorophenol solution in conical flask. The zeolite sample was weighed and placed in flasks containing phenol or 4-chlorophenol solutions at desired concentration.

In order to evaluate kinetic data, separate flasks were prepared for each time interval and only one flask was taken for desired time from 30 min to 24 h. For each adsorption isotherm experiment, a known amount of the adsorbent was added to 50 mL of the solution in a concentration range from 10 to 50 ppm for phenol and from 10 to 100 ppm for 4-chlorophenol. The mixture was shaken in a temperature-controlled shaking water bath at a constant speed of 150 rpm for 24 h. The solution and sorbent were separated by centrifugation at 5000 rpm and analyzed for phenol or 4-chlorophenol concentration for both experiments. The concentration of phenol and 4-chlorophenol was determined by Hitachi UV–vis spectrophotometer at 500 nm [26].

The amount of adsorbed phenol or 4-chlorophenol was calculated according to the following equation:

$$q_e = (C_0 - C_e)\, V/m \tag{1}$$

where q_e is the amount of adsorbed (mg/g), C_0 and C_e are the initial and equilibrium concentrations of liquid phase (mg/L), V is the volume of the solution (L), and m is the mass of the adsorbent.

3. Results and discussion

3.1. Effect of adsorbent dosage

The effect of adsorbent dosage on phenol and 4-chlorophenol removal is shown in Figs. 4 and 5, respectively. These figures show that the removal of phenol and 4-chlorophenol increases with the increase in adsorbent dosage. The phenol removal efficiencies varied from 41 to 74% for HDTMA-zeolite and from 45 to 80% for BDTDA-zeolite at adsorbent concentrations of 20–100 g/L. The 4-chlorophenol removal efficiencies varied from 90 to 98% both for HDTMA-zeolite and BDTDA-

Fig. 5. Effect of BDTA-zeolite dosage on the removal of phenol and 4-chlorophenol.
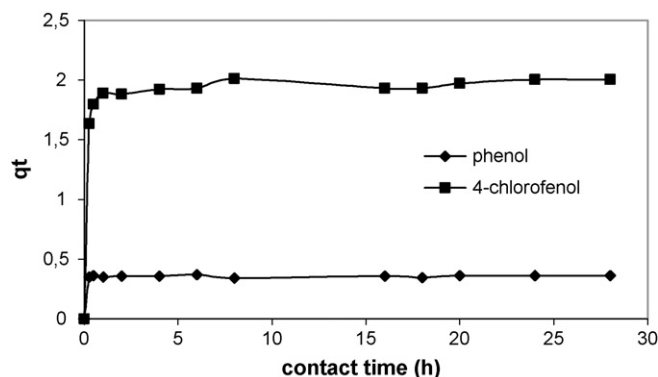

Fig. 6. Effect of contact time on the removal of phenol and 4-chlorophenol on HDTMA-zeolite.

zeolite at adsorbent concentrations of 20–100 g/L. An increase in adsorption with the adsorbent dosage can be attributed to greater surface area and the availability of more adsorption sites, Eq. (6). Although the adsorbed amount increases with adsorbent concentration, this increase is not linear. This result is consistent with the results obtained by Yapar et al. [27].

3.2. Effect of contact time

Figs. 6 and 7 show the plot of phenol and 4-chlorophenol removal against contact time at initial concentration of 50 mg/L. The rate of phenol and 4-chlorophenol removal was found to be
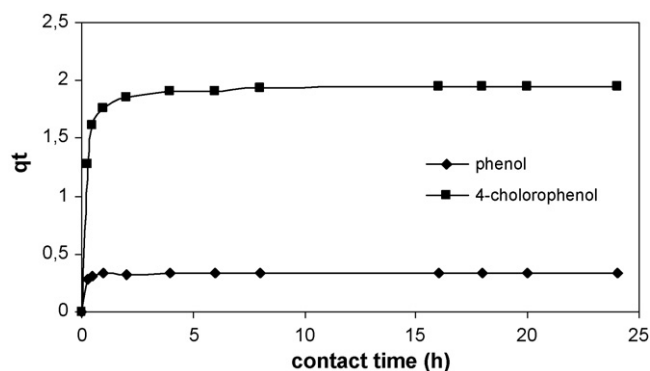

Fig. 7. Effect of contact time on the removal of phenol and 4-chlorophenol on BDTDA-zeolite.

Table 2
Kinetic parameters for the removal of phenol and 4-chlorophenol by surfactant-modified zeolite

Kinetic parameters	Phenol		4-Chlorophenol	
	HDTMA-zeolite	BDTDA-zeolite	HDTMA-zeolite	BDTDA-zeolite
Pseudo-second order				
q_e	0.36046	0.34098	1.9755	1.95963
k_2	41.556	52.220	7.0784	4.8045
R^2	0.9993	1	0.9995	1
Intraparticle diffusion				
k_{id}	[a]	69.5024	73.1139	74.5762
α	[a]	0.0183	0.0335	0.0725
R^2	[a]	0.8592	0.7868	0.7855
Elovich				
α	[a]	2.561×10^{23}	6.593×10^{12}	822020
β	[a]	0.006	0.0613	0.1209
R^2	[a]	0.8661	0.795	0.8205

[a] $R^2 < 0.75$.

very rapid during the initial 30 min and to remain nearly constant thereafter. No significant change in phenol and 4-chlorophenol removal was observed after about 4 h. The phenol removal efficiencies reached up to 71% and 73% for HDTMA-zeolite and BDTDA-zeolite and the 4-chlorophenol removal efficiencies reached up to 81% and 89% for HDTMA-zeolite and BDTDA-zeolite after 24 h.

3.3. Adsorption kinetics

Three kinetic models, pseudo-second order, intraparticle diffusion, and Elovich models were used to investigate the adsorption of phenol and 4-chlorophenol on surfactant-modified zeolite.

3.3.1. Pseudo-second order model

The pseudo-second order reaction model based on sorption equilibrium capacity may be expressed as [28]:

$$dq/dt = k_2(q_e - q_t)^2 \tag{2}$$

After integrating Eq. (2) for the following boundary condition and rearranging it to obtain the linearized form which is shown as follows: $t = 0$, $q_t = 0$, $t = t$, $q_t = q_t$

$$t/q_t = 1/k_2 q_e^2 + 1/q_e t \tag{3}$$

$$h = k_2 q e^2 \tag{4}$$

where q_e is the amount of the solute sorbed at equilibrium (mg/g), k_2 is the equilibrium rate constant of pseudo-second order (g/mg min), h is the initial sorption rate (mg/g min).

These constants can be determined by plotting t/q_t against t.

3.3.2. Intraparticle diffusion model

The intraparticle diffusion model is expressed as [29]:

$$\log R = \log k_{id} + \alpha \log t \tag{5}$$

where R is the percent phenol and cholorophenol adsorbed, t is the contact time (h), α is the gradient of linear plots, and k_{id} may

be taken as a rate factor, i.e., percent phenol and 4-chlorophenol adsorbed per unit time. Higher values of k_{id} illustrate an enhancement in the rate of adsorption, whereas larger α values illustrates a better adsorption mechanism, which is related to an improved bonding between percent phenol and 4-chlorophenol ions and zeolite particles.

3.3.3. Elovich model

The Elovich equation is given as follows [30]:

$$q_t = \beta \ln(\alpha) + \beta \ln t \tag{6}$$

where α (mg/g min) and β (g/mg) are the equilibrium rate constants for Elovich model.

The equations constants can be obtained from the slope and intercept of a straight-line plot of q_t against $\ln t$.

The values of kinetic constants for phenol and 4-chlorophenol sorption onto surfactant-modified zeolite are presented in Table 2. Good correlation coefficients were obtained for the pseudo-second order kinetic model, which shows that the uptake process follows the pseudo-second order rate expression with the correlation coefficients higher than 0.99.

3.4. Effect of initial concentration

The adsorption of phenol and 4-chlorophenol by surfactant-modified zeolite increases as the initial concentration increases. Increasing the initial phenol and 4-chlorophenol concentration would increase the mass transfer driving force and therefore, the rate at which phenol and 4-chlorophenol molecules pass from the solution to the particle surface. This would result in higher phenol and 4-chlorophenol adsorption. However, the percentage adsorption of phenol and 4-chlorophenol decreases as the initial concentration increases [31].

3.5. Adsorption isotherms

The equilibrium sorption isotherm is fundamentally very crucial in design of sorption systems. The equilibrium sorption is usually described by an isotherm equation characterized by cer-
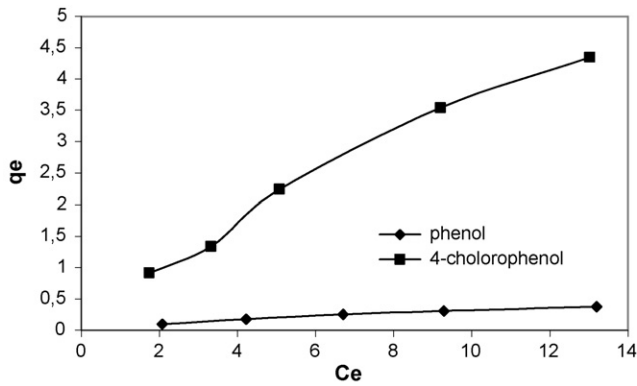
Fig. 8. Equilibrium isotherms for the removal of phenol and 4-chlorophenol on HDTMA-zeolite.
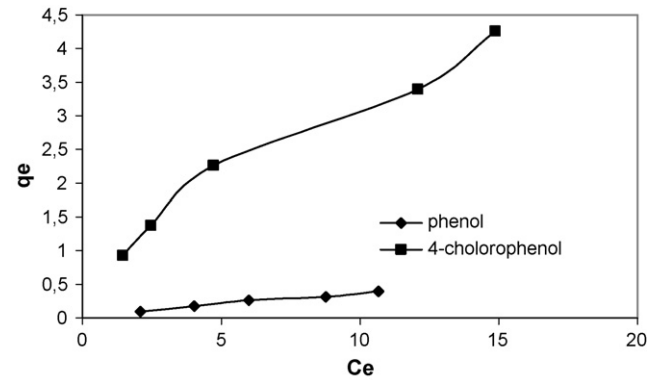

Fig. 9. Equilibrium isotherms for the removal of phenol and 4-chlorophenol on BDTDA-zeolite.

tain parameters which values express the surface properties and affinity of sorbent. The equilibrium relationships between sorbent and sorbate are described by sorption isotherms, the ration between the amount sorbed and that remaining in the solution at a fix temperature at equilibrium [14].

In this study, the sorption of phenol and 4-chlorophenol by surfactant-modified zeolite was analyzed by Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich isotherm models.

3.5.1. Langmuir isotherm

The Langmuir isotherm has been widely applied to pollutants sorption processes. A basic assumption of the Langmuir theory is that the sorption takes place at specific homogenous sites in the sorbent. Moreover, when a site is occupied by a solute, no further sorption can take place at this site. The Langmuir adsorption isotherm can be written as follows [32]:

$$q_e = K_L q_m C_e / 1 + K_L C_e \tag{7}$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), q_m is the adsorption capacity (mg/g), and K_L is the adsorption intensity or Langmuir coefficient (L/mg).

Eq. (7) can be rearranged to the following linear form:

$$C_e / q_e = 1 / K_L q_m + C_e / q_m \tag{8}$$

A plot of C_e / q_e versus C_e gives a straight line with slope $1/q_m$ and intercepts $1/K_L q_m$.

3.5.2. Freundlich isotherm

The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. This experimental model can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption and is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \tag{9}$$

Table 3
Isotherm parameters for the removal of phenol and 4-chlorophenol by surfactant-modified zeolite at 20 °C

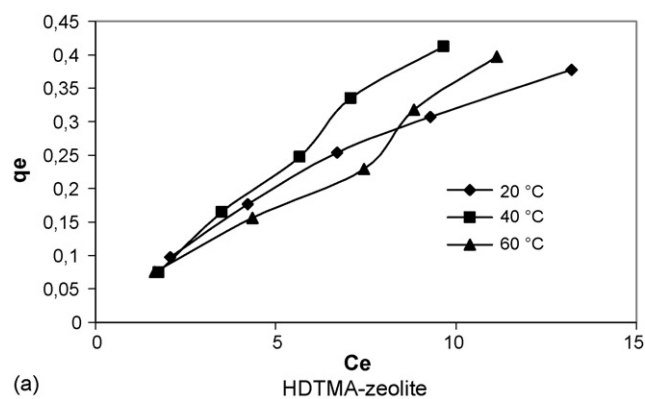| Isotherm parameters	Phenol		4-Chlorophenol	
	HDTMA-zeolite	BDTDA-zeolite	HDTMA-zeolite	BDTDA-zeolite
Freundlich				
K_F	0.0599	0.0538	0.0562	0.7721
$1/n$	0.7276	0.8407	0.8112	0.6261
R^2	0.9903	0.9903	0.9878	0.9871
Langmuir				
q_m	0.7647	1.2977	12.7065	6.4102
K_L	0.0716	0.0393	0.0405	0.1122
R^2	0.9947	0.8484	0.8076	0.9639
Tempkin				
A	0.7538	0.7636	0.7875	1.2008
B	0.1472	0.1746	1.776	1.3668
R^2	0.9903	0.9691	0.9658	0.9716
Dubinin–Radushkevich				
q_0	0.3189	0.3434	3.3324	3.3128
B	1.3599	1.4835	1.1872	0.8733
E	0.6064	0.5806	0.6490	0.7567
R^2	0.9122	0.9169	0.8001	0.8670
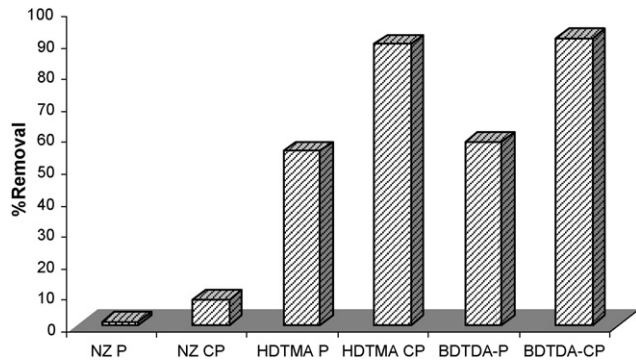
Fig. 10. Comparison of phenol and 4-chlorophenol removal by natural zeolite and surfactant-modified zeolite (20 g zeolite/L, 20 °C, $C_0 = 50$ mg/L) (NZ P: Phenol removal with natural zeolite; NZ CP: 4-chlorophenol removal with natural zeolite; HDTMA P: Phenol removal with HDTMA-zeolite; HDTMA CP: 4-chlorophenol removal with HDTMA-zeolite; BDTDA P: Phenol removal with BDTDA-zeolite; BDTDA CP: 4-chlorophenol removal with BDTDA-zeolite).

where K_F and $1/n$ are the constants that can be related to the adsorption capacity and the adsorption intensity, respectively.
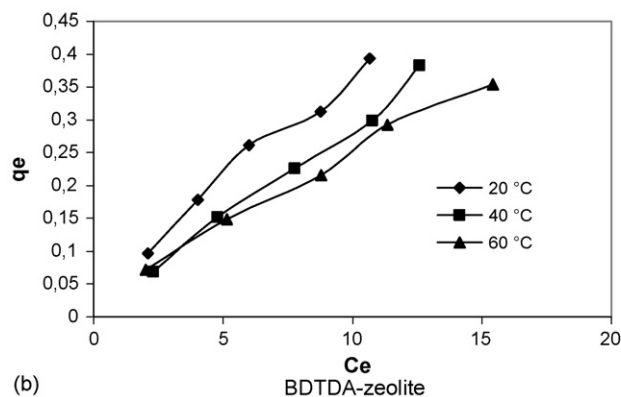
This equation can be rearranged in the linear form by taking the logarithm of both sides as

$$\log q_e = \log K_F + 1/n \, \log C_e \qquad (10)$$

The values of K_F and $1/n$ may be calculated by plotting $\log q_e$ against $\log C_e$. The slope is equal to $1/n$ and the intercept is equal to $\log K_F$.

3.5.3. Tempkin isotherm

Tempkin and Pyzhev considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The Tempkin isotherm has been used in the following form:

$$q_e = RT/b(\ln AC_e) \qquad (11)$$

$$q_e = RT/b \ln A + RT/b \ln C_e \qquad (12)$$

$$B = RT/b \qquad (13)$$

A plot of q_e versus $\ln C_e$ enables the determination of the constants A and B. The constant B is related to the heat of adsorption [33].

3.5.4. Dubinin–Radushkevich isotherm

The empirical equation proposed by Dubinin and Radushkevich has been widely used to describe the adsorption of gases and vapours on microporous solids. In the case of liquid phase adsorption, several studies have shown that the adsorption energy can be estimated according to the Dubinin–Radushkevich equation. Assuming that the adsorption in micropores is limited to a monolayer and the Dubinin–Radushkevich equation is applicable, the adsorption capacity per unit surface area of the adsorbent at equilibrium, q, can be written as [34]:

Fig. 11. Effect temperature on the removal of phenol on HDTMA-zeolite and BDTDA-zeolite.
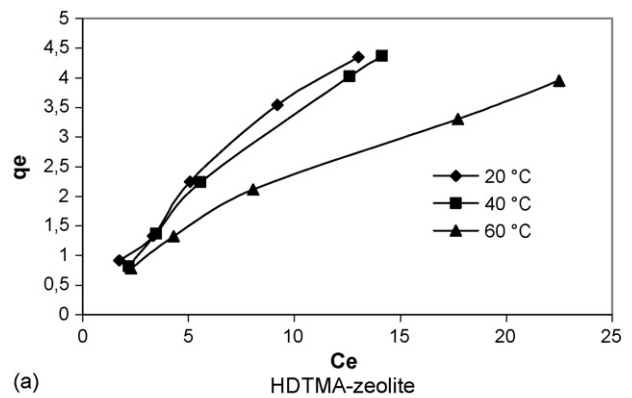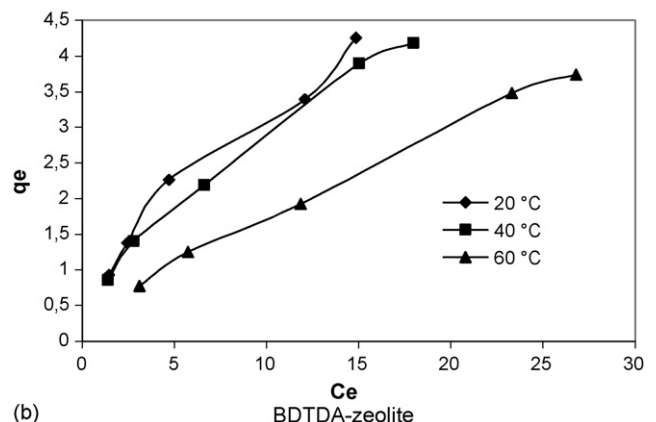
Fig. 12. Effect temperature on the removal of 4-chlorophenol on HDTMA-zeolite and BDTDA-zeolite.

Table 4
Thermodynamic parameters for 4-chlorophenol adsorption

	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)			R^2
			20 °C	40 °C	60 °C	
4-Chlorophenol						
HDTMA-zeolite	1.2162	−0.00548	2.8214	2.9310	3.0405	0.8722
BDTDA-zeolite	5.3094	−0.01825	10.6555	11.0204	11.3853	0.8033

$$q = q_0 \exp(-B\varepsilon^2) \qquad (14)$$

$$\varepsilon = RT \ \ln(1 + 1/C) \qquad (15)$$

where q_0 is the ultimate capacity per unit area in adsorbent micropores, B is the constant related to the adsorption energy, ε is the Polenyi potential, and C is the equilibrium concentration of adsorbate in units of gram per gram. The most probable

energy of adsorption, E, has been chosen to be

$$E = (2B)^{-1/2} \qquad (16)$$

The adsorption isotherms of phenol and 4-chlorophenol by surfactant-modified zeolite are shown in Figs. 8 and 9. Between two phenolic compounds, 4-chlorophenol is more hydrophobic than phenol, having the higher adsorption capacity on surfactant-modified zeolite. The Freundlich equation represents the sorp-

Table 5
Isotherm parameters at different temperatures

	Phenol						4-Chlorophenol					
	HDTMA-zeolite			BDTDA-zeolite			HDTMA-zeolite			BDTDA-zeolite		
	K_F	$1/n$	R^2	K_F	$1/n$	R^2	K_F	$1/n$	R^2	K_F	$1/n$	R^2
Freundlich												
20 °C	0.05990	0.7276	0.9903	0.05380	0.8407	0.9903	0.5617	0.8112	0.9878	0.7721	0.6261	0.9871
40 °C	0.04386	1.0112	0.9938	0.70737	0.9722	0.9950	0.46676	0.7661	0.9896	0.71006	0.6178	0.9974
60 °C	0.04700	0.8530	0.9824	0.04072	0.7919	0.9968	0.56516	0.6930	0.9947	0.33689	0.7318	0.9965

	Phenol						4-Chlorophenol					
	HDTMA-zeolite			BDTDA-zeolite			HDTMA-zeolite			BDTDA-zeolite		
	q_m	K_L	R^2	q_m	K_L	R^2	q_m	K_L	R^2	q_m	K_L	R^2
Langmuir												
20 °C	0.7647	0.0716	0.9947	1.2977	0.0393	0.8484	12.7065	0.0405	0.8076	6.4102	0.1122	0.9639
40 °C	[a]	[a]	[a]	[a]	[a]	[a]	9.3985	0.0433	0.9427	6.5531	0.0939	0.9600
60 °C	[a]	[a]	[a]	[a]	[a]	[a]	7.0373	0.0537	0.9893	8.1235	0.0309	0.9111

	Phenol						4-Chlorophenol					
	HDTMA-zeolite			BDTDA-zeolite			HDTMA-zeolite			BDTDA-zeolite		
	A	B	R^2	A	B	R^2	A	B	R^2	A	B	R^2
Tempkin												
20 °C	0.7538	0.1472	0.9903	0.7636	0.1746	0.9691	0.7875	1.7760	0.9658	1.2008	1.3668	0.9716
40 °C	0.7441	0.1962	0.9586	0.5721	0.1719	0.9352	0.6737	1.5777	0.9705	1.1206	1.3191	0.9578
60 °C	0.8109	0.1565	0.8741	0.7095	0.1361	0.9350	0.6707	1.3722	0.9774	0.4628	1.4070	0.9494

	Phenol								4-Chlorophenol							
	HDTMA-zeolite				BDTDA-zeolite				HDTMA-zeolite				BDTDA-zeolite			
	q_0	B	E	R^2	q_0	B	E	R^2	q_0	B	E	R^2	q_0	B	E	R^2
D–R																
20 °C	0.3189	1.3599	0.6064	0.9122	0.3434	1.4835	0.5806	0.9169	3.3324	1.1872	0.6490	0.8001	3.3128	0.8733	0.7567	0.8670
40 °C	0.3532	1.183	0.6501	0.9162	0.3103	1.7909	0.5284	0.8987	3.8034	1.7547	0.5338	0.9092	3.1797	0.7262	0.8298	0.8031
60 °C	0.2988	0.8376	0.7726	0.8264	0.2746	1.1347	0.6638	0.8508	3.0198	1.4626	0.5847	0.8461	2.8895	2.4475	0.4520	0.8068

[a] $R^2 < 0.75$.

tion process very well; the R^2 value is higher for Freundlich isotherm than for the Langmuir and Tempkin isotherms. The values of isotherm constants for phenol and 4-chlorophenol sorption onto surfactant-modified zeolite are presented in Table 3. The Freundlich exponent $1/n$ gives information about surface heterogeneity and surface affinity for the solute. The Freundlich exponent $1/n$ between 0.6261 and 0.8407 indicates favorable adsorption. Since the degree of favorableness increases as $1/n$ approaches zero, both of the surfactant-modified zeolite samples show a very high affinity for phenol and 4-chlorophenol. Values of q_m, which is defined as the maximum capacity of sorbent, have been calculated from the Langmuir plots. The maximum capacities of surfactant-modified zeolite for phenol and 4-chlorophenol have been calculated in the range of 0.7647–1.2977 mg/g and 6.4102–12.7065 mg/g, respectively.

3.6. Comparison of phenol and 4-chlorophenol removal by natural zeolite and surfactant-modified zeolite

Phenol and 4-chlorophenol removal by natural zeolite and surfactant-modified zeolite was shown in Fig. 10. Phenol and 4-chlorophenol removal efficiency by surfactant-modified zeolite was higher than natural zeolite.

3.7. Effect of temperature and thermodynamic parameters

Temperature has a pronounced effect on the adsorption capacity of adsorbents. Figs. 11 and 12 show the plots of adsorption isotherms, q_e versus C_e for phenol and 4-chlorophenol at different temperatures ranging from 20 to 60 °C. The figures indicate that with the decrease in temperature, the adsorptive of phenol and 4-chlorophenol increases. The increase in the temperature from 20 to 60 °C decreases the adsorption capacity of HDTMA-zeolite and BDTDA-zeolite from 0.39 to 0.37 mg/g and 0.39 to 0.35 mg/g for phenol and from 4.35 to 3.95 mg/g and 4.26 to 3.74 mg/g for 4-chlorophenol. These results confirm the exothermic nature of the adsorption process. The values of isotherm constants for phenol and 4-chlorophenol sorption onto surfactant-modified zeolite at different temperatures are presented in Table 4.

Thermodynamic parameters such as free energy of sorption (ΔG°), the heat of sorption, and standard entropy changes (ΔH° and ΔS°) can be evaluated with the following equations:

$$K_d = q_e/C_e \qquad (17)$$

where K_d is the sorption distribution coefficient.

The K_d values are used in following equation to determine the Gibbs free energy of sorption process at different temperatures.

$$\Delta G^\circ = -RT \ln K_d \qquad (18)$$

where ΔG° is the free energy of sorption (kJ/mol), T is the temperature in Kelvin, and R is the universal gas constant (8.314 J/mol K).

The sorption distribution coefficient may be expressed in terms of enthalpy change (ΔH°) and entropy change (ΔS°) as a function of temperature:

$$\ln K_d = \Delta H^\circ/RT + \Delta S^\circ/R \qquad (19)$$

where ΔH° is the heat of sorption (kJ/mol) and ΔS° is the standard entropy changes (kJ/mol). The values of ΔH° and ΔS° can be obtained from the slope and intercept of a plot of $\ln K_d$ against $1/T$.

Thermodynamic parameters for 4-chlorophenol adsorption on surfactant-modified zeolite were given in Table 5.

4. Conclusion

The present study shows that surfactant-modified zeolite is an effective sorbent for the removal of phenol and 4-chlorophenol from aqueous solution. Adsorption kinetics was found to follow second order kinetic model. The increase in initial concentration of phenol and 4-chlorophenol resulted in an increase in the adsorption by surfactant-modified zeolite. The adsorption of phenol and 4-chlorophenol on surfactant-modified zeolite is favorably influenced by an increase in the temperature. Equilibrium adsorption data for phenol and 4-chlorophenol were best represented by the Freundlich isotherm. It was also found that 4-chlorophenol showed a higher adsorption capacity than phenol on surfactant-modified zeolite.

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