



## The removal of phenol from aqueous solutions by adsorption using surfactant-modified bentonite and kaolinite

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### ABSTRACT

The natural bentonite (BC) and kaolinite (KC) were modified with two surfactant of hexadecyltrimethylammonium bromide (HDTMA) and phenyltrimethylammonium bromide (PTMA) to form four kinds of organic-modified clays, i.e., HDTMA–bentonite (BHM), HDTMA–kaolinite (KHM), PTMA–bentonite (KPM) and PTMA–kaolinite (KPM). The modified minerals were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD) and FT-IR spectroscopy. The surface areas were determined using methylene blue adsorption method. Cation-exchange capacity (CEC) was estimated using an ethylenediamine complex of copper method and the modifier loading was calculated from the total carbon analysis. The ability of raw and organo-modified clays to remove phenol from aqueous solutions has been carried out as a function of contact time, pH and temperatures using a batch technique. The removal of phenol from aqueous solutions by modified clays seems to be more effective than unmodified samples. The adsorption capacity was found to increase with increasing temperature indication that the adsorptions were endothermic. The adsorption of phenol onto these clays was found to be increased by increasing of pH value and the adsorption patterns data are correlated well by Langmuir and Freundlich isotherm models and that the adsorption is physical in nature. The experimental data fitted very well with the pseudo-second-order kinetic model. The thermodynamic study of adsorption process showed that the adsorption of phenol with these six adsorbents was carried out spontaneously, and the process was endothermic in nature.

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### 1. Introduction

The rapidly deteriorating water quality in many of the water resources and increasingly stringent legislation on the purity of drinking water has created a growing interest in the decontamination of water, wastewaters and polluted trade effluents using mineral clays in either crude or modified forms.

Phenolic compounds are common contaminants in wastewater, being generated from petroleum and petrochemical, coal conversion, pulp and paper and phenol producing industries. Phenol are widely used for the commercial production for a wide variety of resins including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives, and polyamide for various applications [1]. Phenols are considered as priority pollutants since they are harmful to organisms at low concentration and many of them have been classified as hazardous pollutants because of their potential harm to human health. Stringent US Environmental Protection Agency (EPA) regulation call for lowering phenol content in the wastewater to less than  $1 \text{ mg L}^{-1}$  [2].

Phenol was selected to represent the phenolic group. It is a common constituent of contaminated soil, ground water or leachate. Phenol is also toxic to plants and aquatic life, which is reflected by low acceptance criteria where these receptors are to be protected [3].

Different water treatment technologies are used to remove phenolic pollutants: destructive process such as destructive oxidation with ozone [4], hydrogen peroxide [5], or manganese oxides [6] and recuperative process such as adsorption into porous solids [7,8], membrane separation [9] and solvent extraction [10].

Organic modification of clay minerals has been shown to significantly increase the attenuation of some organic compounds [11–13]. To increase the ability of mineral clays to remove non-polar and anion water pollutants, it is necessary to modify their surfaces. The permanent negative charge in the crystal structures of some minerals (bentonite, kaolinite, etc.), make them suitable for surface modification by long chain and short chain organic cation surfactants [14–16]. Three-dimensional framework of clay retains the high molecular weight surfactants primarily on the outer surface, whereby at sufficient loading the surfactant forms a bilayer. This bilayer formation results in a reversal of the charge on the external surface of the clay, providing sites where anions will be retained and cations repelled, while neutral species can partition into hydrophobic core. On the other hand, surfactant retention

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occurs in the interlayer space of bentonite and other layer silicates. These modified minerals provide a primarily hydrophobic environment for the retention of organic molecules of low polarity [17].

Over the last three decades, several researchers have investigated the adsorption of phenols on mineral clays, especially bentonite and kaolinite and their organically modified forms that were proved to be very effective in the removal of organic pollutants. Rawajfid and Nsour [18] investigated the interaction of phenol, 4-chlorophenol and 2,4-dichlorophenol with surfactant-modified bentonite clay. Barhoumi et al. [19] studied the influence of nonionic surfactants on the adsorption behaviour of alkylphenols onto kaolinite. The published results so far are limited to certain selected aspects of this phenomenon. The present work is more comprehensive and aims at not only ascertaining the effectiveness of Iraqi clay minerals and their modified forms in removing phenol from water, but extends to studying all the related factors. The maximum exchange capacities, as deduced from the adsorption isotherms, and the thermodynamic parameters of the adsorption process are but few of the comprehensive assessment of this phenomenon that are to be reported in this paper.

The study present in this paper is part of large study aimed at demonstrating the technical feasibility of simple organic modification procedures to increase the organic attenuation capacity of selected Iraqi clay materials. In this part, two cationic surfactant hexadecyltrimethylammonium bromide (HDTMA) and phenyltrimethylammonium bromide (PTMA) were used for the surface modification of natural (raw) Iraqi bentonite and kaolinite, and the adsorption equilibrium and adsorption kinetics of phenol from aqueous solutions onto these modified surfaces, were studied.

## 2. Materials and methods

### 2.1. Materials

Phenol was obtained in excess of 99% purity from Aldrich Chemical Company. Stock solution of 1000 mg L<sup>-1</sup> was made. The stock solution was kept in lightproof container below 5 °C. Sodium azide was used as the bacterial growth retardant in this work. Distilled and deionised water with conductivity value of 1.5 × 10<sup>-6</sup> S cm<sup>-1</sup> was used in all experiments.

HDTMA and PTMA were purchased from Aldrich chemicals and specified to be ≥99% and 98% purity, respectively.

Two mineral clays namely bentonite and kaolinite used in the experiments were received from the General Company for Geological Survey and Mining in Baghdad, Iraq. They were crushed with a hammer and ground in a ceramic mill, the samples was sieved to produce the desired particle size fractions. The samples with a particle size 45 μm was then dried for 24 h at 110 °C in an electric oven and stored in a dessicator until use.

### 2.2. Preparation of organo-modified clays

Both clayey materials were organically modified by adsorption of HDTMA and PTMA and resulted in four organo-modified clays available for further investigation. The surface-modified bentonite and kaolinite samples were prepared as follows.

An aqueous HDTMA or PTMA solutions (50 mmol L<sup>-1</sup>) was added to a 7% aqueous clay suspension. The mixture was stirred in a mixer for 3 h at 350 rpm. The organo-modified clay was separated from the mixture by filtration, washed about five times with distilled water, and dried at 110 °C for 3 h, until constant mass.

The modifier loading was assessed by total carbon analysis (a Leno-2000 CHN analyzer). The difference in carbon content between the unmodified samples and the modified samples was

considered to be entirely due to the exchanged modifier. The total carbon content before, %C<sub>N</sub>, and after, %C<sub>M</sub>, modification, was related to the modifier loading, L<sub>M</sub>, by the following formula [20]:

$$L_M = \frac{1}{\%C_{mW_{mod}}} \left[ \frac{\%C_M - \%C_N}{1 - (\%C_M(mW_{mod}/mWC_{mod}))} \right] \cdot V_{mod} \cdot \frac{100}{1000} \quad (1)$$

where L<sub>M</sub> is modifier loading in milliequivalents per 100 g of unmodified clay, %C<sub>N</sub> is the carbon fraction of the unmodified clay, %C<sub>M</sub> is the carbon fraction of the modified clay, mW<sub>C<sub>mod</sub></sub> is the molecular weight of carbon in the modifying cation, mW<sub>mod</sub> is the molecular weight of the modifying cation and V<sub>mod</sub> is the valency of the modifying cation (1 for both HDTMA and PTMA).

### 2.3. Material characterization

The surface areas for the investigated clays are estimated using methylene blue (MB) adsorption method [21]. This method has advantages over BET gas adsorption measurements in being readily applicable to a wide range of areas and especially to minerals under aqueous conditions [22]. The method is simple, rapid and economical. Different concentration of adsorbate was placed separately in 250 mL stoppered Erlenmeyer flasks and 100 mL of 50 ppm MB solution was added. The mixtures, together with a control sample of MB were left in subdued light at room temperature for the six weeks to be sure that equilibrium is reached. The concentration of equilibrium and standard solution were determined using UV–vis spectrophotometer at 664 nm.

The results of Langmuir adsorption isotherms for MB are used to estimate the monolayer capacity X<sub>m</sub> using Langmuir equation:

$$S = X_m \cdot N_A \cdot A_m \quad (2)$$

where S is the surface area (m<sup>2</sup> g<sup>-1</sup>), N<sub>A</sub> is the Avogadro's number (molecule/mol) and A<sub>m</sub> is the molecular cross sectional area (m<sup>2</sup> molecule<sup>-1</sup>) of MB. The molecular cross sectional area used for MB to estimate the surface area is 1.20 nm<sup>2</sup> [23].

Cation exchange capacity (CEC) of the clays was determined using an ethylenediamine complex of Cu Cu(EDA)<sub>2</sub><sup>2+</sup> method proposed by Bergaya and Vayer [24]. The CEC of the samples examined can be obtained by the difference in Cu content in initial and final solutions as determined by atomic absorption spectrometry (Thermo S1 (UK)) and the CEC calculated from the quantity of Cu(EDA)<sub>2</sub><sup>2+</sup> absorbed (amount initially added to the clay minus amounts remains).

The samples were characterized by X-ray diffraction (XRD) (Phillips 2kW model X-ray spectrophotometer with a nickel filtered copper X-ray radiation (Cu Kα 1.5418 Å)), X-ray fluorescence (XRF) (Phillips PW 1404 X-ray spectrometer wavelength dispersive), and FT-IR spectroscopic analysis (Nexus 870 FTIR spectrophotometer).

### 2.4. Adsorption experiments

Batch adsorption experiments were carried out by allowing an accurately weighted amount (Shimadzu analytical balance model AW 120 measures to the nearest of 0.0001 g) of bentonite or kaolinite or the four organo-modified clays to reach the equilibrium with phenol solution of known concentration. At the end of the desired equilibrium period the contents of the bottles were filtered, centrifuged for 10 min at 5500 rpm using a mLw T5 (Germany) centrifuge and the supernatant was subsequently analyzed for residual concentration of phenol. The concentration of phenol in solutions was typically in the range of 10–100 mg L<sup>-1</sup>. The batch test was conducted by combining 50 mL of phenol solutions with 0.25 g of raw clays or organo-modified samples. The narrow-neck darkly brown coloured bottles were used to prevent photooxidation. The bottles were consequently capped with screw caps fitted with teflon liners and placed on a temperature-controlled GFL 1083 (Germany)



**Table 1**  
Characteristics of bentonite and kaolinite clay.

Analysis	Bentonite	Kaolinite
CEC (meq/100 g)	80	71
Carbon content (%)	0.75	0.23
Surface area (m <sup>2</sup> /g)	123	273
Mineralogy	Quartz (mj), montmorillonite (mi), calcite (mi), Renneite (mi), muscovite (t)	Quartz (mj), kalonite (mi), witherite (mi), muscovite (t)

mj: major, mi: minor, t: trace.

ence of some interlamellar water. After the BC and KC had been treated with HDTMA, a pair of strong bands at 3434 and 3625 cm<sup>-1</sup> for BC and the bands at 3467 and 3654 cm<sup>-1</sup> for KC was observed which can be assigned to the symmetric and asymmetric stretching vibrations of the methylene groups ( $\nu_{\text{CH}_2}$ ) and their bending vibrations are between 1384 and 1470 cm<sup>-1</sup>, which supporting the intercalation of surfactant HDTMA molecules between the silica layers, but these stretching bands are not observed in the raw BC and KC. Due to these observations of the changes in the IR spectra it is thought that the surfaces of BC and KC had been replaced by HDTMA. Figs. 1 and 2 clearly show that the medium strong vibration of the bonded OH of BC and KC appearing at 3432 and 3625 cm<sup>-1</sup> and 3467 and 3621 cm<sup>-1</sup> of BC and KC respectively, has shifted to 3439 and 3630 cm<sup>-1</sup> and 3470 and 3629 cm<sup>-1</sup> in BPM and KPM. Also the appearance of new absorption bands at 693 and 695 cm<sup>-1</sup> for BC and KC respectively, belonging to the mono-substituted benzene group of PTMA. These observations can be interpreted as being the covering of PTMA molecules the surfaces of these two clays.

The chemical composition of BC and KC samples as determined by XRF technique (wt%) are found as follows: BC: SiO<sub>2</sub>, 49.70; Al<sub>2</sub>O<sub>3</sub>, 20.30; Fe<sub>2</sub>O<sub>3</sub>, 14.60; CaO, 8.87; TiO<sub>2</sub>, 1.60; V<sub>2</sub>O<sub>5</sub>, 0.10; SrO, 0.096; ZrO<sub>2</sub>, 0.056; ZnO, 0.095; K<sub>2</sub>O, 0.63; L.O.I., 9.5. KC: SiO<sub>2</sub>, 51.30; Al<sub>2</sub>O<sub>3</sub>, 31.70; Fe<sub>2</sub>O<sub>3</sub>, 4.11; CaO, 0.37; TiO<sub>2</sub>, 5.87; V<sub>2</sub>O<sub>5</sub>, 0.23; ZrO<sub>2</sub>, 0.27; PdO, 5.80; L.O.I., 12.10. It seems from the chemical compositions of the raw samples the predominant exchangeable cation was calcium. The loss on ignition (L.O.I.) figures indicates the loading of mineral by the organic compounds. The ratio of Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> show interesting behaviour. It was 0.41 for BC compared with 0.61 for KC.

The main characteristics of raw BC and KC clays are given in Table 1. The characteristic XRD peaks for the two clays are shown in this table. The clay mineral constituents of the samples are determined, and identified as major (mj), minor (mi) and trace (t) amounts. The raw BC and KC samples contain mainly quartz with the other minerals as minor and trace amounts. The carbon content of both clayey is considered to be predominantly related to organic matter.

The two clayey are organically modified by adsorption of HDTMA and PTMA and resulted in four organo-modified clays labeled as BHM, BPM, KHM and KPM respectively. HDTMA was chosen as a representative long chain modifier and PTMA was chosen as a representative short chain modifier. The main characteristics of these four organo-modified clays are listed in Table 2.

### 3.2. Contact time

The adsorption data for the uptake of phenol versus contact time at constant initial concentration is presented in Fig. 3. As seen from

**Table 2**  
Physical characteristics of organically modified clay adsorbents.

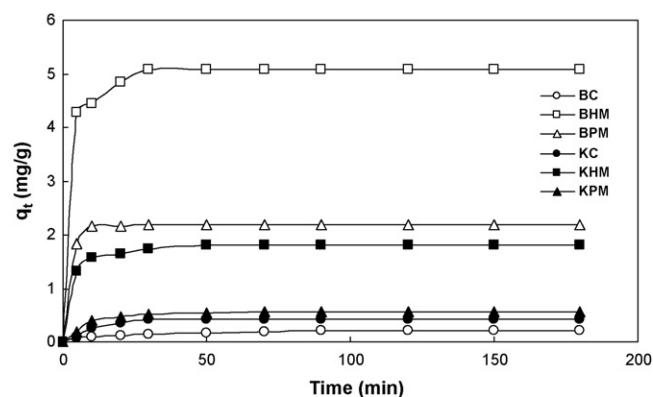
Analysis	BHM	BPM	KHM	KPM
CEC (meq/100 g)	19	27	15	45
Carbon content (%)	9.76	4.73	8.87	2.22
%CEC exchange	76	66	79	37
Modifier loading (meq/100 g)	48	37	42	17
Surface area (m <sup>2</sup> /g)	108	104	246	265

Fig. 3 that equilibrium time required for the adsorption of phenol on BC and KC is almost 2 h. It also seen that the remaining concentration of phenol becomes asymptotic to the time axis after 2 h. HDTMA and PTMA modification covered the BC and KC surfaces and increased molecular interaction between phenol molecules and the BC and KC surfaces. Therefore, adsorption capacities increased from 0.247 mg g<sup>-1</sup> on raw BC clay to 8.435 and 3.481 mg g<sup>-1</sup> for BHM and BPM, respectively, and from 0.468 mg g<sup>-1</sup> on raw KC clay to 2.351 and 0.675 mg g<sup>-1</sup> for KHTM and KPTM respectively. The modification of the clays by HDTMA and PTMA increased adsorption capacities for phenol, reached equilibrium after 30 and 50 min of contact time, respectively. After the equilibrium time, the increasing rate of adsorption of phenol decreased, and the amount of phenol adsorbed remained almost the same.

### 3.3. Effect of pH

The adsorption of phenol by BC and KC and the four modified clays was investigated, phenol solution of 100 mL in volume and 60 mg L<sup>-1</sup> in concentration were used at pH values of 2, 6.5 and 10. In the experiments, clay content was kept constant (0.25 g) and adsorption was carried out until equilibrium. The results obtained are listed in Table 3. The pH was measured before and after adsorption process and it has been found that the difference between the two measurements values of pH is less than 0.3 for all samples.

It is evident that the amount of adsorption strongly depends on solution pH. The adsorption capacity of phenol with all unmodified and modified clays is increased with increase of pH values. Adsorption of clays at higher pH is higher and is may be explained on the assumption that HDTMA and PTMA modification covered the clay surfaces with positive charges and increased electrochemical interaction between phenol molecules and the modified clay surfaces. It is well known the dependency of phenol ionization on the pH value. Obviously, phenol will be dissociated to C<sub>6</sub>H<sub>5</sub>O<sup>-</sup> at pH > pK<sub>a</sub> (phenol is a weak acid, pK<sub>a</sub> = 9.92) and such negatively charged species is easy to be adsorbed on positively charged clay surfaces due to attractive forces prevailing at higher pH values. The high adsorption capacity is due to the strong electrostatic interaction between the N<sup>+</sup>(D or



**Fig. 3.** Comparison of phenol adsorption by raw BC and KC and BHM, BPM, KHM and KPM (temperature, 25 °C; pH, 6.5; C<sub>0</sub>, 60 mg L<sup>-1</sup>).



**Table 3**  
Adsorption capacities at equilibrium ( $q_e$ ) for phenol.

	BC (mg g <sup>-1</sup> )	BHM (mg g <sup>-1</sup> )	BPM (mg g <sup>-1</sup> )	KC (mg g <sup>-1</sup> )	KHM (mg g <sup>-1</sup> )	KPM (mg g <sup>-1</sup> )
Temperature (°C)	C <sub>0</sub> , 60 mg L <sup>-1</sup> ; pH, 6.5					
25	0.247	8.435	3.481	0.468	2.351	0.675
35	0.231	7.712	3.325	0.422	1.987	0.532
45	0.214	7.229	3.169	0.344	1.688	0.377
pH	C <sub>0</sub> , 60 mg L <sup>-1</sup> ; T, 25°C					
2	0.208	6.922	3.234	0.390	2.013	0.506
6.5	0.247	8.435	3.481	0.468	2.351	0.675
10	0.292	10.338	4.740	0.579	2.600	0.818

Ph)(CH<sub>3</sub>)<sub>3</sub> of BHM, KHM, BPM or KPM and phenoxide. On the contrary, at lower pH more protons will be available, thereby increasing electrostatic repulsions, causing decrease in phenol adsorption. Similar behaviour has been reported by Karadag et al. [29] and Denizil et al. [30].

### 3.4. Effect of temperature

Temperature study on adsorption of phenol on clays is carried out at three different temperatures, i.e., 25, 35 and 45 °C. The results obtained are listed in Table 3. The equilibrium adsorption capacities of phenol increased with an increase in temperature from 25 to 45 °C. Increasing adsorption capacity with increasing temperature indicates that the adsorption of phenol is controlled by an endothermic reaction.

### 3.5. Adsorption isotherms

Several models have been published in the literature to describe experimental data adsorption isotherms. The Langmuir [31] and Freundlich [32] are the most frequently employed models. In this work, both models were used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration in solutions at different temperatures and pH values. The adsorption isotherms obtained for phenol on the four modified clays and two unmodified clays are presented in Fig. 4 as a representative example at 25 °C and pH, 6.5.

#### 3.5.1. Langmuir isotherm

This model supposes that the adsorption take place at a specific surface with the single coating layer on this surface. The attraction between molecules decreases as getting further from the adsorption surface [33]. Langmuir isotherm model can be represented by

the following relation:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (4)$$

where  $q_e$  is the amount of phenol adsorbed onto clay at equilibrium (mg g<sup>-1</sup>),  $q_{\max}$  is the theoretical monolayer capacity (mg g<sup>-1</sup>),  $K_L$  is the Langmuir equilibrium constant related to the affinity of binding sites and energy of adsorption and  $C_e$  is the equilibrium solution concentration (mg L<sup>-1</sup>).

The linear form of the Langmuir equation can be written as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad (5)$$

The values of  $q_{\max}$  and  $K_L$  can be evaluated from the intercept and the slope of the linear plot of experimental data of  $C_e/q_e$  versus  $C_e$  (Fig. 5).

One of the essential characteristics of the Langmuir equation could be expressed by dimensionless constant called equilibrium parameter  $R_L$  which is defined as [34]:

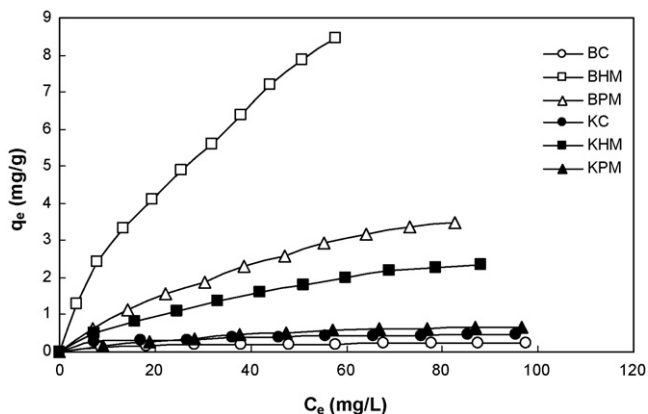
$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

where  $C_0$  is the highest initial concentration (mg L<sup>-1</sup>). The value of  $R_L$  indicates the type of isotherm to be irreversible adsorption ( $R_L = 0$ ), favourable adsorption ( $0 < R_L < 1$ ), unfavourable adsorption ( $R_L > 1$ ) and linear adsorption ( $R_L = 1$ ). As seen from Tables 4 and 5, the adsorption of phenol on modified and unmodified clays is favourable [35].

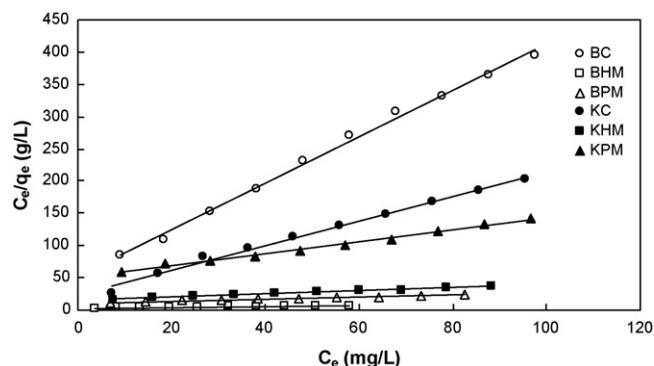
#### 3.5.2. Freundlich isotherm

Freundlich isotherm is used for modelling the adsorption on heterogeneous surfaces. Freundlich isotherm can be defined according to the following formula:

$$q_e = K_F C_e^{1/n} \quad (7)$$



**Fig. 4.** Adsorption isotherms for phenol onto BC, BHM, BPM, KC, KHM and KPM at 25 °C and pH, 6.5.



**Fig. 5.** Langmuir plot for the adsorption of phenol onto BC, BHM, BPM, KC, KHM and KPM at 25 °C.

**Table 4**  
Langmuir and Freundlich isotherm parameters for adsorption of phenol onto BC, BHM and BPM at different temperatures and pH values.

		Langmuir				Freundlich		
		$R^2$	$q_{max}$	$K_L$	$R_L$	$R^2$	$K_F$	$n$
$T, ^\circ C$	BC, pH, 6.5							
	25	0.996	0.278	0.068	0.128	0.922	25.704	2.632
	35	0.999	0.265	0.062	0.139	0.944	20.044	2.757
	45	0.998	0.251	0.055	0.154	0.920	19.928	3.125
pH	BC, $T, 25^\circ C$							
	2	0.992	0.238	0.056	0.152	0.917	9.419	4.762
	6.5	0.996	0.278	0.068	0.128	0.922	25.704	2.632
	10	0.986	0.325	0.074	0.119	0.920	29.419	2.551
$T, ^\circ C$	BHM, pH, 6.5							
	25	0.998	23.888	0.024	0.294	0.946	4.499	1.511
	35	0.997	19.231	0.011	0.476	0.957	3.388	1.925
	45	0.996	14.286	0.009	0.526	0.924	2.720	2.176
pH	BHM, $T, 25^\circ C$							
	2	0.999	10.173	0.004	0.714	0.986	3.457	1.699
	6.5	0.998	23.888	0.024	0.294	0.946	4.499	1.511
	10	0.996	25.573	0.028	0.263	0.936	7.778	1.305
$T, ^\circ C$	BPM, pH, 6.5							
	25	0.996	8.306	0.016	0.385	0.997	11.013	1.234
	35	0.993	7.143	0.011	0.476	0.995	7.871	1.333
	45	0.991	6.258	0.008	0.556	0.994	5.888	1.429
pH	BPM, $T, 25^\circ C$							
	2	0.986	6.452	0.009	0.526	0.994	5.248	1.471
	6.5	0.996	8.306	0.016	0.385	0.997	11.013	1.234
	10	0.997	10.137	0.007	0.588	0.999	17.762	1.190

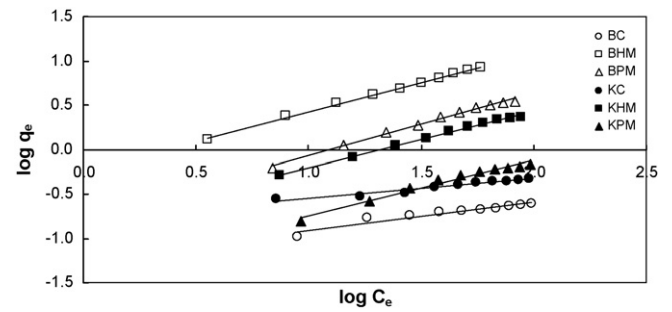
where  $K_F$  is the Freundlich constant ( $Lg^{-1}$ ) and  $1/n$  is the adsorption intensity.

The logarithmic linear form of the Freundlich equation is given as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

**Table 5**  
Langmuir and Freundlich isotherm parameters for adsorption of phenol onto KC, KHM and KPM at different temperatures and pH values.

		Langmuir				Freundlich		
		$R^2$	$q_{max}$	$K_L$	$R_L$	$R^2$	$K_F$	$n$
$T, ^\circ C$	KC, pH, 6.5							
	25	0.995	0.520	0.083	0.108	0.943	5.370	5.376
	35	0.998	0.484	0.068	0.128	0.965	4.385	6.578
	45	0.998	0.417	0.048	0.172	0.974	4.266	7.246
pH	KC, $T, 25^\circ C$							
	2	0.997	0.416	0.144	0.065	0.931	3.507	6.667
	6.5	0.995	0.520	0.083	0.108	0.943	5.370	5.376
	10	0.996	0.613	0.134	0.069	0.964	6.385	4.535
$T, ^\circ C$	KHM, pH, 6.5							
	25	0.997	3.846	0.021	0.323	0.987	15.642	1.357
	35	0.992	3.571	0.015	0.400	0.981	10.162	1.459
	45	0.992	3.279	0.011	0.069	0.984	6.803	1.582
pH	KHM, $T, 25^\circ C$							
	2	0.994	3.436	0.035	0.222	0.969	10.803	2.083
	6.5	0.997	3.846	0.021	0.323	0.987	15.642	1.357
	10	0.998	3.972	0.015	0.400	0.979	17.906	1.235
$T, ^\circ C$	KPM, pH, 6.5							
	25	0.990	1.111	0.019	0.345	0.973	19.124	1.473
	35	0.998	0.909	0.015	0.400	0.977	18.261	1.449
	45	0.997	0.714	0.013	0.436	0.939	13.823	1.401
pH	KPM, $T, 25^\circ C$							
	2	0.998	1.023	0.010	0.500	0.969	15.884	1.835
	6.5	0.990	1.111	0.019	0.345	0.973	19.124	1.473
	10	0.997	1.144	0.026	0.278	0.988	21.804	1.320



**Fig. 6.** Freundlich plot for the adsorption of phenol onto BC, BHM, BPM, KC, KHM and KPM at  $25^\circ C$ .

Fig. 6 shows the dependence of  $\log q_e$  on  $\log C_e$  ( $K_F$  and  $1/n$  were calculated from the intercept and slope of the plot of  $\log q_e$  versus  $\log C_e$ ).

Two regression curves were fitted to each data set, based on the two linear equations of Langmuir and Freundlich. The adsorption equations, estimated from the results of the batch equilibrium adsorption tests for phenol to unmodified and modified clays.

The Langmuir and Freundlich isotherm constants at different temperatures and PH values for the adsorption of phenol on BC, BHM, BPM and KC, KHM and KPM are presented in Tables 4 and 5 respectively. Jaynes and Boyd [36] proposed that the adsorption conforms to the Langmuir and Freundlich models when the value of correlation coefficient ( $R^2$ ) is greater than 0.89. The  $R^2$  values shown in Tables 4 and 5 are greater than 0.89, indicating that both the Langmuir and Freundlich isotherm models can adequately describe the adsorption data. The applicability of the two isotherm models to the all investigated systems implies that both monolayer adsorption (i.e., only a limited number of surface sites are adsorbing sites for the phenol molecule) and heterogeneous surface conditions exist under the experimental conditions studied. The adsorption of phenol on these surfaces is thus complex, involving more than one mechanism. Similar observations have been reported by Rawajfih and Nsour [18] and Barhoumi et al. [19] for the adsorption of phenol by unmodified and organo-modified bentonite and kaolinite clays.  $K_F$  and  $q_{max}$  are related to adsorption capacity, and they can be used to distinguish adsorption performance [37]. Comparing the  $K_F$  and  $q_{max}$  values indicates that increasing temperature increased the adsorption capacities of phenol. On the other hand,  $q_{max}$  values indicate that the optimum pH for phenol is 10.

One of the Freundlich constants  $K_F$  indicates the adsorption capacity of the adsorbent. The other Freundlich constants  $n$  is a measure of the deviation from linearity of the adsorption. If a value for  $n$  is equal to unity, this implies that adsorption process is chemical, but a value for  $n$  is above to unity, adsorption is favourable a physical process (Tables 4 and 5) [12].

It is obvious observation of the adsorption isotherms, and the adsorption coefficients, that the organically modified clays are much more efficient adsorbents of phenol than the unmodified bentonite and kaolinite. Clays that are organically modified with short chain organic cations ( $C_{<10}$ ) are often referred to as “adsorbent complexes”; while clays modified with long chain modifiers are called “partitioning complexes”. The mechanism in both unmodified clays and in their adsorbent complexes is considered to be of the surface adsorption type; hence has a limited capacity due to the finite surface area available. On the other hand the mechanism for “partitioning complexes” is considered to be organic partitioning; hence has no such limitation. This explains the higher values of  $q_{max}$  of the surfactant-modified clays in comparison to the unmodified clays [18].

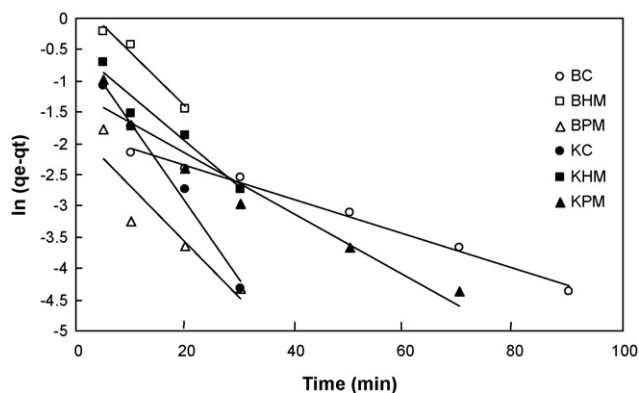


Fig. 7. Pseudo-first-order kinetics of phenol adsorption (temperature, 25 °C; pH, 6.5;  $C_0$ , 60 mg L<sup>-1</sup>).

### 3.6. Kinetics of adsorption

Two kinetic models; Lagergreen (pseudo-first-order) and pseudo-second-order reaction were used to test experimental data to predict to the adsorption kinetic.

#### 3.6.1. Pseudo-first-order reaction kinetic

The adsorption rate constant proposed by Lagergreen [38] using first order reaction kinetic is shown below:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (9)$$

where  $k_1$  is the adsorption rate constant (min<sup>-1</sup>) for the first order adsorption,  $q_t$  is the amount of phenol adsorbed at time  $t$  (mg g<sup>-1</sup>) and  $q_e$  is the amount of phenol adsorbed at equilibrium (mg g<sup>-1</sup>).

If it is supposed that  $q = 0$  at  $t = 0$ , then

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (10)$$

#### 3.6.2. Pseudo-second-order reaction kinetic

Adsorption data was also evaluated according the pseudo-second-order reaction kinetic proposed by Ho and McKay [39]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (11)$$

where  $k_2$  is the second order reaction constant (g mg<sup>-1</sup> min<sup>-1</sup>). If the differential equation is integrated with boundary conditions ( $t = 0 \rightarrow t$  and  $q_t = 0 \rightarrow q_e$ ) the following expression is obtained

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (12)$$

The rate constants  $k_1$ ,  $k_2$  and  $q_e$  were calculated from the slopes and intercepts of the linear plot of  $\ln(q_e - q_t)$  or  $t/q_t$  against  $t$  respectively (Figs. 7a and 8). The values of  $q_{e, \text{calculated}}$ ,  $k_1$  and  $k_2$  are listed in Table 6. As the difference between  $q_{e, \text{calculated}}$  and  $q_{e, \text{experimental}}$  values is considered, it is seen that phenol removal with all clays is well described by the second order reaction kinetic. Moreover, all

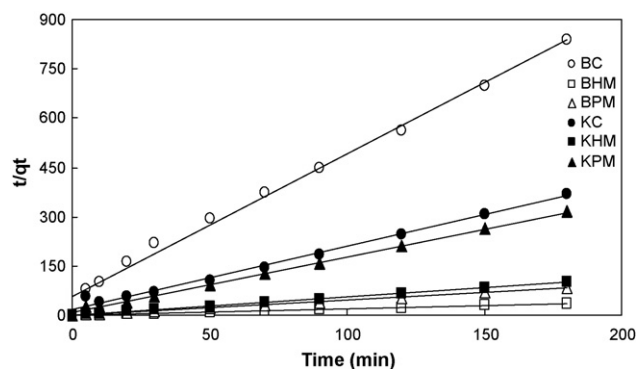


Fig. 8. Pseudo-second-order kinetics of phenol adsorption (temperature, 25 °C; pH, 6.5;  $C_0$ , 60 mg L<sup>-1</sup>).

the correlation coefficients  $R^2$ , of second order reaction kinetic are higher than that of the first order reaction kinetic.

### 3.7. Thermodynamic parameters

The amount of adsorption of phenol by raw and modified BC and KC were measured in temperature 298.15–318.15 K. The equilibrium constant  $K$  for the adsorption process at each temperature was calculated from the Langmuir equation [40]:

$$\frac{C_e}{q_e} = \frac{K}{q_{\text{max}}} + \frac{C_e}{q_{\text{max}}} \quad (13)$$

where  $K$  is the equilibrium constant related to Langmuir constant  $K_L$ , and is defined by the following equation [41]:

$$K = \frac{q_e}{C_e} \quad (14)$$

The following relationships have been used to evaluate the thermodynamic parameters enthalpy,  $\Delta H$ , Gibbs free energy,  $\Delta G$  and entropy,  $\Delta S$  [42]:

$$\Delta G = -RT \ln K \quad (15)$$

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (16)$$

A plot of  $\ln K$  versus  $1/T$  (Fig. 9) should be linear with a slope equal  $\Delta H/R$  and with intercept equal  $\Delta S/R$ . The changes in Gibbs free energy were calculated at each temperature from Eq. (15).

The calculated values of adsorption enthalpies, free energies and entropies of phenol on modified and unmodified clays are presented in Table 7.

Generally, the change of free energy for physisorption is between  $-20$  and  $0$  kJ mol<sup>-1</sup>, but chemisorption is a range of  $-80$  to  $-400$  kJ mol<sup>-1</sup> [43]. The over all free energy change during the adsorption process was negative for the experimental range of temperature (see Table 6), corresponding to a spontaneous physical process of phenol adsorption and that the system does not gain energy from an external source. The negative value of  $\Delta G$  also indicate the feasibility of the process and also suggest the adsorption

Table 6

Pseudo-first-order and pseudo-second-order adsorption rate constants and calculated  $q_{e, \text{calculated}}$  values of phenol onto clays at 25 °C and pH 6.5.

Clay	$q_{e, \text{experimental}}$ (mg g <sup>-1</sup> )	Pseudo-first-order			Pseudo-second-order		
		$k_1$ (min <sup>-1</sup> )	$q_{e, \text{calculated}}$ (mg g <sup>-1</sup> )	$R^2$	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$q_{e, \text{calculated}}$ (mg g <sup>-1</sup> )	$R^2$
BC	0.247	0.027	0.164	0.991	0.328	0.230	0.998
BHM	8.435	0.086	1.364	0.975	0.128	7.968	0.997
BPM	3.481	0.113	0.294	0.878	0.675	3.203	1.000
KC	0.468	0.126	0.658	0.988	0.369	0.449	0.998
KHM	2.351	0.073	0.604	0.955	0.487	1.821	0.999
KPM	0.675	0.049	0.306	0.948	0.391	0.589	0.998

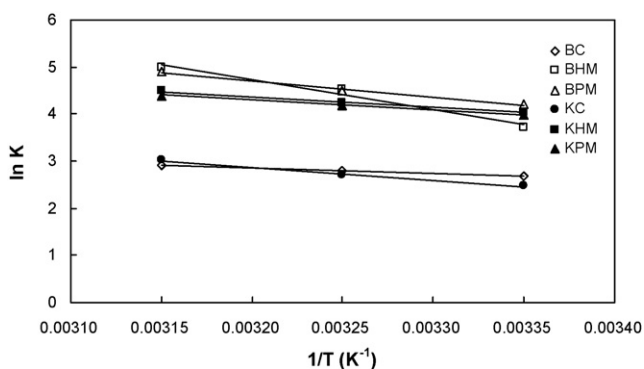


Fig. 9. Plot of  $\ln K_c$  vs.  $1/T$  for estimation of thermodynamic parameters for the adsorption of phenol onto BC, BHM, BPM, KC, KHM and KPM.

Table 7

Thermodynamic parameters calculated for the adsorption of phenol onto clays.

Clay	$\Delta G$ (kJ/mol)			$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J K <sup>-1</sup> mol <sup>-1</sup> )
	298.15 K	308.15 K	318.15 K		
BC	6.664	7.124	7.672	8.351	50.316
BHM	9.245	11.554	12.460	38.909	162.248
BPM	10.250	11.554	12.771	27.346	126.148
KC	6.170	6.887	8.032	21.523	92.659
KHM	9.576	10.759	11.929	25.499	117.651
KPM	9.824	10.759	11.487	14.998	83.364

of phenol on all clays is spontaneous. Such negative value in all temperatures under study suggests that the adsorption is more spontaneous also results in increase in retention time of phenol by adsorbents. When the temperature decreases from 45 to 25 °C, the magnitude of free energy change shifts to high negative value suggested that the adsorption was more spontaneous at low temperature [44].

The mean adsorption enthalpy,  $\Delta H$  values for these study systems are positive, indicated the uptake of phenol on all adsorbents to be a physical sorption and is also endothermic. The endothermic enthalpy gives clear indication of strong interaction between adsorbates and adsorbents. This can be explained by the fact that each molecule of sorbate has to displace more than one molecules of solvent. The net result corresponds to an endothermic process.

The positive values of  $\Delta S$  show the increased randomness of the solid-solution interface during the sorption of phenol on clays. These positive values of entropy may be due to some structural changes in both adsorbates and adsorbents during the adsorption process.

#### 4. Conclusions

In this work, surface modification of bentonite and kaolinite with HDTMA and PTMA was studied. An assessment of the adsorption of phenol by four modified clays indicates that the modification employed resulted in an increase in adsorption capacity from the raw clays of approximately thirty and twelve order of magnitude for BHM and BPM and an increase of approximately four and one order of magnitude for KHM and KPM. It is also determined that the adsorption is completed in relatively short time period. Optimum contact time are 30 min for removal of phenol by BHM and BPM and 50 min by KHM and KPM.

An increase in adsorption temperature resulted in an increase in amount of phenol adsorbed, which showed that the adsorption of phenol is controlled by an endothermic reaction. The equilibrium adsorption capacity of phenol onto raw and modified clays showed a maximum at pH 10.

The empirical values are evaluated according to the Langmuir and Freundlich that are generally used to describe the adsorption processes. Both isotherm models fit the experimental data very well. The  $q_{max}$  values are increased with an increase of temperature from 25 to 45 °C, while increased with increase of pH from 2 to 10.

Phenol adsorption onto all clays is well described with the pseudo-second-order reaction kinetics. In the second-order-reaction kinetic,  $q_{e,calculated}$  and  $q_{e,experimental}$  values are quite close to each other. Negative values of the change in free energy  $\Delta G$ , indicate that adsorption of phenol by all clays is spontaneous. Changes in enthalpy  $\Delta H$  indicate positive values, and therefore, the adsorption mechanism is found to be endothermic. The positive values of  $\Delta S$  for phenol suggest that randomness increases during adsorption.

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