

A Comparison Study on the Removal of Phenol From Aqueous Solution Using Organomodified Bentonite and Commercial Activated Carbon

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The potential of bentonite modified with cationic surfactant (CTAB-Bent) and commercial Activated Carbon (AC) for the removal of phenol removal was assessed. Batch kinetics and isotherm studies were carried out to evaluate the effects of contact time (t), phenol initial concentration (C_0), adsorbent dose (C_{ads}), and pH of the solutions. Kinetics and isotherm of the adsorption were also determined using the most frequent models. The results of the study showed that increasing C_0 could result in the increase of adsorption capacity of both types of adsorbents. The optimum pHs for CTAB-Bent and AC were determined as 10 and 8, respectively. The equilibrium data of the phenol adsorption from the aqueous solutions was well fitted by the Langmuir isotherm models. The kinetics study revealed that pseudo-second-order kinetics gives better description of adsorption process. The adsorption capacities, as deduced from the adsorption isotherm were 22.68 and 112.36 mg/g for CTAB-Bent and activated carbon, respectively. However, considering the market price of these adsorbents, low-cost modified bentonite can be a promising adsorption technology and an alternative adsorbent to commercial activated carbon in the future.

Keywords: Phenol; Surface-Active Agents; Adsorption; Bentonite

1. Introduction

Phenol has specific characteristics which makes it useful in many industries such as production of different resins, including phenolic resins, epoxy resins, and adhesives as well as polyamides with various applications. Thus, wastewaters containing phenol were discharged from many such industries like petroleum and petrochemical plants, coal conversion, plastics, pulp, paper, and phenol producing industries (1, 2). Despite its widespread use in industries, phenol and phenolic compounds were classified as priority pollutants by health agencies such as U.S. environmental protection agency (EPA), because these compounds have potential health threats for both human and other organisms at such a low concentration of 1 mg/L. Furthermore, in high concentrations it considered as a known or suspected carcinogen.

Therefore, to protect environment from various harmful effects of these compounds, these wastewaters should be treated with appropriate methods before discharging to the environment or water bodies. Different methods were evaluated to remove phenol from waste streams, among them, advanced oxidation processes (AOPs) (3, 4), aerobic and anaerobic biological processes (5, 6), and adsorption by different adsorbents were frequently used (7). Adsorption by activated carbon is the best and most frequently used method because activated carbon has large surface

area, microporous nature, high adsorption capacity, high purity, and easy availability (8). However, the costs of starting material for preparation of activated carbon is considered a limiting factor (8). Therefore, the technical feasibility of using cheaper adsorbents such as clay; organomodified Tirebolu bentonite (9); and carbon prepared from biomass materials (8), sugarcane bagasse (10) or *Tectona grandis* saw dust (11) have been examined recently. It was shown that organic modification of clay minerals significantly increases the ability of bentonite to remove nonpolar and anion water contaminants through surface modification of the adsorbent (12). Removal of tannin from aqueous solutions by cationic surfactant-modified bentonite clay was assessed by Anirudhan and Ramachandran (13), which showed that the modified bentonite has a capacity of about 70 $\mu\text{mol/g}$ in tannin removal. Thus, the main objectives of this study were to compare the efficiency of modified bentonite (with Cetyl Trimethyl Ammonium Bromide [CTAB]) with commercial Activated Carbon (AC) with respect to the removal of phenol and to study the effects of contact time (t), phenol initial concentration (C_0), adsorbent dose (C_{ads}), and pH on the adsorption processes. Batch kinetics and isotherm studies were also conducted to evaluate the adsorption capacity of activated carbon (AC) and CTAB-Bent in order to explore the mechanisms of adsorption process.

2. Materials and Methods

2.1. Adsorbate, Adsorbents, and Working Solutions

Analytical-reagent grade phenol (hydroxybenzene or carboic acid, CAS No.:108-95-2) (purchased from Sigma-Aldrich) was used as the adsorbate. CTAB ($C_{19}H_{42}BrN$, CAS No: 57-09-0) was used as the cationic surfactant for modifying bentonite (purchased from Merck Co.). These chemicals were used without further purification. Commercial activated carbon (AC, untreated, granular, CAS No.: 7440-44-0) (supplied by Sigma-Aldrich) along with bentonite from a quarry located in Zanjan, west of Iran (as a gift) were used as adsorbents. Natural bentonite was modified using CTAB according to the methods, which was well-described in other studies (14, 15). A stock solution of desired concentration was prepared by dissolving the required amount of phenol in double-distilled water. Working solutions of the desired concentrations in different phases of the study were obtained by successive dilutions.

2.2. Adsorption Experiments

In adsorption equilibrium, experiments were conducted in a set of 250 mL Erlenmeyer flasks, containing 100 mL of solution, with different initial concentrations of 100 to 1000 mg/L using CTAB-Bent and AC. Four gram of AC and 20 g of CTAB-Bent were added to phenol solutions and each sample was left 6 to 48 h to reach equilibrium. Temperature and pH of the solutions were not controlled. The initial and final concentrations of phenol in the solutions were determined using UV- VIS spectrometer (DR-5000, Hatch). This method was based on the color developed as a result of the reaction of phenol with 4-aminoantipyrine as detailed in the Standard Methods (16). In order to minimize the interference of the adsorbents with the analysis, the samples were centrifuged at 15000 rpm for at least 15 min. After that, the supernatant was filtered through a 0.45- μ m filter paper. All experiments were duplicated under identical conditions. The amount of adsorption at equilibrium, q_e (mg/g), was calculated using Equation 1:

(1)

$$q_e = \frac{(C_0 - C_e)V}{M}$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of phenol, respectively. V (L) is the volume of the solution and M (g) is the mass of the adsorbents.

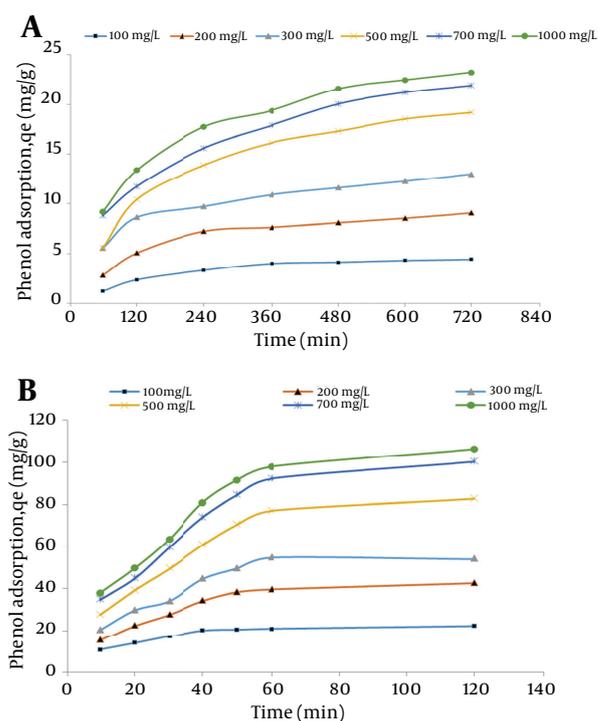
Adsorption equilibrium isotherms were determined using adsorbent dosages of respectively 4 and 20 g for AC and CTAB-Bent per 100 mL of aqueous solutions containing the initial concentrations of phenol in the range of 100 - 1000 mg/L, at an optimum pH. The initial pH of the solutions was adjusted by addition of 0.1 N H_2SO_4 or 0.1 N NaOH. All of the experiments were conducted at room temperature ($\approx 25^\circ C$) and the flasks were shaken with constant speed of about 150 rpm (found in the literature) (11) for a minimum contact time required to attain the equilibrium.

3. Results and Discussion

3.1. Effect of Contact Time and Initial Phenol Concentration

The effect of contact time for adsorption process was carried out to determine the equilibrium point for a period of 0 - 120 minutes for AC and 0 - 720 minutes for CTAB-Bent with different initial phenol concentrations (Figure 1). The other parameters of the study were kept constant. It was found for all sets of experiments that the adsorption was rapid in the initial stages of the process because of higher driving forces resulted from the largest amount of phenol (13) and later on became slow, and finally the systems reached equilibrium after around 60 and 360 minutes for AC and CTAB-Bent, respectively. However, to ensure equilibrium the samples of AC and CTAB-Bent were left for 6 and 48 hours, respectively. The adsorbed amount (mg/g) increased with longer contact time until it reached equilibrium and the curves of phenol adsorption with respect to time got smooth and continuous indicative of saturation. As shown in Figure 1, the required time to reach equilibrium was selected as the contact time for further experiments of CTAB-Bent and AC.

Figure 1. Effect of Initial Phenol Concentration on the Sorption Kinetics of Phenol by (A) CTAB-Bent and (B) AC



CTAB-Bent: dose = 20 g/L, shaking time = 360 min, and AC: dose = 4 g/L, shaking time = 60 min.

Based on the figure, the necessary time to reach equilibrium was variable and depended on the initial concentration of the phenol, which was increased with the increases of initial concentration and was about 240 min and 480 min for C_0 of 100 and 300 mg/L for CTAB-Bent, respectively. It should be noted that the more the initial phenol concentration the more would be the adsorption capacity of adsorbents, but the adsorption efficiency of adsorbent was inversely related to the initial phenol concentration and the removal efficiencies decreased as the concentration increased at a fixed adsorbent dosage (11, 17). The results showed that an increase in initial phenol concentration would lead to a decrease in the rate of constants values, which are in agreement with the study of Benguella and Benaissa (18).

3.2. Effect of pH

Hydrogen ion concentration of the solution plays an important role in the adsorption processes (11, 18, 19). The effect of pH on the adsorption capacity of phenol was shown in Figure 2. At higher pH, adsorption of bentonite was greater which might be explained on the assumption that the surfactant modification covered the adsorbent surfaces with positive charges and increased electrochemical interaction between phenol molecules and the modified bentonite surfaces (11, 19). The ionization degree of phenol depends on the pH values of the solution. If pH of the solution was more than the pK_a of phenol (≈ 9.92), phenol would dissociate to negatively charged species such as $C_6H_5O^-$, which could be easily adsorbed on positively charged CTAB-Bent surfaces and favored in higher pH values. But when the pH was lower than pK_a , more electrostatic repulsions would decrease phenol adsorption due to the more availability of protons (20). As clearly seen in Figure 2, when the pH is lower than 8, AC has more removal efficiency as its particles have active sites with negative charges at relatively acidic pH and phenol was undissociated. Hence, the dispersion interaction predominated. Furthermore, the higher concentration of H^+ ions within low solution pH can neutralize those negative sites, reduces the hindrance to diffusions of phenol ions from the aqueous solution and consequently increases the chances of their adsorption. However, at the high solution pH, OH^- concentration ions dominates, which can in turn increase the hindrance to the diffusions of phenol ions and thus reduce the chances of their adsorption (21-23). Therefore, based on the experimental results, pH values of 10 and 8 were selected as the optimum values for further experiments on CTAB-Bent and AC, respectively. Similar trend was also observed in the study conducted by Alkaram et al. (24) for phenol removal from aqueous solutions using surfactant-modified bentonite and kaolinite.

3.3. Effects of Adsorbent Dosages

As observed in Figure 3 A and 3B, the efficiency of phenol removal was increased with the increase of adsorbent dose up to an optimum dosage and remained almost

unchanged with the further increase of adsorbent dosages. For instance, for a given reaction time of 360 minutes, when CTAB-Bent concentration increased from 5 to 20 g/L, the phenol adsorption increased from 45.33% to 66.36%. As it was expected, a further increase of adsorbent concentration to 40 g/L, however, increased efficiency only about 3.26%. Similar trend was also observed for activated carbon adsorption process (Figure 3 B). In fact, as the sorbent particles surrounding the phenol increases, at a fixed phenol concentration, they provide greater availability of the exchangeable sites or surface area, so more phenol molecules have the chance to attach to these particles (25). Beyond the optimum point, the removal efficiency decreased due to the partial aggregation or overlapping of adsorbent surfaces (26).

3.4. Adsorption Isotherms

The equilibrium isotherms were determined through contacting a constant amount of each adsorbent with different initial concentrations of 100 to 1000 mg/L. The adsorbents and phenol solutions were agitated in a series of 250 mL Erlenmeyer flasks for a period of 24 h at room temperature. After this period, the final concentration of unbound phenol was calculated using Equation 1. The most frequently employed models i.e., Langmuir and Freundlich ones were used to assay experimental data adsorption isotherms (27). In the Langmuir isotherm, it was assumed that the monolayer adsorption of adsorbate onto a homogeneous adsorbent surface takes place with the single coating layer on this surface. According to this model, as the distance from adsorption surfaces increases, the attraction between molecules decreases (28). Langmuir isotherm model can be determined by Equation 2:

$$(2) \quad \frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L}$$

where C_e (mg/L) is the equilibrium concentration of phenol, q_{max} (mg/g) is the maximum adsorbed phenol, q_e (mg/g) is the amount of phenol adsorbed per unit weight of modified bentonite at equilibrium time and K_L (L/mg) is the Langmuir constant related to the affinity of binding sites computed from the plot of C_e/q_e against C_e , which gives a straight line with a slope of $1/q_{max}$ and an intercept of $1/(q_{max}K_L)$. Based on this graph, the maximum capacity of phenol removal by CTAB-Bent and activated carbon were calculated as 22.88 and 112.36 mg/g, respectively (Table 1). Furthermore, according to Table 2, adsorption capacity obtained in this study was relatively high in comparison with similar studies.

The Freundlich isotherm is an empirical equation based on the assumption of multilayer formation of adsorbate and that adsorption takes place on heterogeneous surface (28). The linear form of Freundlich isotherm model

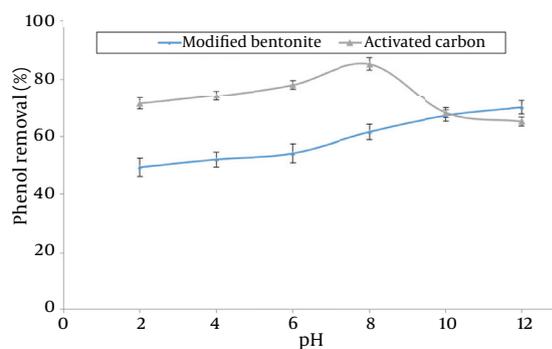
was presented in Equation 3:

$$(3) \quad \log q_e = \log k_f + \frac{1}{n} \log C_e$$

Where K_f and n are Freundlich constants showing the adsorption capacity (mg/g) and intensity, respectively, calculated from the plot of $\log q_e$ versus $\log C_e$.

The adsorption isotherms obtained for phenol on the AC and CTAB-Bent are shown in Figure 4 and the isotherm parameters are presented in Table 1.

Figure 2. The Influence of pH of the Solution on the Phenol Adsorption by Different Adsorbents



CTAB-Bent: dose = 20 g/L, shaking time = 360 min, $C_0 = 500$ mg/L and AC: dose = 4 g/L, shaking time = 60 min, $C_0 = 500$ mg/L.

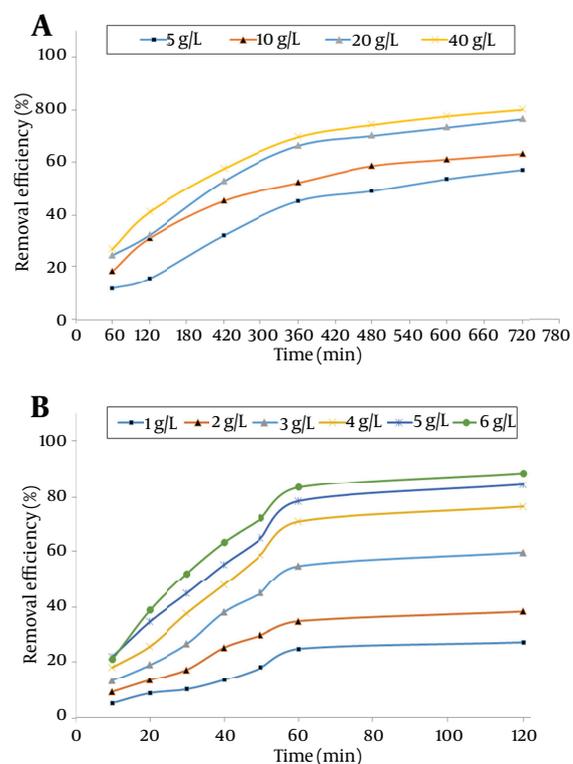


Figure 3. The Influence of Adsorbent Dosage on the Phenol Adsorption by (A) CTAB-Bent ($C_0 = 500$ mg/L, pH = 10, Shaking Time = 360 min), and (B) AC ($C_0 = 500$ mg/L, pH = 8, Shaking Time = 60 min)

Table 1. Langmuir and Freundlich Isotherm Parameters for Adsorption of Phenol Onto AC and CTAB-Bent

Adsorbent	Langmuir Isotherm			Freundlich Isotherm		
	$q_m, \text{mg/g}$	$K_L, \text{L/mg}$	R^2	n	K_f	R^2
CTAB-Bent	22.88	0.011	0.9956	31.84	3.40	0.958
AC	112.36	0.0128	0.996	1.28	3.03	0.981

Table 2. Comparison of Different Pollutants Removal by Bentonite and Phenol Removal by Various Adsorbents

Pollutant	Adsorbent	Isotherm Parameters for Adsorption		Reference
		$q_{max}, \text{mg/g}$	$K_L, \text{L/mg}$	
Phosphate	Bent (HO-CaBen)	29.1	0.15×10^{-2}	(29)
Nitrate	Bent (Surfactant)	13.79	-	(30)
Aniline	Granular activated carbon	52.26	2.90×10^{-3}	(31)
Phenol	Bent (Surfactant)	8.35	3.3×10^{-1}	(19)
Phenol	Bent (Surfactant)	22.88	1.1×10^{-2}	This study
Phenol	Granular activated carbon	112.36	1.3×10^{-2}	This study

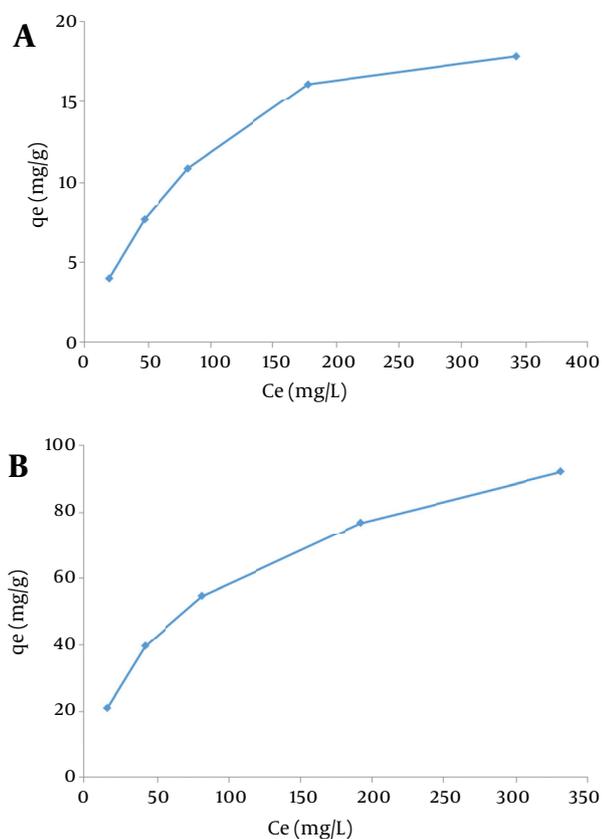


Figure 4. The Amounts of Phenol (mg) Adsorbed on Adsorbent (g) at Equilibrium: (A) CTAB-Bent and (B): AC

3.5. Adsorption Kinetics

Kinetics of phenol adsorption with CTAB-Bent was modeled by two common models of pseudo-first-order and pseudo-second-order rate equation (28), as Equations 4 and 5 respectively:

$$(4) \quad \ln(q_e - q_t) = \ln q_e - k_1 t$$

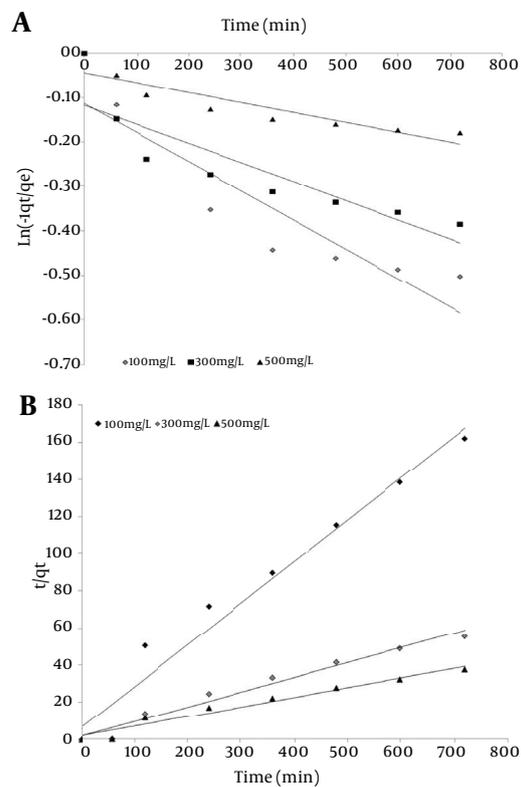
Where q_e and q_t (mg/g) are the amounts of phenol adsorbed at equilibrium and at any time (minute), respectively. The constant k_1 (minute⁻¹) is the adsorption rate constant of pseudo-first-order model, which was determined from the plot of $\ln(q_e - q_t)$ against t .

$$(5) \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where q_e and q_t are defined above, and the constant k_2 (g/mg · minute) is the adsorption rate constant of pseudo-second-order model.

As shown in the Figure 5, straight lines were obtained indicating that phenol adsorption and CTAB-Bent data were best fitted to the pseudo-second-order rate equation.

Figure 5. Linearization of Phenol Sorption Kinetics by CTAB-Bent



(A) Pseudo-first-order rate and (B) pseudo-second-order rate kinetics plots.

4. Conclusions

Results showed that phenol adsorption efficiency is strongly affected by parameters such as initial phenol concentration, pH of the solution, and adsorbent dosages. The efficiency rises with the increase in the adsorbents dosages but adsorption capacity has inverse correlation with the increase in adsorbents dosages. The linearity of the plots t/q_t versus t , confirmed that the process followed a pseudo-second-order rate kinetics. Regarding the experimental results of the Langmuir and Freundlich models, the former model gives a better correlation coefficient with corresponding capacities of about 22.68 and 112.36 mg/g for CTAB-Bent and AC, respectively.

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Authors' Contributions

Mostafa Leili, as a coordinator of the study, managed adsorption studies of phenol and writing of the manu-

script. Javad Faradmal contributed in experiment design and analyzing of data. Farzaneh Kosravian and Mahdieh Heydari involved in laboratory removal experiments. All authors read and approved the final manuscript.

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