Original Article

Adsorption Isotherm and Kinetics Study: Removal of Phenol Using Adsorption onto Modified Pistacia mutica shells

Ramin Sarvani[1] Elhamh Damani[2] **Shahin Ahmadi[3]***

1. Assistance professor in Biotechnology, Cellular and Molecular Research Center and Department of Clinical Biochemistry, School of Medicine, Zahedan University of Medical Sciences, Zahedan, Iran
2. MSC in public Health, Department of Environmental Health, School of Public Health, Zahedan University of Medical Sciences, Zahedan, Iran
3. Instructor Department of Environmental Health, School of Public Health, Zabol University of Medical Sciences, Zabol, Iran

***Correspondence to**: Shahin Ahmadi
sh.ahmadi398@gmail.com

Abstract

Background and purpose: Phenol is an aromatic hydrocarbon and one of the banzan derivatives which has a higher dissolution rate in water. Therefore, it must be removed for water pollution prevention. The aim of this study was to investigate the possibility of Pistaciamuticabio mass as an alternative adsorbent for phenol removal from aqueous solution.

Materials and Methods: The effect of various parameters including contact time (10-102 min), pH(2-8), adsorbent dosage (0.4-1.5g/L), phenol concentration (50-150mg/L) were investigated in this experimental-lab study. Also, the isotherm and kinetic investigations were performed for phenol adsorption process. The adsorption equilibriums were analyzed by Langmuir, Temkin, Freundlich and Harkins Jura isotherm models.

Results: It was found that the data fitted to Langmuir (R^2=0.98) better than other isotherm models. Batch kinetic experiments showed that the adsorption followed Pseudo second-order kinetic model with correlation coefficients greater than 0.998.

Conclusion: It was revealed that P. mutica was not only an inexpensive absorbent, but also a quite effective factor in removal of phenol from water and wastewater.

Keywords: Adsorption; Aqueous solution; Pistacia mutica; phenol

1. Introduction

Phenol and its derivatives are used as intermediates for the manufacturing of various synthetic compounds, such as dye stuffs, rubbers, pesticides, plastics, and paints (1-2). Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations (3, 4) due to their toxicity and carcinogenicity properties. The US Environmental Protection Agency (EPA) regulations call for lowering phenol content in the wastewater to less than 1 mg/L (5). Thus, it is fully recommended to remove the phenol from industrial effluents before entering the water stream (6).Several treatments methods for the removal of phenol from contaminated waters, including oxidation, biodegradation, chemical coagulation, solvent extraction, incineration, reverse osmosis, and adsorption and other processes, among which adsorption is one of the most effective techniques in either laboratory or industrial scale (7, 8, 9). Recently, physicochemical methods have been used for removal organic material in wastewaters. Consequently, amongst numerous techniques, adsorption techniques seem to have the most potential for future use in industrial wastewater treatment because of their proven efficiency in the removal of organic and mineral pollutants and for economic considerations (10). The previous studies have indicated that the adsorption onto activated carbon was a reliable, inexpensive and significantly effective technique to remove the phenol; however, the high cost of activated carbon limits the use of activated carbon (11). Many low-cost adsorbents have been investigated on phenol removal, such as lemnaminor (12), coconut shell, rice husk, corncobs, bamboo, saw dust, activated carbon, (13, 14), coal fly ash, and clays (15), which are normally used. This pistacia mutica is the most economically important tree in many parts of Iran including the Zagros Mountains, where it is managed as a valuable forest tree (15, 16). Pistacia mutica is the most economically important species for rural people in areas of natural forest (16). The fruit of p. mutica is also an important source of food, although the fruits are smaller and not as commercially valuable as those produced in orchards (primarily from cultivars of Pistacia Vera L). Old trees may have trunks measuring 2 m (6 ft 7 in) in diameter; it may take 200 years for a tree to reach 1 m wide (17,18). The main purpose of this study was to investigate the P.mutica shells efficiency in the removal of phenol from aqueous solution. The impact of various factors such as the contact time, adsorbent dosage, pH and initial concentration of phenol were studied to determine the optimal conditions. Finally, the adsorption isotherm and kinetic models have been studied.

2. Materials and methods:
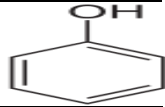
2.1. Preparation of adsorbent

Pistacia mutica was collected from Zahedan city, Iran. It was washed thoroughly with distilled water, dried at 105ºC for 24 hours. Each 10 gr of P.mutica was activated by using 20 ml of sulphuric acid for 24 h. Then, it was rinsed 3 times by distilled water. Next, it was dried in 110ºC for 1 h. After that the P.mutica was grinded and sieved by using a 100 mesh sieve (19).

2.2. The characteristics of phenol

The used phenol was the analytical grade which was purchased from Sigma Aldrich Co, Germany. The stock solution (1000mg/L) was a prepared and desired concentration of phenol solution which was prepared by dilution of stock solution. The general characteristics and chemical structures of phenol are presented in Table1.

Table1. Characteristics of phenol (9)

Name	Molecular weight	λ_{max}(nm)	Molecular formula	Structure
phenol	94.11g/mol	500nm	C_6H_5OH	

2.3. Batch adsorption experiments

The batch adsorption system was employed in the present study, and the most effective factors for adsorption process including contact time (10-105 min), pH (2,4,6,8), adsorbent dose (0.4-1.5 g L^{-1}), and initial concentration of phenol (50- 150 mgL^{-1}) were assessed. The stock solution of phenol was prepared with a concentration of 1000 ppm in double distilled water. The optimum pH was then determined by varying the pH in the range of 2-8 and keeping constant the other variables (contact time, adsorbent dose, and initial phenol concentration). The experiments were performed in 100 milliliter beaker with a constant concentration of phenol. Then, this mixture was shacked with a shaker device of enforce model with 150 rpm and the room temperature of 20 – 25°C. The HCl and NaOH were used to adjust the pH solution. In the next step, the optimum adsorbent dose was estimated by keeping constant the contact time and initial phenol concentration and also the obtained optimum pH. After determining the optimum pH and adsorbent dose, the various concentrations of the phenol in the specified times of contact were investigated. The final phenol concentration in the solution was measured by the UV-Visible spectrophotometer at a wavelength 500nm and with regard to standard curve, respectively (20, 21).

The removal efficiency and sorption capacity of the Pistacia mutica were determined by Eq. (1) and (2), respectively (22, 23):

$$R=[\frac{(C_0-C_f)}{C_0}] \times 100 \ (1) \quad Qe =\frac{(C_0-C_e)V}{M} \quad (2)$$

Where; R (%) and qe (mg/g) are the removal efficiency and adsorption capacity, respectively. C_0 (mg /L) and C_f are the initial and final concentration, Ce (mg/ L) is concentration at the equilibrium, m (g) is the mass of the adsorbent, and V (L) is the volume of the solution.

2.4. Isotherm and Kinetics

The equilibrium adsorption isotherm is important in the design of adsorption systems. Although several isotherm equations are available, but four important isotherms including Langmuir, Temkin, Harkins Jura, and Freundlich isotherms were selected. The Isotherms equations are presented in Table 2.

Table2. The equation of isotherms (24, 25)

model	equation	
Langmuir	$\dfrac{c_e}{q_e} = \dfrac{1}{q_m k_l} + \dfrac{c_e}{q_m}$	(3)
Freundlich	$\text{Log } q_e = \dfrac{1}{n} \log c_e + \log k_f$	(4)
Temkin	$q_e = B_T \ln A_T + B_T \ln C_e$	(5)
Harkins Jura	$\dfrac{1}{q_e^2} = \left[\dfrac{B_{HJ}}{A_{HJ}}\right] - [\dfrac{1}{A_{HJ}}] \log C_e$	(6)

Kinetic models are used to examine the rate of adsorption process and the potential rate of controlling step. In the present work, the obtained kinetic data from batch studies were analyzed using the pseudo second-order, Intraparticle diffusion, and pseudo first-order model. The study of kinetic models was conducted in contact time between 10-105 min with aniline and phenol concentration of 50 mg/l and optimum amount of pH and adsorbent dose. To evaluate the differences in the biosorptionrates and uptakes, the kinetic data were described with Intraparticcle diffusion, pseudo first-, and pseudo second-order models. The linearized form of model is shown in Table 3.

Table3. The equation of kinetics (26, 27)

model	equation	
pseudo-first-order	$\text{Log } (q_e - q_t) = \log(q_e) - \dfrac{k_1}{2.303} t$	(7)
pseudo second-order	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q^2} + \dfrac{t}{q_e}$	(8)
Intra-particle diffusion	$q_t = K_{pi} t^{0.5} + c$	(9)

3. Results

3.1. Effect of pH and initial phenol concentration

As is seen in Figure 1, the pH value of the solution was an important controlling parameter in the adsorption process. The effect of pH on phenol uptake in the batch process was studied by varying the pH level from 2 to 8. It was shown in Figure 1 that on the basis of the maximum removals of phenol for contact time of 10 min carried out at pH4, the removal percent of 81.9% was obtained at biosorbent dosage from 0.6 g/L.

To determine the effect of initial phenol concentration on the adsorption process, the initial concentration of phenol was varied from 50 to 150 mg/L at the fixed pH level of 4, adsorbent dose of 0.6g/L, and contact time of 10 min.
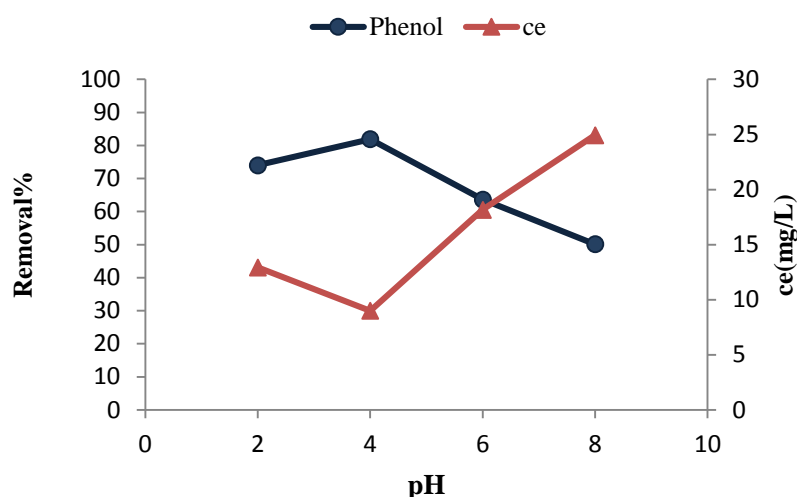
Figure 1. Effect of pH on removal efficiency of phenol
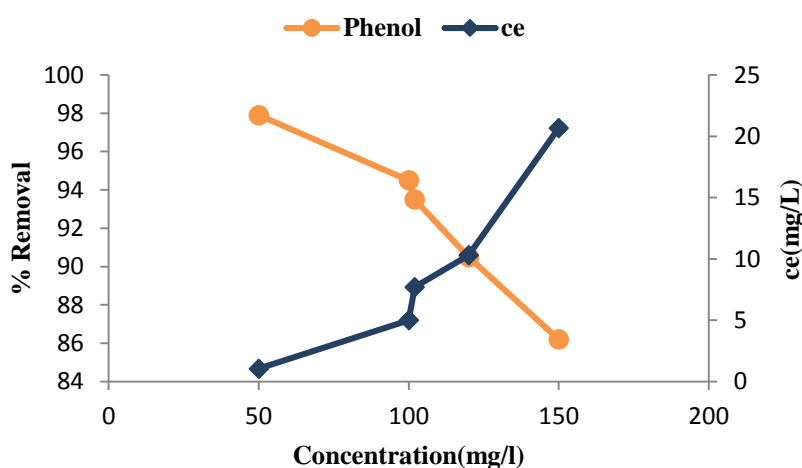(Contact time =10 min, dosage: 0.6g/L, initial concentration: 50 mg/L)

Figure 2. Effect of phenol concentration on removal efficiency of phenol
(Time = 10 min, dosage: 0.6g/l, pH =4)

3.2. Effect of adsorbent dose and contact time

The effect of adsorbent dose on removal of phenol was studied by varying the dose of adsorbent from 0.4 to 1.5 g/L. As shown in Figure 3, the adsorbent dose significantly influenced the amount of adsorbed. In fact, the percentage of phenol removal steeply increased with the adsorbent loading up to 1 g/L, but qe adsorbed decreased as the dose of adsorbent increased from 0.4 to 1.5 g/L. The contact time between adsorbate and adsorbent is one of the most important design parameters that affect the performance of adsorption processes. Figure 4 shows the effect of contact time on the percent removal efficiency of phenol onto the P.mutica constant initial phenol concentration (50 mg/L) and optimum adsorbent dosage and pH. The uptake of phenol on P. atlantica was rapid in the first 45 min (%99), then the adsorption rate finally reached equilibrium in about 60 min.
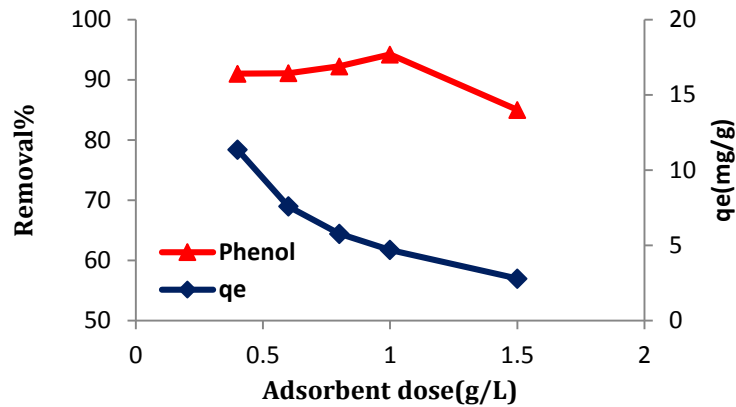
Fig 3. Effect of adsorbent dose on removal efficiency of phenol
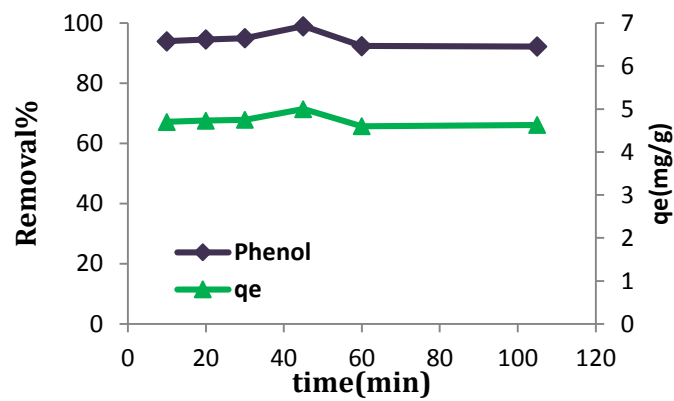(Contact time = 10 min, pH 4, phenol concentration: 50ppm)

Fig 4. Effect of contact time on removal efficiency of phenol
(pH, dosage and concentration: optimum)

3.3.Adsorption isotherms and kinetics

The results and correlation coefficients for isotherms model are presented in Table 4 and Figure 5. The findings showed that phenol on dried baneh fitted according to Langmuir Model isotherm model (R^2=0.985). Furthermore, it was found to agree with Tempkin isotherm (R^2=0.98) more than with Freundlich (R^2=0.967) and Harkins Jura Models (R^2=0.94).

Table4. The adsorption isotherms constants for the removal phenol

Langmuir				Freundlich		
q_m	R_L	K_L	R^2	n	K_F	R^2
8	0.006	3	0.9847	2.8	8.18	0.9678
Temkin				Harkins Jura		
B_T	A_T	b_T(Kj/mol)	R^2	B_{HJ}	A_{HJ}	R2
4.57	5.07×10^2	0.55	0.9799	1.5	158.7	0.9406

The results and correlation coefficients for Kinetic Model are presented in Table 5, and Figure 6. By comparing the correlation coefficients R^2, it can be seen that the experimental equilibrium sorption data are better described by the pseudo second-order model than by the other models**.**

Table5. The adsorption kinetic model constants for the removal phenol

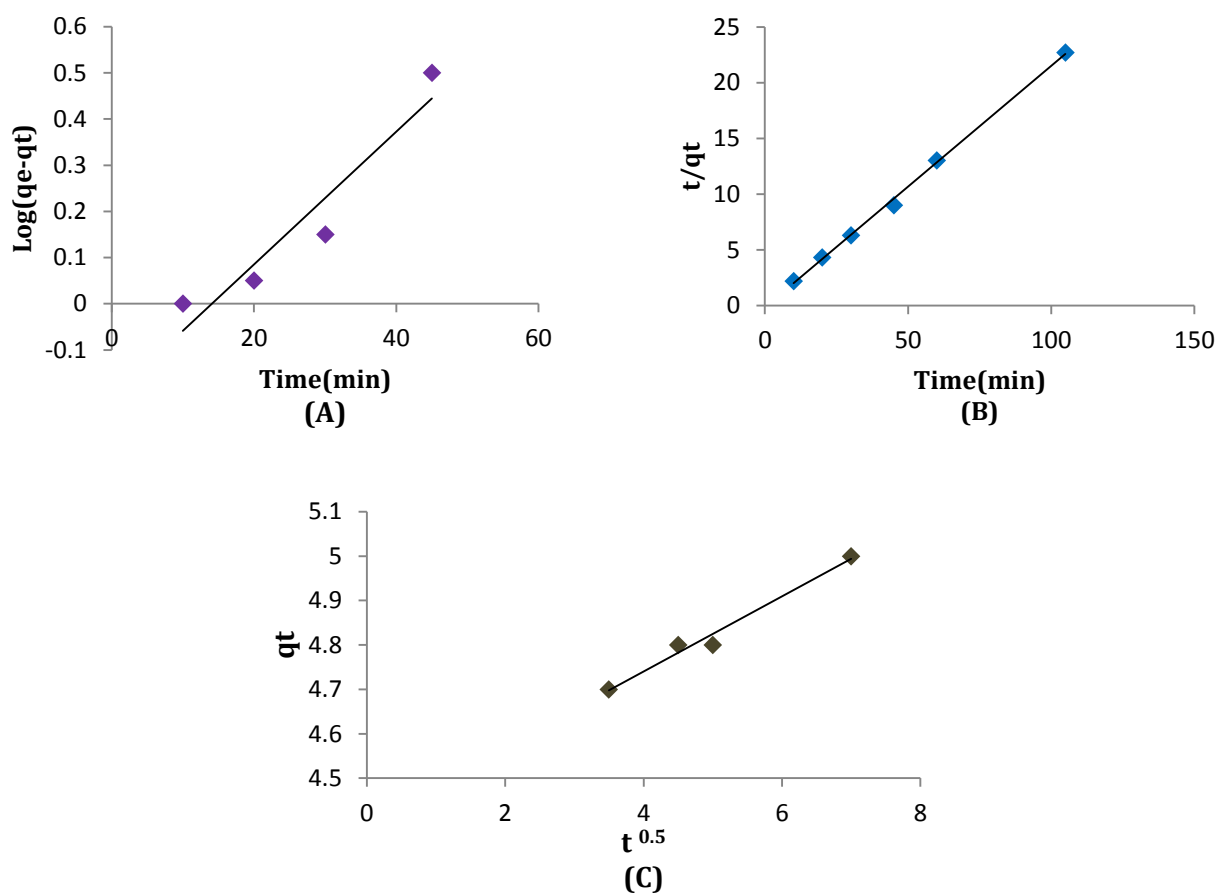| C_O(mg/l)	Pseudo second-order			Pseudo First-order			Intra-particle diffusion		
	K_2(g/mg min)	Qe(mg/g)	R^2	$K_{1(1/min)}$	Qe(mg/g)	R^2	K_{pi}	c	R^2
Phenol	0.285	50	0.998	0.033	1.6	0.908	0.085	4.4	0.979

Fig6. Kinetic isotherms (a); pseudo first order (b); pseudo-second-order (c), Intra-particle diffusion

4. *Discussion*

Generally, solution pH affects the surface charge of adsorbent and degree of ionization of the adsorbate. Phenol as a weak acid compound with pKa ≈9.5 is dissociated at pH> pKa (1). Therefore, the adsorption decreases at high pH values due to ionization of adsorbate molecules. The reason could also be due to the electrostatic repulsions between the negative surface charge and the phenol anions in solution (22). At the same time, at acidic pH, the percentage removal was higher because phenol was undissociated and the dispersion interaction predominated. This result can be supported by results of various studies (5). Another effective parameter on phenol removal adsorption was

documented to be the initial phenol concentration which has been studied in this work. Initial concentration effect on the adsorption of phenol is shown in Figure 2. By increasing the initial concentration of 50 to 150 mg/L, the removal phenol decreased. This may be due to the limited number of active sites on the adsorbent that becomes saturated at high concentration of phenol. In other words, at low concentrations, the availability of phenol molecules to adsorption sites is more than high concentrations (23). The study of Ahmadi et al. showed that using Baneh, the level of aniline decreased to 81.6% with an increase in removing concentration to 150 mg/L (16) and the adsorption rate decreased by increasing the adsorbent dose from 1 to 1.5 g/L, which was due to the limited number of active sites on the adsorbent and decreasing the active surface of adsorbent (24, 28). The optimum contact time was found to be 45 min which can probably be explained by the greater contact surface of baneh adsorbent, because any increase in the specific surface area could lead to more adsorption percentage in lower time (20,29). The R^2 of kinetic models suggested that the pseudo second-order model mechanism is predominant, which meant that the uptake process followed the pseudo-second-order expression with correlation coefficients always greater than 0.998. The correlation coefficient in pseudo second-order model was better than the first-order model correlation coefficients, and similar results are shown using removal organic compounds on another adsorbent (30,31). Overall, the current study investigated the adsorption of phenol from aqueous solutions onto dried P.atlantica biomass. The results showed that the solution pH played a significant role in influencing the capacity of an adsorbent towards phenol molecules. An increase in the pH of solutions led to a decrease in the sorption capacities of phenol. The sorbed amounts of phenol also increased with any increase in contact time, reaching a maximum value after 45 min. The Langmuir isotherm was demonstrated to provide the best correlation for the adsorption of phenol. The pseudo-second-order kinetic model provided the best correlation of the experimental data. The findings of the study also showed that baneh biomass can be effectively used as adsorbent for the removal of phenol from aqueous solutions. Moyo1 et al. in a previous study had also reported the adsorption potential of phenol claiming that the adsorption capacity was greater. Hence, the equilibrium data fitted well to the Langmuir Model with correlating constant (R2) higher than 0.99(32).

Acknowledgments

Conflict of interest

The Authors have no conflict of interest.

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