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Removal of Phenolic Compounds from Aqueous Solution by Using Agricultural Waste (Al-Khriet)

Hayder A.K. Al-jandeel
Chemical Engineering Department, College of Engineering, University of Baghdad

Abstract

Adsorption techniques are widely used to remove organics pollutants from waste water particularly, when using low cost adsorbent available in Iraq. Al-Khriet powder which was found in legs of Typha Domingensis is used as bio sorbent for removing phenolic compounds from aqueous solution. The influence of adsorbent dosage and contact time on removal percentage and adsorb ate amount of phenol and 4- nitro phenol onto Al-Khriet were studied. The highest adsorption capacity was for 4-nitrophenol 91.5% than for phenol 82% with 50 mg/L concentration, 0.5 gm. dosage of adsorbent and pH 6 under a batch condition. The experimental data were tested using different isotherm models. The results show that Freundlich model resulted in the best fit also the kinetic study make it clear that the adsorption process proceeded according to the pseudo second order model.

Key Words: Al-Khriet, Agricultural waste adsorbent, Bio sorption, phenolic compound, isotherm kinetic model

Introduction

Phenols and their derivatives are known to be highly toxic for human beings and the aquatic life [1]. They result from different industrial processes such as, synthetic rubber, petrochemical industry, plastics, coking, paper, phenolic resin industries, and oil refineries [2, 3]. The use of water contained phenol can result in retardation of the central nervous system (CNS), impairment of the liver, kidney and irritation of the eyes, skin and mucous membrane [4]. It had been concluded from earlier studies that the skin is a route of entrance of phenol [5]. A 32 years old man died soon after spilling strong solution of phenol above his shoulder and other part of his body. Chronic phenol poisoning is diagnosed by the disfunction of different body system such as the nervous system. The human eyes is very sensitive to the chemical especially the phenol causing swelling and burns as well as the cornea may become white or even loosen sensation. Loss of vision has happened in some case [6]. According to the world health organization (WHO), the recommended concentration of phenolic compound in drink water is 1 mg/L [7] and that is why it is strongly recommended to remove phenolic compounds from wastewater. For this reason different environment friendly process had been used. Several physicochemical and biological treatment techniques such as chemical oxidation [8], ultrasonic

degradation [9], photo catalytic degradation using son photo chemical [10], enzymatic polymerization [11], ion exchange by resin [2] and adsorption [12] but the most efficient process and economically feasible technology for removal phenol in adsorption, especially when using locally available adsorbent. Many research have studied the feasibility of inexpensive adsorbents such as Al-Khriet, (a powder which has been found in the legs of Typa Domingensis) agricultural waste and it is easily available in the waste could be an alternative for cheaper raw materials that are used to treat waste water. According to the literature there is no present study on the biosorptive removal of phenolic compound from aqueous solution using Al-Khriet. , they were selected for this research because they represent commonly encountrated phenolic pollutants in waste water treatment. The aim of this study is to look closely into the adsorption of Al-Khriet for removing phenol and 4-nitrophenol from aqueous solution. The effect of various factors, such as time of contact, bio sorbent dosage and initial adsorbent concentration on the adsorption process is investigated under batch experiments. Kinetic and equilibrium models were used to fit experimental data.

Material and Adsorbent Properties

Al-Khriet, a powder was collected from the marshes in the south of Iraq, first it was washed with dionized water several times to remove impurities and dried in air for two days before drying in oven at 100°Cover night finally Al-Khriet powder was stored in dictator.

Experimental Work

Different concentrations of phenol and 4-nitrophenol aqueous solution were prepared from stock of 500 mg/L by dissolving a proper amount of phenol and 4-nitrophenol in deionized water. The properties of phenol and 4-nitrophenol are shown in Table 1.

Another reason for choosing these compounds is their difference in molecular structure; phenol is two dimensional, flat structures, while 4-nitrophenol is three dimensional.

Table 1, Physical properties of adsorbents [13]

Adsorb ate	Phenol	4-nitrophenol
Molecular weight (g/mol.)	94.1	139.1
Water solubility (g/ L_{H2O})	93	17
Molecular dimensions, (A^0)	5.76*4.17	6.84*4.17

Adsorption was performed in a batch mode. The equilibrium isotherm was determined by mixing 0.5 gm of Al-Khriet with 25 ml of phenol and 4-nitrophenol solution with different initial concentration (50-200) mg/L in conical flask. The flask was shaken in shaker at room temperature of 25°C for 3 hrs. Such a time is indeed to reach equilibrium according to series of experiments. The suspension of Al-Khriet was then filtered and the residual phenol concentration was measured by uv-visible (Shimadzu uv-160A) spectrophotometer. The latter was calibrated at a wavelength of 270 nm, 320 nm for phenol and 4-nitrophenol respectively using a number of aqueous solutions of phenol and 4-nitrophenol at known concentration in order to calculate the calibration curve.

The adsorbed amount at equilibrium, q_e (mg/g) and removal percentage of phenol and 4-nitrophenol onto Al-Khriet were calculated according to the following equation [14].

$$q_e = \frac{(C_0 - C_e)V}{w} \quad \ldots (1)$$

$$R\% = \frac{C_0 - C_e}{C_0} * 100 \quad \ldots (2)$$

Where R is the removal percentage, C_0 and C_e are the initial and equilibrium concentrations of adsorb ate (mg/L) respectively, V is the volume of solution (L), w is the weight of adsorbent used (gm.).

The adsorption kinetics was analyzed by adding 0.5gm of Al-Khriet to 25 ml of 50 mg/L of phenol and 4-nitrophenol solutions. The sample was shaken and examined at different time intervals. The effect of adsorbent dosage and the initial concentration of feed solution were also studied by using different amount of adsorbent (0.2-1) gm for the 50 mg/L solution of phenol and 4-nitrophenol.

Results and Discussion

Effect of Contact Time

As shown in Fig.1 the percent removal of phenol and 4-nitrophenol by adsorption onto Al-Khriet increases with contact time until attain equilibrium of about 3 hr. Removal percent equal to 91.5% and 82% for 4-nitrophenol and phenol respectively at pH 6 and of 50 ppm ions concentration for each adsorb ate and 0.5 gm. of adsorbents. The result indicates that the rate of sorption of 4-nitrophenol and phenol on Al-Khriet were fast because of a largest amount of two compounds attached to the adsorbent within 1 hr of adsorption. The similar results have been reported by Khorsravi R. et al [15].

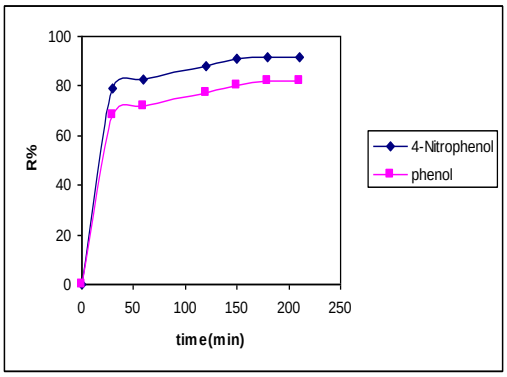

Fig.1 Effect of time on removal efficiency using Al-Khriet as adsorbent

The Effect of Adsorbent Dosage

The adsorption of phenol and 4-nitrophenol on Al-Khriet was carried out by various adsorbent dosages. The relationship between adsorbent dosage and percent of removal is presented in Fig.2. It can be perceived the percent of removal increased with increasing of Al-Khriet dosage while the loading capacity q_e(mg/g) decreased, this is due to increase surface area, more adsorption sites are available. The optimum weight of adsorbents was found (0.5) gm. for Al-Khriet.

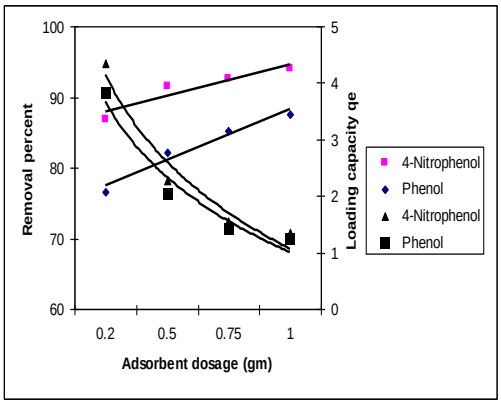

Fig.2 Effect of adsorbent dosage on percent removal for phenol and 4-nitrophenol by Al-Khriet, contact time 3 hr. initial concentration for both ions 50 ppm

It is appears from this figure that the removal percent of 4-nitrophenol is higher than phenol that is due to its lower water solubility and larger molecular weight of 4-nitrophenol when compared to phenol according to Table 1. In general, the adsorptive capacity was related to the electron-with drawing or electron- donating functional groups, water solubility of the compound and the molecular structure of the adsorb ate. The less soluble compounds are easier to be adsorbed [2].

Effect of Phenol and 4-nitrophenol Concentration

The effect of phenol and 4-nitorphenol concentration on percent of removal was studied. The

concentration was varied from (50-200) ppm on 0.5 gm. of Al-Khriet at room temperature. The result in Fig. 3 shows that the percent removal decreased as the concentration of phenol and 4-nitorphenol increased, indicating the less favorable sites and available for adsorb ate with increasing concentration. Removal percent equal to 85 % and 74% for 4-nitrophenol and phenol respectively at 200 ppm concentration, using 0.5gm of Al-Khriet and pH of 6. The pH value were 6 before and after mixing with adsorbent. 0.1M of NaOH and HCl were used for pH adjustment to fix the pH value in all experiments.

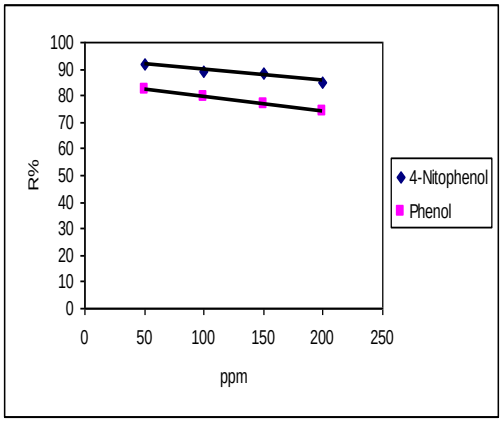

Fig.3 Removal of phenol and 4- nitro phenol using different concentration of ions

Kinetic Studies

Different kinetic models including the pseudo first order model (PFOM) and pseudo second order model (PSOM) were examined for the experimental data to estimate the adsorption kinetics. The PFOM and PSOM may be represented by the following equations respectively [16].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad \ldots (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \qquad \ldots (4)$$

Where q_e, q_t is the amount of adsorbed at equilibrium (mg.g^{-1}), k_1 and k_2 is the rate constant for PFOM and PSOM respectively. The slope and intercept of plots $\ln(q_e - q_t)$ versus time were used to determine the k_1 while the slope and intercept of plot of $\frac{t}{q_t}$ versus t were used to calculate k_2.

The PFOM and PSOM plots are shown in Fig. 4 and Fig. 5 respectively. A comparison of kinetics model is included in Table 2, based on their correlation coefficient (R^2). The adsorption of phenolic compounds onto Al-Khriet is suitable for PSOM, based on higher correlation coefficients.

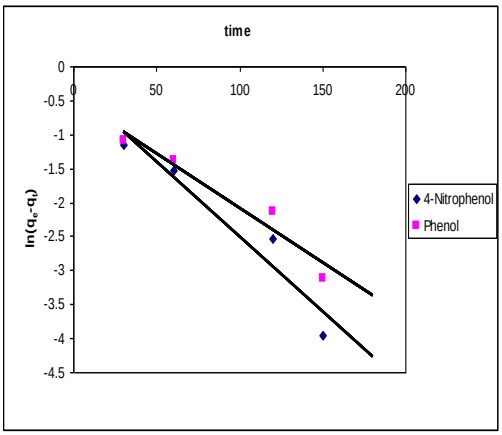

Fig.4 PFOM plots for phenol and 4-nitrophenol

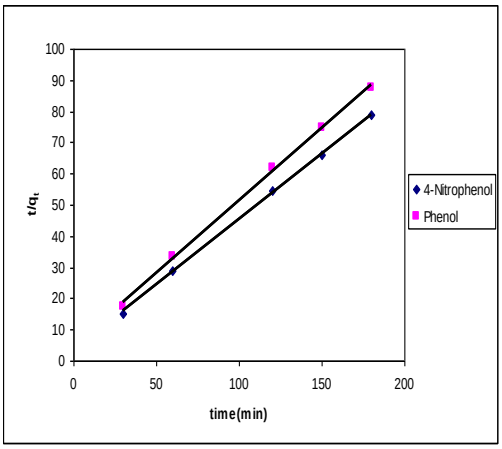

Fig.5 PSOM plots for phenol and 4-nitrophenol

Table 2, The rate constant and correlation coefficient for pseudo first and second order for the kinetic models

Kinetic model	Parameters	Nitrophenol	Phenol
PFOM	$k_1(min^{-1})$	0.022	0.016
	q_e (mg/g)	0.733	0.613
	R_1^2	0.926	0.94
PSOM	k_2 ($mg.g^{-1}.min^{-1}$)	0.055	0.048
	q_e (mg/g)	2.37	2.14
	R_1^2	0.999	0.998

Equilibrium Isotherms

Langmuir (LM), Freundlich (FU) and Dubinin-Rodushkevich (D-RU) were chosen in this study to assess the relationship between the equilibrium concentration and the amount of phenol and 4-nitrophenol adsorbed on Al-Khriet. The LM assumes that the adsorption occurs at specific homogenous sites within the adsorbent and has found successful application in many studies of monolayer adsorption. The LM equation is given by the following equation [17].

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

Where q_e is the solid phase adsorbate concentration in equilibrium (mg/g), $q_{\max}$ the maximum adsorption capacity corresponding to complete monolayer coverage (mg/g), C_e the concentration of adsorb ate at equilibrium (mg/L) and K_L is the Langmuir constant L/mg. The K_L and $q_{\max}$ can be evaluated from the slopes and intercept of linear plots C_e/q_e versus C_e as shown in Fig. 6, the parameter of these model were tabulated in Table (3).

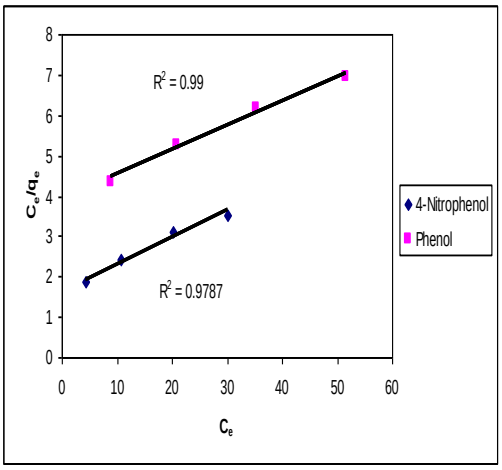

Fig.6, Adsorption isotherm of phenol and 4-nitrophenol at pH (6) by using Langmuir

Table 3, Parameter of isotherms for phenol and 4-nitrophenol and correlation coefficient for Langmuir isotherm R^2

Kinetic model	Parameters	4-nitrophenol	phenol
Langmuir	$q_{\max}$ (mg/g)	15.24	16.6
	K_L L/mg	0.0.039	0.015
	R^2	0.979	0.99

Freundlich model is present by following equation [18].

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad \ldots (6)$$

Freundlich describes the adsorption on an energetically heterogeneous surface on which the adsorbed molecules are interactive. This isotherm dose not predict any saturation of the sorbent by sorbate, indicating multilayer sorption where K_f is the Freundlich constant (mole/gm.) and n stands for the adsorption intensity. The value of K_f and 1/n were calculated from slope and intercept of the plot between $\ln q_e$ and $\ln C_e$ as shown in Fig. 7. The value of K_f and n were tabulated in Table (4).

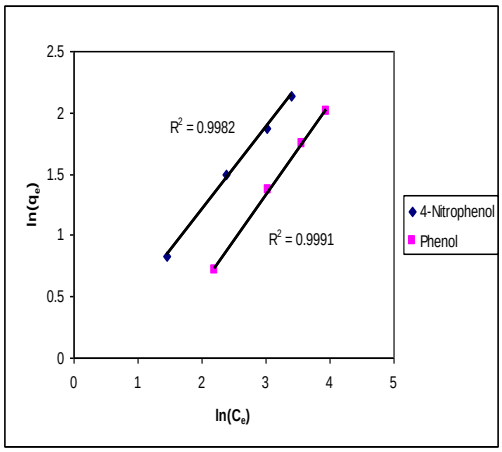

Fig.7 Adsorption isotherm of phenol and 4-nitrophenol at pH (6) by using Freundlich

Table 4, parameter of isotherms for phenol and 4-nitrophenol and correlation coefficient for Freundlich isotherm R2

Kinetic model	Parameters	4-nitrophenol	phenol
Freundlich	$K_f \frac{mg}{g}(\frac{L}{mg})^{\frac{1}{n}}$	0.886	0.414
	n	1.50	1.36
	R^2	0.998	0.999

The Dubinin-Rodushkevich model is an empirical equation employed to determine if the adsorption occurred by a physical or chemical process. The Dubinin-Rodushkevich[19] equation is more general than Langmuir because it does not assume a homogenous surface or a constant sorption potential. The linear form of this model is represented by

$$\ln q_e = \ln q_m - B\varepsilon^2 \quad \ldots (7)$$

B ($mol^2.Kj^{-2}$) is the constant related to sorption energy while ε is the polanyi sorption potential.

$$\varepsilon = RT\ln(1+\frac{1}{C_e}) \quad \ldots (8)$$

R is the gas constant 8.314 $J.mol^{-1}K^{-1}$, T is the temperature in Kelvin. The value of B, q_m were calculated from the slopes and intercept of the plots $\ln q_e$ versus ε^2 as shown in Fig. 8 and 9 [19], the parameter of these models were tabulated in Table (5).

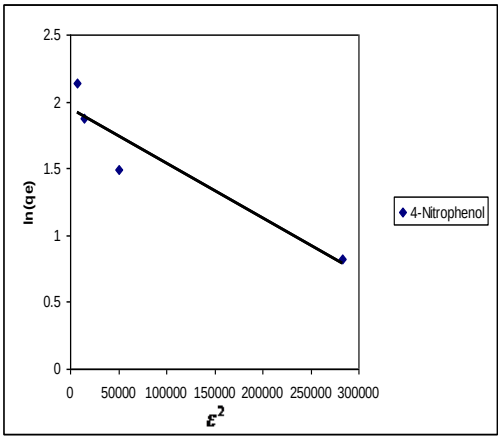

Fig.8 Adsorption isotherm of 4-nitrophenol at pH (6) by using Dubinin-Rodushkevich

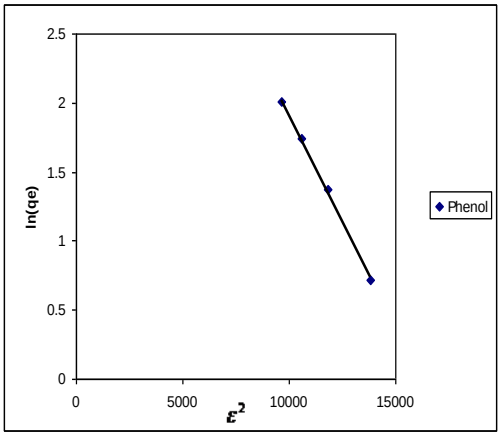

Fig.9 Adsorption isotherm of phenol at pH (6) by using Dubinin-Rodushkevich

Table (5) parameter of isotherms for phenol and 4-nitrophenol and correlation coefficient for Dubinin-Rodushkevich isotherm R^2

Kinetic model	Parameters	4-nitrophenol	phenol
Dubinin-Rodushkevich	$B*10^4$	0.04	3
	q_m	7	147.7
	R^2	0.886	0.998

The experimental data yielded excellent fit within the following isotherm

FU>LM> D-RU

Based on its R^2 value as it gave the maximum R^2 value among the conceded model.

Conclusion

Al-Khriet can be used for first time as effective, locally available adsorbents for the removal of phenol and nitrophenol from waste water. The adsorption of phenol and nitrophenol on Al-Khriet is dependent on contact time**,** initial concentration and adsorbent dosage. It was observed that the removal process increase with contact time and attain equilibrium about 180 minute. In the study of kinetics of adsorption, the pseudo-second order mode provides better correlation than pseudo first order model. Also Freundlich model was found to fit the present experimental data with high correlation factor. Finally Al-Khriet under consideration is not only economical, but also an agriculture waste and locally available which would be useful for economical treatment of waste water containing phenol compounds.

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