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## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

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Rokayia S. Al-Khalisy<sup>a</sup>; Abdul Muhsen A. Al-Haidary<sup>a</sup>; Ammar H. Al-Dujaili<sup>a</sup>

<sup>a</sup> Department of Chemistry, College of Education, Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq

Online publication date: 02 June 2010

**To cite this Article** Al-Khalisy, Rokayia S. , Al-Haidary, Abdul Muhsen A. and Al-Dujaili, Ammar H.(2010) 'Aqueous Phase Adsorption of Cephalexin onto Bentonite and Activated Carbon', *Separation Science and Technology*, 45: 9, 1286 – 1294

**To link to this Article:** DOI: 10.1080/01496391003689017

**URL:** <http://dx.doi.org/10.1080/01496391003689017>

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# Aqueous Phase Adsorption of Cephalexin onto Bentonite and Activated Carbon

Rokayia S. Al-Khalisy, Abdul Muhsen A. Al-Haidary, and Ammar H. Al-Dujaili

Department of Chemistry, College of Education, Ibn Al-Haitham, University of Baghdad,  
Baghdad, Iraq

The adsorption of cephalexin in aqueous solution has been investigated using bentonite and activated carbon as the adsorbents. Batch kinetics and isotherm studies were carried out to evaluate the effect of contact time, adsorbent dosage, pH, particle size, and temperature. Adsorption equilibrium data were well represented by the Langmuir and Freundlich isotherm models. The adsorption intensity was found to be increased as the aqueous phase pH increased, and had a maximum at pH = 6.1. The pseudo-first order, pseudo-second order, and intraparticle diffusion kinetic models were used to describe the kinetic data. The experimental data fitted very well with the pseudo-second-order kinetic model and also followed the simple external and intraparticle model.

**Keywords** activated carbon; adsorption; bentonite; cephalexin; isotherm

## INTRODUCTION

The medical importance of the active surface materials is based on their adsorptive properties, which have many applications, like isolation and purification of antibiotics (1), pharmaceutical products (2), enzymes (3), vitamins, and proteins (4).

Adsorption chromatography recommended for the extraction and purification of various hydrophilic bioproducts (5), can be competitive of beta-lactams, particularly the cephalosporin group of antibiotics (6).

The first adsorbent used was activated carbon, but regeneration problems make its use inappropriate in several cases. However, because of its low cost and easy availability, it does have prospect for use in the adsorption of cephalosporins, particularly at low pH conditions, under which cephalosporins are markedly hydrophobic (7). The most important application of these adsorbents in medicine is to use them as physical antidotes in the treatment of actual poisoning by toxic substances and drug overdose (8).

There are in fact no antidotes for the majority of drugs that cause the poisoning. Certain clay antagonists are of value, and examples of these specific antidotes are kaolinite (9) and attapalguite (10) clays, that can be used in the treatment of poisoning with overdosage drug poisoning. Limit values of cephalexin antibiotic overdosage, as set by the American Academy of Clinical Toxicology and European Association of Poisons Center and Clinical Toxicologists, is 100 mg/kg human body weight (11).

In this paper, we report the equilibrium and kinetic of the behavior of the cephalexin on Iraqi bentonite clay as well as activated carbon with the emphasis on understanding the solute-sorbent interaction. We believe such a study will be useful for the design of an appropriate adsorbent for a specific duty and would be useful in developing adsorptive separation process.

## EXPERIMENTAL

### Materials

The cephalexin monohydrate ( $C_{16}H_{17}N_3O_4S \cdot H_2O$ ) (see Fig. 1 for its structure) and hydrochloric acid, were obtained from Aldrich Chemicals. Activated carbon (100–200 mesh) was obtained from Sigma-Aldrich Chemicals, and had a specific surface area of  $1500 \text{ m}^2 \text{ g}^{-1}$ , pore volume of  $1.5 \text{ cm}^3 \text{ g}^{-1}$  (dry basis), a porosity of 48% and an apparent density of  $390 \text{ kg m}^{-3}$ . It was washed with distilled water and dried in an oven overnight at around  $110^\circ\text{C}$  and then kept in airtight containers. The bentonite clay was obtained from the General Company for Geological Survey and Mining, Baghdad, Iraq. It was 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 ranging from  $75 \mu\text{m}$  to  $250 \mu\text{m}$  was then dried for 24 hours at  $110^\circ\text{C}$  in an electric oven and stored in a dessicator until use. It was washed with an excessive amount of distilled water to remove the soluble materials. The surface area of the bentonite was determined by using the BET,  $N_2$  adsorption method. The measurements were performed with a Micrometrics Gemini (V) (U.S.A.) apparatus. It was found to have a

Received 19 July 2009; accepted 26 January 2010.

Address correspondence to Ammar H. Al-Dujaili, Department of Chemistry, College of Education, Ibn Al-Haitham, University of Baghdad, Aladhmyia, P.O. Box 4185, Baghdad, Iraq. E-mail: ahdujaili@yahoo.com

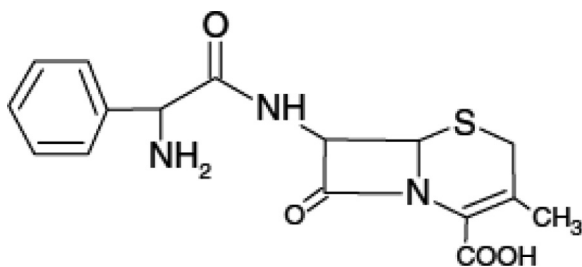


FIG. 1. Structure of cephalexin.

specific area of  $199 \text{ m}^2/\text{g}$ . The surface area was also determined using the adsorption of Methylene Blue on the solid sorbents (12). The specific surface area estimated by this method was found to be  $72 \text{ m}^2/\text{g}$ . The chemical composition of bentonite as determined by XRF technique (wt%) is found as follows:  $\text{SiO}_2$ , 49.70;  $\text{Al}_2\text{O}_3$ , 20.30;  $\text{Fe}_2\text{O}_3$ , 14.60;  $\text{CaO}$ , 8.87;  $\text{TiO}_2$ , 1.60;  $\text{V}_2\text{O}_5$ , 0.10;  $\text{SrO}$ , 0.096;  $\text{ZrO}_2$ , 0.056;  $\text{ZnO}$ , 0.095;  $\text{K}_2\text{O}$ , 0.63; L.O.I, 9.5. It seems from the chemical compositions of the raw sample that the predominant exchangeable cation was calcium. The characteristic XRD peaks for the bentonite show that it contains mainly quartz with the other minerals as minor and trace amounts.

### Adsorption Experiments

Equilibrium isotherms were obtained by contacting 100 mL of solution with 0.25 g of each of the activated carbon or bentonite adsorbents in thermostated shaker bath controlled at  $37.5 \pm 0.5^\circ\text{C}$ . For estimation of thermodynamic parameters, equilibrium experiments were conducted at different temperatures, i.e., 10, 25, 37.5, and  $50^\circ\text{C}$ . The initial concentration of cephalexin in the aqueous solutions ranges from 10 to  $90 \text{ mg L}^{-1}$ . The pH of the solution was varied between 1.2 and 6.1 using appropriate dose of HCl. The adsorption studies were also conducted at different size fractions (75, 150, and  $250 \mu\text{m}$ ), pH value (2.1, 2.5, 4.0, and 6.1) and temperatures (10, 25, 37.5 and  $50 \pm 0.5^\circ\text{C}$ ).

The equilibrium time was 60 and 75 min. for activated carbon and bentonite respectively. For all systems and in all subsequent investigations, a shaking time of 240 minutes was conveniently adopted followed by the standing overnight in the thermostated bath. After attainment of equilibrium the mixture was allowed to settle, centrifuged, and the supernatant liquid was filtered to remove any particulate matter. The clear solution so obtained was analyzed by a T7 UV-visible PG Instruments (UK) spectrophotometer calibrated at 265 nm (13,14).

The amount of cephalexin per gram of adsorbent,  $q_e$  ( $\text{mg g}^{-1}$ ) was calculated as follows:

$$q_e = \frac{(C_i - C_e) \cdot V}{m} \quad (1)$$

Where  $C_i$  is the initial concentration ( $\text{mg L}^{-1}$ );  $C_e$  is the equilibrium or residual cephalexin concentration ( $\text{mg L}^{-1}$ );  $V$  is the volume of the solution (L); and  $m$  is the mass of adsorbent (g).

Experiments on the kinetic were conducted at  $\text{pH} = 6.1$ . In stirred 250 mL Erlenmeyer flask. The liquid volume was 100 mL with 0.25 g of adsorbents the initial concentration of the cephalexin was  $60 \text{ mg L}^{-1}$  at  $37.5 \pm 0.5^\circ\text{C}$ . The mixture was stirred in a mixer for 3 hours at 350 rpm. The samples were taken at different intervals of time. This solution aliquot was filtered and centrifuged the supernatant was analyzed for cephalexin by UV-visible spectrophotometer. Experiments on the adsorption process were found in details in our previous work (15).

## RESULTS AND DISCUSSION

### Contact Time

The adsorption data for the uptake of cephalexin versus contact time at constant initial concentration is presented in Fig. 2. As seen from Fig. 1 that equilibrium time required for the adsorption of cephalexin on activated carbon and bentonite are 60 and 75 minutes respectively. It is also seen that the remaining concentration of cephalexin becomes asymptotic to the time axis after this time. The adsorption capacities increased from  $6.746 \text{ mg g}^{-1}$  on activated carbon to  $8.457 \text{ mg g}^{-1}$  and from  $5.432 \text{ mg g}^{-1}$  to  $7.362 \text{ mg g}^{-1}$  on bentonite clay. The rate curves exhibit a rapid initial uptake followed by a relatively slow approach to equilibrium.

### Effect of pH

The influence on the extent of adsorption of the pH of the solution is exhibited in Fig. 3. The adsorption extent of cephalexin on bentonite and activated carbon increased with increasing pH of the solution. The maximum

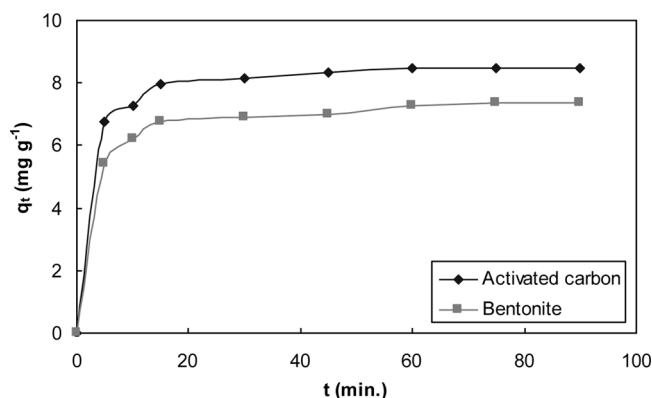


FIG. 2. Effect of equilibrium time on the adsorption of cephalexin on activated carbon and bentonite. Initial concentration,  $60 \text{ mg L}^{-1}$ ; pH 6.1; clay dosage, 0.25 g/100 mL and temperature,  $37.5^\circ\text{C}$ .

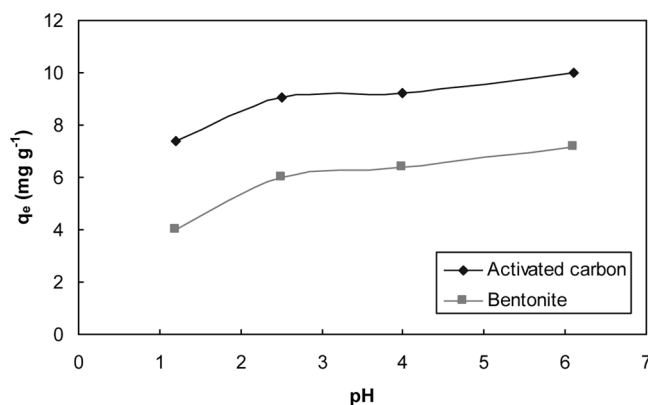


FIG. 3. The effect of initial solution pH on the adsorption of cephalalexin on activated carbon and bentonite. Initial concentration, 60 mg L<sup>-1</sup>; clay dosage, 0.25 g/100 mL and temperature, 37.5°C.

quantities of the drug adsorbed on the two surfaces at 37.5°C followed the order:

$$\text{pH } 6.1 > \text{pH } 4 > \text{pH } 2.5 > \text{pH } 1.2$$

These results may be considered as a consequence of the competition between the hydrogen ions and cephalalexin at low pH values (11). The changes in these interactions are due to the variation in the degree of dissociation of acidic or basic functional groups of the solute, the solvent, and the surface. This in turn affects the polarization of these species and subsequently affects the adsorption extent (16). The cephalalexin is amphoteric in nature. The values of  $\text{pK}_{a1}$  and  $\text{pK}_{a2}$  are 2.56 and 6.88 for this drug (17). The reduction in adsorption capacity of cephalalexin on bentonite and activated carbon with increase of pH has been interpreted from a model incorporating hydronium-ion concentration and dissociation constant, attributable to both the carboxylic and amino functional groups (18). This behavior indicates that the neutral form of the cephalalexin should necessarily be adsorbed. As the pH rose above the  $\text{pK}_{a2}$  value, the anionic forms of cephalalexin predominate, so that the amino affinity forms of the cephalalexin predominate, and therefore the anion affinity is more towards the aqueous phase. The amino species can experience electrostatic repulsion from anions in the surface layer of adsorbents (19).

#### Effect of Particle Size

Experiments were conducted with samples having three different average particle sizes for adsorbents ranging from 75 to 250  $\mu\text{m}$  in order to determine the effect of particle size on adsorption. The adsorption capacity for cephalalexin increases with the decrease in the particle size as shown in Fig. 4. This is due to the fact that adsorption being a

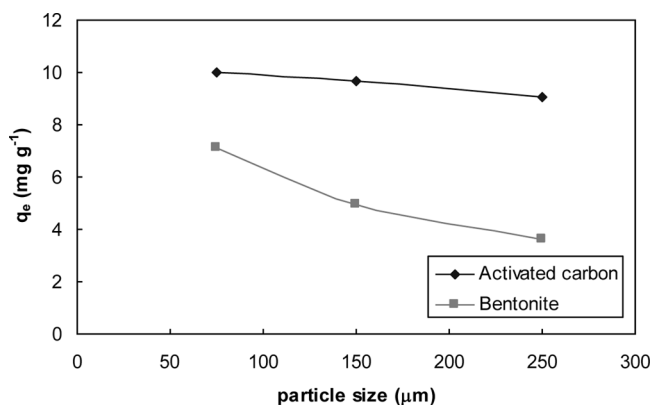


FIG. 4. The effect of particle size on the adsorption of cephalalexin on activated carbon and bentonite. Initial concentration, 60 mg L<sup>-1</sup>; pH 6.1; 0.25 g/100 mL and temperature, 37.5°C.

surface phenomenon, the smaller adsorbent size offered a comparatively larger surface area and hence higher cephalalexin removal at equilibrium. So the smaller clay particle sizes for a given mass of adsorbents have more surface area and therefore the number of available sites is more (20).

#### Effect of Temperatures

The effect of temperature variation on the adsorption extent of the drug on the bentonite and activated carbon has been studied at pH 6.1. Figures 5 and 6 illustrate the data and the general shapes of cephalalexin adsorption isotherms at 10, 25, 37.5, and 50°C.

The adsorption capacity of cephalalexin on activated carbon decreasing with increasing temperature indicates that the adsorption of cephalalexin is controlled by an exothermic reaction. In contrast, the adsorption on bentonite was endothermic (an increase in adsorption extent with

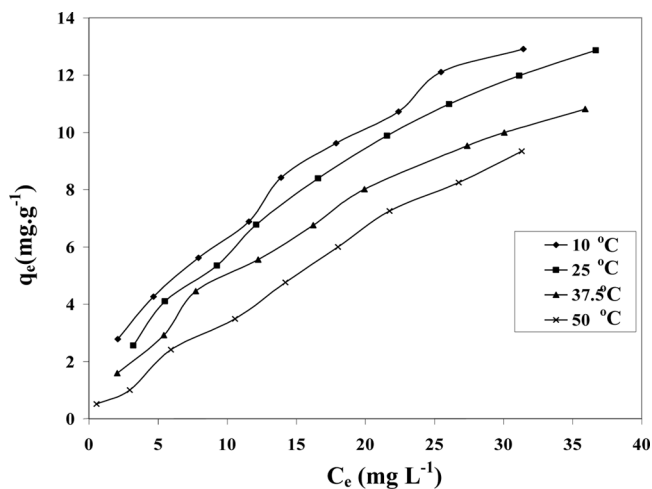


FIG. 5. Adsorption isotherms of cephalalexin on activated carbon at different temperatures.

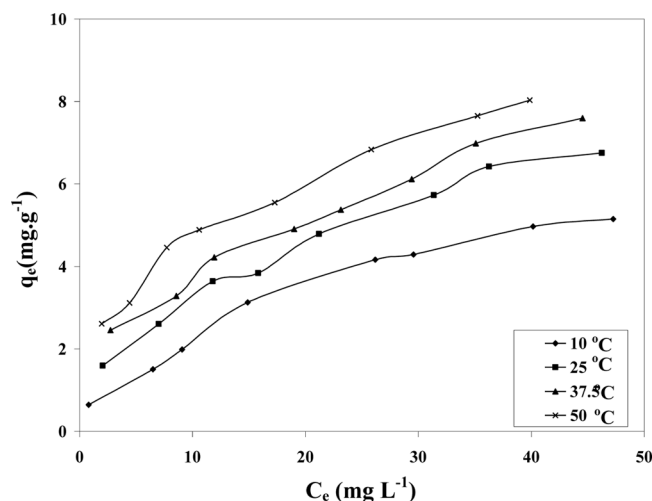


FIG. 6. Adsorption isotherms of cephalexin on bentonite at different temperatures.

increasing temperature). This result may be attributed to a different specific chemical interaction between the activated carbon or bentonite and the drug molecules, which absorbs or release an appreciable energy in order for adsorption to take place (21). Endothermic drug uptake may also be interpreted as a consequence of the possible absorption process (the adsorbent molecule diffuse inside the pores and crystal network for the clay, the diffusion speed increase with increase of temperature), or a sorption process by the surface.

### Effect of Adsorbents Dosage

The percentage of cephalexin adsorption with varying amounts of bentonite and activated carbon is presented in Fig. 7. In general, an increase in the adsorbent dosage increased the adsorption capacity of adsorbate. This is consistent with the expectation that higher adsorbent dosages

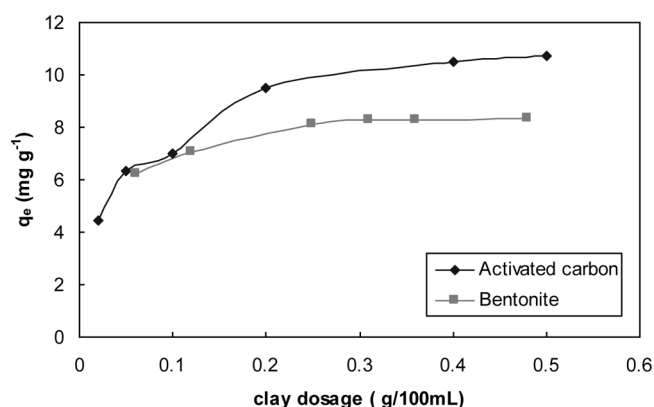


FIG. 7. The effect of adsorbent dose on the adsorption of cephalexin on activated carbon and bentonite. Initial concentration, 60 mg L<sup>-1</sup>; pH 6.1; and temperature, 37.5 °C.

will result in lower  $q_e$  values. The increase in the efficiency can be explained by increasing surface area where the adsorption takes place. As seen in Fig. 6 optimum adsorbent dosages that can be used in bentonite and activated carbon are 0.4 and 0.3 g, respectively.

### Adsorption Isotherms

Various isotherms have been used to interpret data on clays and activated carbon adsorption in the aqueous phase. The two most common isotherm types for describing this type of system are the Langmuir and the Freundlich isotherm.

The most important model of monolayer adsorption came from the work of Langmuir (22). This isotherm is given as Eq. (2):

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

The constants  $q_{\max}$  and  $K_L$  are characteristics of the Langmuir equation and can be determined from the a linearized form of Eq. (2)

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad (3)$$

where  $q_e$  is the amount of cephalexin adsorbed onto clay or activated carbon 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 (L mg<sup>-1</sup>), and  $C_e$  is the equilibrium solution concentration (mg L<sup>-1</sup>). The dependence of  $C_e/q_e$  on  $C_e$  was obtained using the experimental results (Fig. 8).

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor,  $R_L$ , which is defined as:

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (4)$$

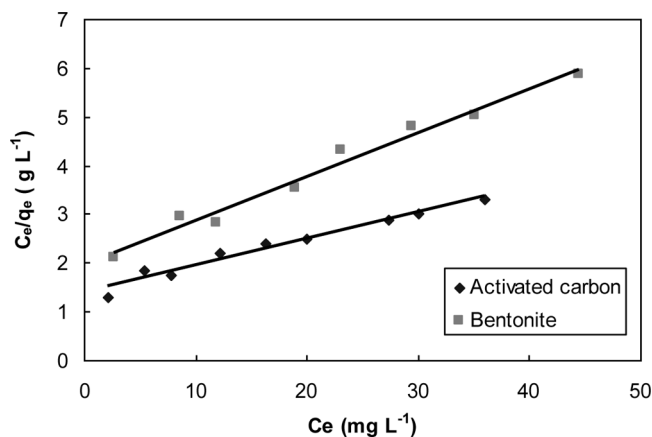


FIG. 8. Langmuir isotherms for cephalexin on activated carbon and bentonite. pH 6.1; and temperature, 37.5 °C.

TABLE 1  
Langmuir and Freundlich isotherm constants for the adsorption of cephalexin onto activated carbon and bentonite at 37.5°C

Adsorbent	Langmuir				Freundlich		
	$q_{\max}$ (mg g <sup>-1</sup> )	$K_L$ (L mg <sup>-1</sup> )	$R_L$	$R^2$	$K_F$ (L g <sup>-1</sup> )	$n$	$R^2$
Activated carbon	17.361	12.518	0.009	0.951	1.018	1.488	0.989
Bentonite	10.384	5.438	0.023	0.999	0.734	1.627	0.901

Where  $C_o$  is the highest initial concentration (mg L<sup>-1</sup>). The  $R_L$  values were found to be 0.009 and 0.023 for activated carbon and bentonite, respectively. They are in range of 0–1 which indicates favorable adsorption (23) (Table 1).

The Freundlich isotherm (24) derived to model the multiplayer adsorption and for the adsorption on heterogeneous surfaces. The Freundlich model is formulated as Eq. (5):

$$q_e = K_F C_e^{1/n} \quad (5)$$

Where  $K_F$  is the Freundlich constant (mg g<sup>-1</sup>) and  $1/n$  is the adsorption intensity. The equation may be linearized by taking the logarithm of both sides of Eq. (5) and the linear form of the Freundlich isotherm can be given as Eq. (6):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

Figure 9 shows the dependence of  $\log q_e$  on  $\log C_e$ . The Freundlich constants  $K_F$  and adsorption intensity  $1/n$  for cephalexin are calculated from the slopes and intercept of this figure.

It is seen that the Langmuir and Freundlich isotherms curves are linear in cephalexin adsorption on activated carbon and bentonite. The Langmuir and Freundlich

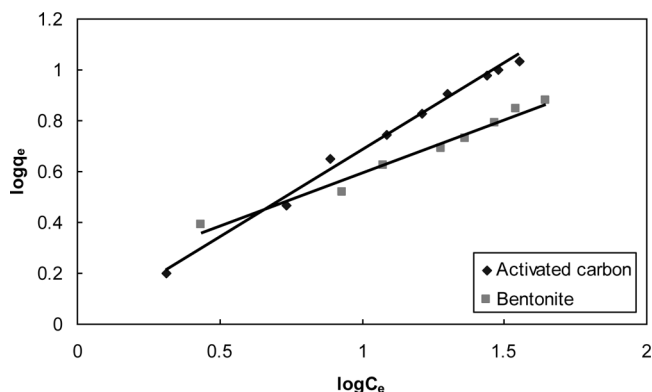


FIG. 9. Freundlich isotherms for cephalexin on activated carbon and bentonite. pH 6.1; and temperature, 37.5°C.

constants are calculated from the slopes and intercepts of Figs. 8 and 9 and listed in Table 1.

The applicability of the two isotherm models to the cephalexin-activated carbon and cephalexin-bentonite systems implies that both monolayer and heterogeneous surface conditions exist under the experimental condition studies. The adsorption of cephalexin on activated carbon and bentonite is thus complex, involving more than one mechanism (25).

It is worthwhile to compare the adsorption affinity of cephalexin on activated carbon obtained in this work with the published results. Dutta et al., (26) reported the adsorption affinity ( $q_e/C_e$ ) of cephalexin on activated carbon and some polymeric resins. They were found that the adsorption affinity for polymeric resins, XAD-2, XAD-4, XAD-7, and XAD-16 and activated carbon are 0.190, 0.489, 0.116, and 0.224 and 0.470 g/L. The results obtained in this work for the adsorption of cephalexin onto activated carbon and bentonite are 0.381 and 0.511, respectively, which are comparable with Dutta's results. Unfortunately, no data available in the literature concerning the adsorption of cephalexin by bentonite clay.

### Kinetics of Adsorption

Kinetic of adsorption is one of the most important characteristics to be responsible for the efficiency of adsorption diffusion. Various kinetic models such as Lagergren pseudo-first order, pseudo-second order, and intraparticle diffusion have been applied for the experimental data to predict the adsorption kinetics.

The pseudo first-order rate expression of Lagergren model (27) is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (7)$$

This can be integrated into:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

where  $q_t$  is the amount of cephalexin adsorbed at time  $t$  (mg g<sup>-1</sup>),  $q_e$  is the amount of cephalexin adsorbed at equilibrium (mg g<sup>-1</sup>), and  $k_1$  is the pseudo-first-order rate

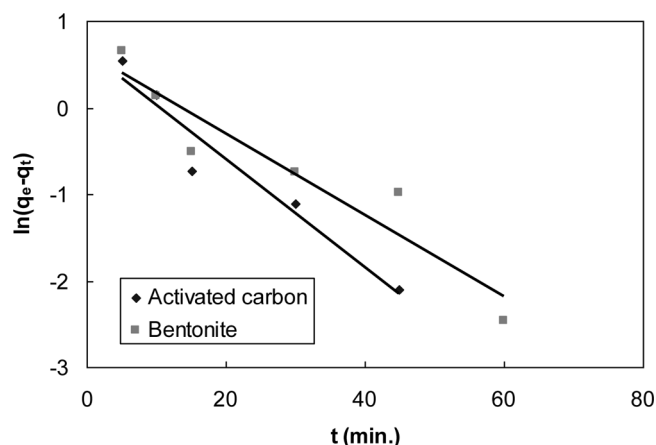


FIG. 10. Pseudo-first order reaction kinetics for the adsorption of cephalalexin on activated carbon and bentonite. Initial concentration, 60 mg L<sup>-1</sup>; pH 6.1; clay dosage, 0.25 g/100 mL and temperature, 37.5°C.

constant (min<sup>-1</sup>) for the first-order adsorption. Values of  $k_1$  calculated from the slope of the plot of  $\ln(q_e - q_t)$  versus  $t$  (Fig. 10) are shown in Table 2.

If the adsorption rate is pseudo-second order, the pseudo second-order kinetic rate equation is expressed as (28):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (9)$$

This can be integrated to

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

where  $k_2$  is the equilibrium rate constant of pseudo-second order adsorption (g mg<sup>-1</sup> min<sup>-1</sup>). Values of  $k_2$  and  $q_e$  were calculated from the slopes and intercepts of the linear plot of  $t/q_t$  against  $t$  (Fig. 11). The rate constants  $k_1$ ,  $k_2$ ,  $q_e$  and the correlation coefficient  $R^2$  of cephalalexin under different conditions were calculated from the relevant plots are given in Table 2.

The pseudo-first-order and pseudo-second-order kinetic models can not identify the diffusion mechanism and the kinetic results can be used to test the presence or absence of intraparticle diffusion and to determine whether intraparticle diffusion is the rate-limiting step for adsorption. The diffusion mechanism, includes four steps:

1. migration of adsorbate molecules from bulk solution to the surface of the adsorbent;
2. diffusion through the boundary layer to the surface of the adsorbent;
3. adsorption at a site and
4. intraparticle diffusion into the interior of the adsorbent (29).

The intraparticle diffusion equation (30) can be written as follows:

$$q_t = k_p t^{1/2} + I \quad (11)$$

where  $I$  is the intercept and  $k_p$  is the intraparticle diffusion rate constant (mg g<sup>-1</sup> min<sup>-1/2</sup>). According to this model, the plot of uptake  $q_t$ , versus the square root of time ( $t^{1/2}$ ) (Fig. 12) should be linear if intraparticle diffusion is involved in the adsorption process of cephalalexin by activated carbon and bentonite. The two curves had the same features, i.e., an initial curve portion followed by a linear portion and later a plateau. If these lines pass through the origin then intraparticle diffusion is the rate controlling step (31). When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further show that the intraparticle diffusion is not the only rate limiting step. But also other kinetic models may be controlled by the rate of adsorption, all of which may be operating simultaneously. Two linear portions in each curve were obtained. Their  $k_{id}$  values ( $k_{id1}$  and  $k_{id2}$  for first stage and second stage, respectively), which were determined from the slopes of the lines are given in Table 2.

The parameter values obtained from the application of kinetic models were used to predict the variation of adsorbed cephalalexin with time. The resulting kinetic

TABLE 2

Kinetic parameters of adsorption of cephalalexin on activated carbon and bentonite according to Lagergren pseudo-first order, pseudo-second order and intraparticle diffusion rate expressions

Adsorbent	$q_{e, experimental}$ mg g <sup>-1</sup>	Pseudo-first order			Pseudo-second order			Intraparticle diffusion model		
		$k_1$ min <sup>-1</sup>	$q_{e, calculated}$ mg g <sup>-1</sup>	$R^2$	$k_2$ g mg <sup>-1</sup> min <sup>-1</sup>	$q_{e, calculated}$ mg g <sup>-1</sup>	$R^2$	$k_{id1}$ g mg <sup>-1</sup> min <sup>-1/2</sup>	$k_{id2}$ g mg <sup>-1</sup> min <sup>-1/2</sup>	$R^2$
Activated carbon	8.457	0.062	1.924	0.940	0.107	8.547	1.000	0.742	0.112	0.996
Bentonite	7.362	0.047	1.901	0.899	0.082	7.463	0.999	0.812	0.133	0.995

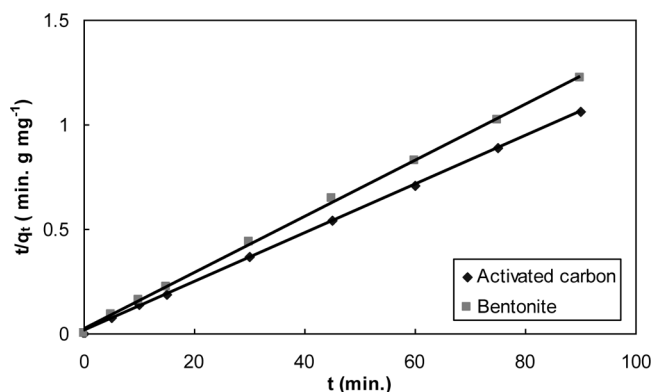


FIG. 11. Pseudo-second order reaction kinetics for the adsorption of cephalixin on activated carbon and bentonite. Initial concentration, 60 mg L<sup>-1</sup>; pH 6.1; clay dosage, 0.25 g/100 mL and temperature, 37.5°C.

parameters are presented in Table 2. As seen, the correlation coefficient  $R^2$  of the pseudo-second-order model are higher than in all other models, indicating that the pseudo-second-order model best describe the adsorption of cephalixin on activated carbon and bentonite. Moreover, as the difference between  $q_{e,calculated}$  and  $q_{e,experimental}$  values is considered, it is seen that cephalixin removal with all both adsorbents is well described by the second-order reaction kinetic. Considering all the above results, the kinetic of cephalixin adsorption on activated carbon and bentonite can be described in the order of fitting; the pseudo-second order, intraparticle diffusion, and the pseudo-first order equation.

### Thermodynamic Parameters

The thermodynamic parameters including change in the Gibbs free energy,  $\Delta G$  enthalpy  $\Delta H$  and entropy,  $\Delta S$  are calculated from the variation of the thermodynamic

equilibrium constant  $K_d$  with changes in temperature.  $K_d$  for the adsorption reaction can be defined (32):

$$K_d = \frac{q_e}{C_e} \quad (12)$$

Values of  $K_d$  are obtained by plotting  $\ln q_e/C_e$  versus  $q_e$  and extrapolating  $q_e$  to zero.

Gibbs free energy changes  $\Delta G$  for interactions are calculated from the relationship:

$$\Delta G = -RT \ln K_d \quad (13)$$

Where  $R$  is the universal gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>) and  $T$  is the temperature in Kelvin

The enthalpy changes  $\Delta H$  and entropy changes  $\Delta S$  are then determined from the slope and intercept of the following Eq. (14) plot of  $\ln K_d$  versus  $1/T$  (Fig. 13).

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (14)$$

The values obtained are shown in Table 3, the negative Gibbs free energy changes  $\Delta G$  confirms that the adsorption process has a natural tendency to proceed spontaneously. The values of the  $\Delta G$  also confirm that maximum adsorption is obtained with the cephalixin onto activated carbon higher than of bentonite. 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> (33). The overall free energy change during the adsorption process was negative for the experimental range of temperature (see Table 3), corresponding to a spontaneous physical process of cephalixin adsorption and that the system does not gain energy from an external source.

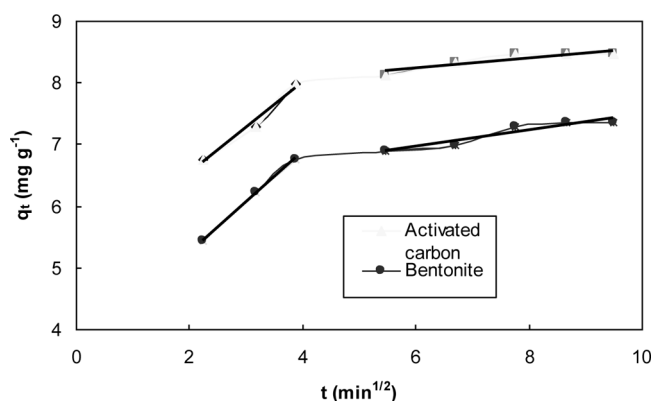


FIG. 12. Intraparticle diffusion kinetic plots for the adsorption of cephalixin on activated carbon and bentonite. Initial concentration, 60 mg L<sup>-1</sup>; pH 6.1; clay dosage, 0.25 g/100 mL and temperature, 37.5°C.

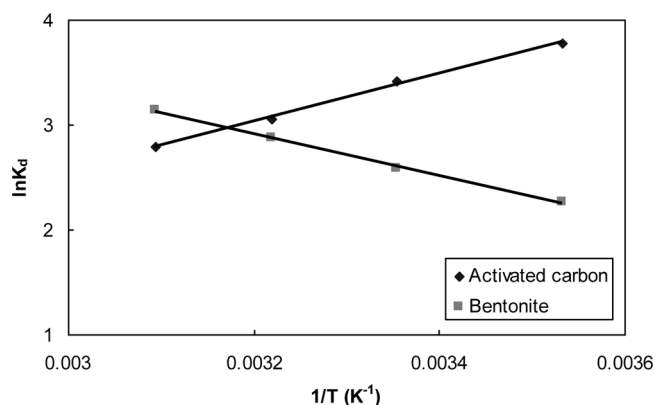


FIG. 13. Plot of  $\ln K_d$  versus  $1/T$  for estimation of thermodynamic parameters for the adsorption of cephalixin on activated carbon and bentonite.



TABLE 3  
Thermodynamic parameters calculated for the adsorption of cephalexin on activated carbon and bentonite

T/°C	Activated carbon			Bentonite		
	$\Delta G$ kJ mol <sup>-1</sup>	$\Delta H$ kJ mol <sup>-1</sup>	$\Delta S$ JK <sup>-1</sup> mol <sup>-1</sup>	$\Delta G$ kJ mol <sup>-1</sup>	$\Delta H$ kJ mol <sup>-1</sup>	$\Delta S$ JK <sup>-1</sup> mol <sup>-1</sup>
10	-8.891	-18.937	-35.343	-5.325	16.706	89.904
25	-8.455			-6.393		
37.5	-7.888			-7.433		
50	-7.509			-8.424		

It is clear from these results that the overall enthalpy change  $\Delta H$  of the adsorption of cephalexin onto activated carbon is negative which indicates that the adsorption of cephalexin on activated carbon is exothermic and the product is energetically stable with high binding of cephalexin to the available sites. The negative value of  $\Delta S$  might be associated with the adsorption of cephalexin to the activated carbon, which resulted in a decrease in freedom degree of the system during the adsorption. In contrast, the mean adsorption enthalpy,  $\Delta H$  value for adsorption of cephalexin on bentonite is positive, and indicated the uptake of cephalexin on this adsorbent to be a physical sorption and is also endothermic. The endothermic enthalpy gives clear indication of a strong interaction between the adsorbates and the adsorbents. This can be explained by the fact that each molecule of the sorbate has to displace more than one molecule of the solvent. The net result corresponds to an endothermic process. The positive values of  $\Delta S$  shows the increased randomness of the solid-solution interface during the sorption of cephalexin on bentonite. Generally, the sign of entropy values may be due to some structural changes in both the adsorbate and adsorbents during the adsorption process.

## CONCLUSIONS

The adsorption of cephalexin on activated carbon and bentonite from aqueous solution was demonstrated in this study. In general activated carbon provides higher adsorption intensity than bentonite. The adsorption capacity increased with an increase in pH and adsorbent dosages, but decreased with an increase in particle size of adsorbents.

Both Langmuir and Freundlich models represent well the adsorption isotherm. The Langmuir model exhibited a slightly better fit to the adsorption data of cephalexin than the Freundlich model. The rate of adsorption onto activated carbon and bentonite appears to be followed pseudo-second order adsorption kinetic. Both intraparticle diffusion and kinetic models might affect the adsorption rate.

Thermodynamic analysis indicates that the adsorption process was exothermic in case of activated carbon, while

endothermic with the adsorption of cephalexin on bentonite. The relatively low Gibbs free energy and enthalpy suggest that the adsorption of cephalexin might be physical in nature.

## ACKNOWLEDGMENTS

Prof. A. H. Al-Dujaili thanks the International Institute of Education (IIE), New York, USA, for the award of a fellowship at the University of Jordan.

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