

Adsorption Kinetics and Isotherms of a Pesticide on Polyester Fibers by Carrier Finishing

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ABSTRACT: The effective management and control of mosquitoes in human living environments are crucial to minimize vector-borne diseases in homes. Pesticides, such as pyrethroids, are considered powerful tools in the control of mosquitoes and are intended to be incorporated into textiles. The adsorptive behavior of the pesticide ZX-1 [the main component is 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl) ethane] in aqueous solution on polyesters fibers at different treatment times, temperatures, and concentrations are discussed in this article. The second-order model was found to be the most suitable for describing the kinetic diffusion process, and the intraparticle diffusion was the rate-controlling

process. The Langmuir, Freundlich, and Dubinin–Radushkevich adsorption models were applied to these approaches. The results show that the Langmuir model appeared to fit the adsorption of ZX-1 on the polyester fibers better than other adsorption models. In addition, thermodynamic parameters, such as the free energy of adsorption (ΔG^0), enthalpy (ΔH^0), and entropy, were calculated. Positive values of ΔH^0 and ΔG^0 indicated the endothermic and nonspontaneous nature of ZX-1 adsorption on the polyester fibers. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1208–1215, 2011

Key words: kinetics (polym.); polyesters; thermodynamics

INTRODUCTION

Insecticide-treated mosquito-repellent nets are a major tool for malaria control, especially in sub-Saharan Africa, where the infection rate of vector diseases is the greatest in the world.¹ However, the nets have to be treated regularly with insecticides to offer long-lasting and desired protection for people because these functions on the nets are not durable to laundering and storage.^{2,3} Despite the popularity of the nets themselves, the treatment of bed nets is not easy, particularly for achieving powerful and durable functions. However, bed nets pretreated with durable functions by textile mills have improved performance over those that are treated by users.⁴ On the other hand, mosquitoes, such as *Anopheles gambiae* in western and eastern Africa and *Anopheles funestus* in South Africa, are becoming more resistant to pyrethroid insecticides.^{5–8} The recent failure of insecticide-treated nets and the indoor spraying of pesticides to kill or protect against pyrethroid-resistant *A. gambiae* in southern Benin⁹ showed the urgency of finding alternative insecticides and repellents to supplement or replace the widely overused pyrethroids.¹⁰ A recent study

on impregnating nets with DEET repellent revealed some promising approaches for overcoming the problems.^{11–13} However, DEET is not a powerful mosquito repellent, and it is hard to achieve very durable functions on polyester nets with DEET.

In 2007, in view of the necessity of malaria control and in overall consideration of pesticides in mosquito control, the World Health Organization reinstated the use of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl) ethane as an indoor residual spray.¹⁴ It has several unique features, including the longest residual efficacy and repellency to mosquitoes, although human and environmental health concerns still exist.¹⁵ Considering these special properties of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl), we thought its use in treated textiles, such as bed nets and meshes, may have great advantages over that in indoor residual sprays. These textile products can only be used indoors and have to be placed in specific areas without easy human skin contact. Because of the long-lasting repellency to mosquitoes of the chemical, chemically treated fibers could slowly release the pesticide to the environment and provide even longer repellency, possibly for years. Such an approach could be environmentally friendly and safer to users. Thus, we tried to develop polyester fabrics treated with the pesticide ZX-1 [its main component is 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)]. In this article, we discuss an investigation on the adsorption behavior of ZX-1 in aqueous solution onto polyester fibers at

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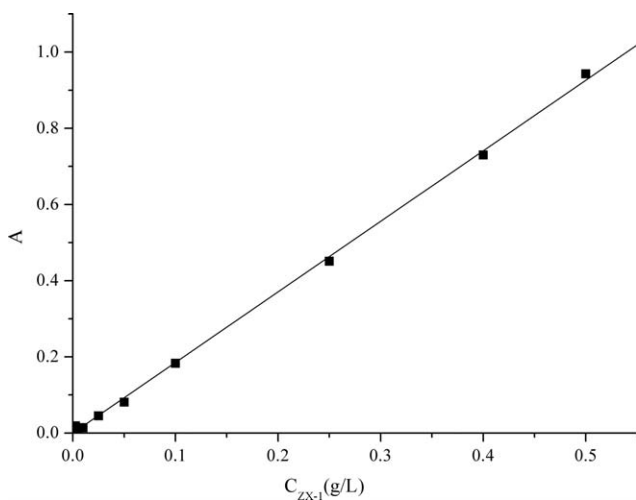


Figure 1 Standard working plot of ZX-1 in a cyclohexane solution.

various times, temperatures, and concentrations, and obtaining a high efficient rate in mosquito-resistant nets and other household textiles.

EXPERIMENTAL

Materials

Polyester net fabric was obtained from Jiangsu AB Group Co., Ltd. (Suzhou, China). Industrial-grade ZX-1 was purchased from Tianjin Chemical Plant, (Tianjin, China). All other chemicals were analytical grade and were used as received without further purification.

Purification of ZX-1

The commercial pesticide was purified to remove precursors of chlorobenzene and trichloroaldehyde according to the following procedure. ZX-1 was purified with deionized water for 30 min at room temperature to extract trichloroaldehyde; then, the indissoluble materials were treated with absolute alcohol for 15 min to remove chlorobenzene. Then, the pure sample was dried.

Adsorption experiments

The ultraviolet-visible absorbance values of ZX-1 were measured three times for each sample with an ultraviolet-visible spectrophotometer (Shimadzu UV-3000, Tokyo, Japan) at $\lambda_{max} = 278$ nm. The amounts of ZX-1 adsorbed on the polyester fibers at different times (t 's) were calculated from the concentrations in solution before and after adsorption, and the amount of ZX-1 adsorbed (mol/g) on the polyester fibers was calculated from the mass balance equation:

$$q_t = (C_0 - C_e) \frac{V}{m} \tag{1}$$

where q_t is the amount of adsorbed ZX-1 on the polyester fiber at different times (mg/g); C_0 and C_e are the initial and equilibrium liquid-phase concentrations of ZX-1 (mg/L), respectively; V is the volume of ZX-1 solution (L); and m is the mass of the polyester fiber (g).¹⁶⁻¹⁸

Standard working plot of ZX-1 in a cyclohexane solution

A series of ZX-1 standard solutions in cyclohexane were prepared at different concentrations from 0.001 to 0.5 g/L for 10 min in a sonicator operated at 250 W and 50 kHz at room temperature ($25 \pm 1^\circ\text{C}$). The values of UV absorbance at λ_{max} were recorded, and the relation between the absorbance value and the concentrations of (CZX-1) is shown in Figure 1. On the basis of the straight line shown in Figure 1, the concentrations of ZX-1 were calculated at specific time intervals; then, the concentrations of ZX-1 on the polyester fiber at specific time intervals was calculated.

Effect of the concentration of ZX-1

The antimosquito effect was determined directly by the concentration of ZX-1. To determine the detailed concentration of ZX-1, a series of ZX-1 concentrations were prepared from 0.1 to 1.7 g/L. The results are shown in Figure 2.

Figure 2 shows that the ZX-1 concentration on the fiber (CZX-1f) increased withincreasing ZX-1 concentration in solution (CZX-1s) until it reached the saturation value, and this concentration was 1.2 g/L in solution. This result shows that the pesticide ZX-1 entered the polyester fabric cavities and reached saturation. According to the limit of the ZX-1 dosage, the optimal concentration was 0.6 g/L, namely, 3% (on the basis of the weight of the fiber).

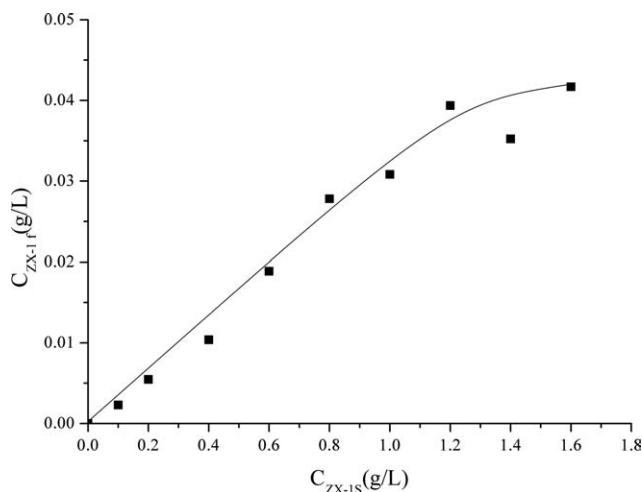


Figure 2 Effect of the concentration of ZX-1 on the carrier finishing process.

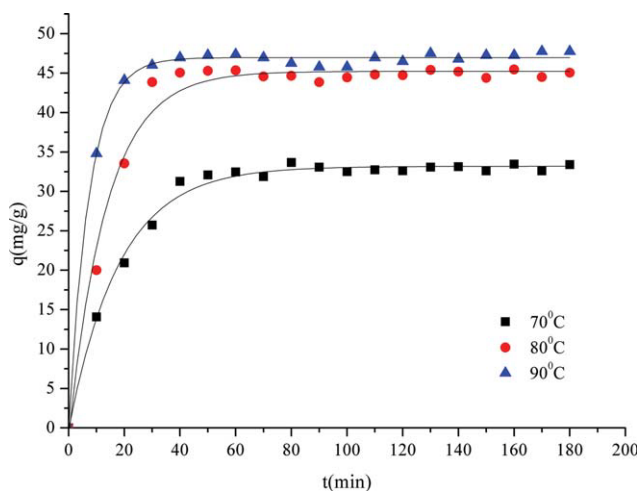


Figure 3 ZX-1 adsorption on polyester fibers at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Adsorption kinetics

The amount of adsorption of ZX-1 on the polyester fibers determined the efficacy of the mosquito repellent performance of the bed nets. To determine the affecting factors of ZX-1 on the fibers, the adsorption kinetics were investigated. Both the treatment temperature and time were important factors affecting the processes; they influenced the amount of ZX-1 adsorbed on polyester fibers, as shown in Figure 3. The equilibrium adsorption increased when the temperature increased, but the adsorption equilibrium time decreased. The amount of ZX-1 adsorption continued to increase with increasing treatment time until it reached the saturation point. Polyester fibers have a glass-transition temperature (T_g) at 71.9°C, above which the adsorption equilibrium time should be shortened according to the structural changes of the polyester.¹⁹

As shown in Figure 3, the maximum adsorption capacity of ZX-1 on polyester fibers was increased from 34.6 mg/g at 70°C to 47.8 mg/g at 90°C because, under temperatures above T_g , the polyester molecules had increased chain movements and openness, which allowed more ZX-1 molecules to enter. Such a process is quite similar to the disperse dyeing of polyesters.^{20,21} So the optimal temperature was chosen as 90°C to carry out adsorption of pesticides in polyester fibers.

Three main kinetic models, namely, a first-order equation, a pseudo-second-order equation, and an intraparticle diffusion equation, were used to interpret the experimental data:^{22–24}

The first-order rate expression is given as Eq. (2):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where q_e and q_t are the amounts of ZX-1 adsorbed on the adsorbent at equilibrium and at different times t (mg/g^{-1}) and k_1 is the rate constant of the first-order model for the adsorption process (min^{-1}).

The pseudo-second-order kinetic model is expressed as Eq. (3):

$$\frac{dq}{dt} = k_2(q_2 - q_t)^2 \quad (3)$$

The integrated form is given as Eq. (4):

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \quad (4)$$

where q_2 is the maximum adsorption capacity for the pseudo-second-order adsorption (mg/g) and k_2 is the rate constant of the pseudo-second-order model for the adsorption process ($\text{g mg}^{-1} \text{min}^{-1}$).

The intraparticle diffusion equation can be written as Eq. (5):

$$q_t = k_p t^{1/2} + B \quad (5)$$

where B is the intercept and k_p is the intraparticle diffusion rate constant ($\text{g mg}^{-1} \text{min}^{-1/2}$).

The plots of $\ln(q_e - q_t)$ versus t for the first-order reaction and t/q_t against t for the pseudo-second-order reaction (Fig. 4) for the adsorption of ZX-1 on polyester fibers helped us obtain the rate parameters. The kinetic parameters of ZX-1 under different conditions were calculated from these plots and are given in Table I. The correlation coefficients for the first-order kinetic model (R_1^2 's) were between 0.312 and 0.567, and the correlation coefficients for the pseudo-second-order kinetic model (R_2^2 's) were between 0.996 and 0.999. It seemed that the

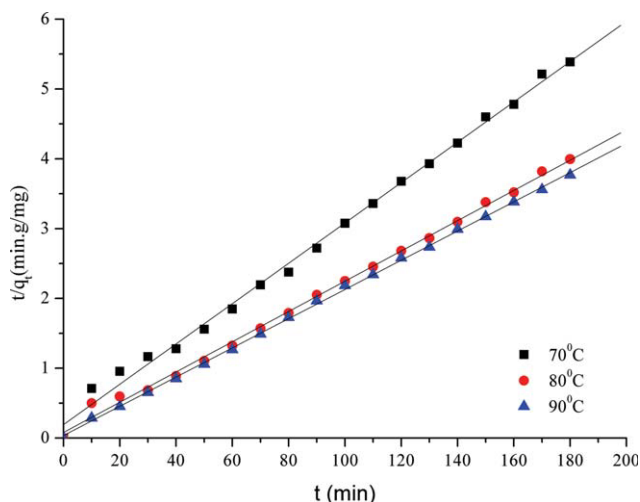


Figure 4 Pseudo-second-order kinetic adsorption of ZX-1 on the polyester fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Kinetic Parameters of ZX-1 Adsorption on Polyester Fibers at Various Temperatures

Kinetic model	Temperature		
	70°C	80°C	90°C
First-order			
$C_0 \times 10^3$ (mg/L)	1.2	1.2	1.2
$k_1 \times 10^{-2}$ (min ⁻¹)	-1.197	-1.011	-1.630
q_e (mg/g)	7.83	4.22	4.17
R_1^2	0.567	0.312	0.522
SE (%)	63.38	75.49	75.93
Pseudo-second-order			
$k_2 \times 10^{-3}$ (g mg ⁻¹ min ⁻¹)	4.323	5.938	11.902
q_2 (mg/g)	34.60	46.08	47.85
R_2^2	0.996	0.997	0.999
SE (%)	4.85	3.61	1.60
Intraparticle diffusion			
k_p (g mg ⁻¹ min ^{-1/2})	1.320	1.318	0.615
B	18.39	30.52	40.37
R_p^2	0.600	0.411	0.406

adsorption system was more fitted to the pseudo-second-order kinetic model. A similar phenomenon was observed in the adsorption of disperse dyes by polyester fibers.²⁵ The k_2 values indicated a steady increase in k_2 from 4.323×10^{-3} to 1.1902×10^{-2} with an increase in the temperatures from 70 to 90°C (Table I). Such a result revealed that the adsorption of ZX-1 onto the polyester fiber possibly followed a physisorption mechanism; increasing temperature generally increased the rate of approach to equilibrium and the equilibrium adsorption capacity.

Because the first-order and pseudo-second-order models could not confirm the potential diffusion mechanism of ZX-1 onto the polyester fibers, an intraparticle diffusion model was used to further study the mechanism. If this diffusion process did occur, the plot of uptake, q_t versus $t^{1/2}$ (square root of time), should have been linear and should have passed through the origin. Thus, the intraparticle diffusion would have been the sole rate-limiting process.^{26,27} Values of k_p ²⁸ were obtained from the slopes of the linear portions of the plots and are listed in Table I. The correlation coefficients for the intraparticle diffusion model (R_p^2) were 0.600, 0.411, and 0.406. These values indicated that the adsorption of ZX-1 on the polyester fibers did not fit the intraparticle diffusion model.

The validity of the studied models was further verified with the sum of squared errors [SE (%)], as given by Eq. (6):

$$SE = \frac{100}{n - 1} \sum \frac{|Q_{e,exp} - Q_{e,pre}|}{Q_{e,exp}} \quad (6)$$

where n is the number of data points. $Q_{e,exp}$ is the experimental concentration at any time; $Q_{e,pre}$ the corresponding predicted concentration according to the equation under study with best fitted parame-

ters; It was reported that the fit is better when the SE values are below 5.²⁹ The experimental results (Table I) show relatively low SE values for the pseudo-second-order compared to the first-order model. This indicated that the predicted values of Q_e in the case of the second-order model were very close to the experimental values. These results confirmed that the adsorption of ZX-1 on polyester fiber was best described by the pseudo-second-order model. Similar phenomena were observed for drin pesticide adsorption by acid-treated olive stones.

In general, the plot of q_t versus $t^{1/2}$ may be multilinear, which might be caused by two or more steps in the adsorption processes.³⁰⁻³² Figure 5 indicates that two linear stages were involved with a rapid diffusion and saturation of the diffusion, whereas intraparticle diffusion was the rate-controlling process in the first stage. Thus, predominantly, ZX-1 adsorption took place rapidly by surface adsorption and was followed by intraparticle diffusion. The second step corresponded to the final equilibrium adsorption process, where the intraparticle diffusion started to slow down because of the extremely low solute concentration in solution.

Adsorption isotherms

Adsorption isotherms were used to describe the equilibrium of the ZX-1 between the aqueous solution and the solid phase. Depending on the nature of the adsorption system, the isotherm model could determine maximum adsorption capacity and several thermodynamic parameters of ZX-1 on the fibers; this knowledge could be used for a better understanding of the binding mechanism. According to the results of the kinetic study and to achieve a compromise between the adsorption efficiency and

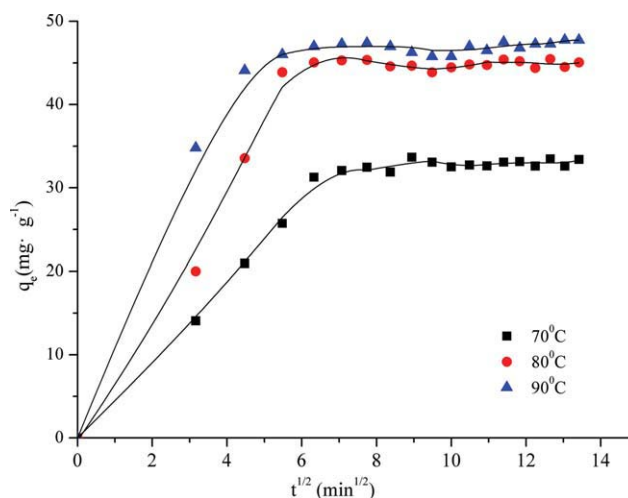


Figure 5 Intraparticle diffusion plot for ZX-1 adsorption on polyester fibers at different temperatures. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

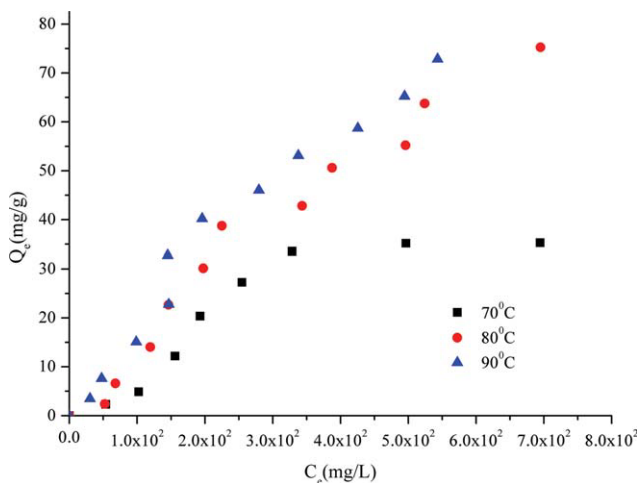


Figure 6 Experimental adsorption data at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the duration of the full analysis, 1.5 h was chosen as the equilibrium time for obtaining the adsorption isotherms. Figure 6 shows the adsorption isotherms of the studied ZX-1 (initial concentration = 0.1–2.0 g/L) at various temperatures (70, 80, and 90°C). We observed that the higher temperature improved the uptake capacity of ZX-1 on the polyester fibers; this could have been a result of more openness in the polymer molecules at temperatures above T_g .³³ The adsorption data were analyzed with the Nernst, Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm model equations.^{34–37} Their expressions are shown by eqs. (7)–(10), respectively:

Nernst equation:

$$q_e = K_N C_e \quad (7)$$

Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m K_L} \right) \frac{1}{C_e} \quad (8)$$

Freundlich equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (9)$$

D–R equation:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (10)$$

where q_e is the equilibrium ZX-1 concentration on the adsorbent (mg/g^{-1}); C_e is the equilibrium ZX-1

concentration in the solution (mg/L^{-1}); q_m is the monolayer capacity of the adsorbent (mg/g); K_N is the Nernst constant (L/mg); K_L is the Langmuir constant (L/mg) and is related to the free energy of adsorption (ΔG^0); K_F is the Freundlich constant [$\text{g}^{-1} \text{L}^{1/n} \text{mg}^{(1-1/n)}$]; n is the heterogeneity factor, which has a lower value for more heterogeneous surfaces (dimensionless); β is a constant related to ΔG^0 per mole of the adsorbate (mol^2/kJ^2); and ε is the Polanyi potential, which is equal to Eq. (11):

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (11)$$

where R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$) and T is the absolute temperature (K). Hence, by plotting $\ln q_e$ versus ε^2 , we could obtain the value of q_m (mg/g^{-1}) from the intercept and the value of β from the slope in Figure 9 (shown later), and the value of adsorption energy (E) could be correlated to β with the following relationship:³⁸

$$E = \frac{1}{(2\beta)^{1/2}} \quad (12)$$

The Nernst, Langmuir, Freundlich, and D–R parameters for the ZX-1 adsorption on the polyester fibers are listed in Table II. The fit of the data suggested that the ZX-1 adsorption on the polyester fibers was closer to the Langmuir model (Fig. 7) than to the Freundlich (Fig. 8) or D–R models (Fig. 9); this is shown by a comparison of the correlation coefficients for the Nernst, Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm model (R_N , R_L , R_F , R_{D-R}) values in Table II.

TABLE II
Isotherm Constants of ZX-1 Adsorption on Polyester Fibers at Various Temperatures

Isotherm model	Temperature		
	70°C	80°C	90°C
Nernst			
$K_N \times 10^{-2}$	0.578	1.122	1.319
$R_N \times 10^{-1}$	8.873	9.790	9.769
Langmuir			
q_m (mg/g)	57.84	167.79	114.27
K_L (L/mg) $\times 10^{-3}$	3.1419	1.1137	2.7114
R_L	0.928	0.984	0.990
Freundlich			
n	0.868	0.836	0.994
$K_F \times 10^{-2}$ ($\text{g}^{-1} \text{L}^{1/n} \text{mg}^{(1-1/n)}$)	3.155	4.159	15.04
R_F	0.939	0.957	0.980
D–R			
q_m (mg/g)	37.39	59.13	65.00
$\beta \times 10^{-3}$ (mol^2/kJ^2)	2.74	2.46	1.75
R_{D-R}	0.990	0.982	0.947
E (kJ/mol)	13.51	14.26	16.90

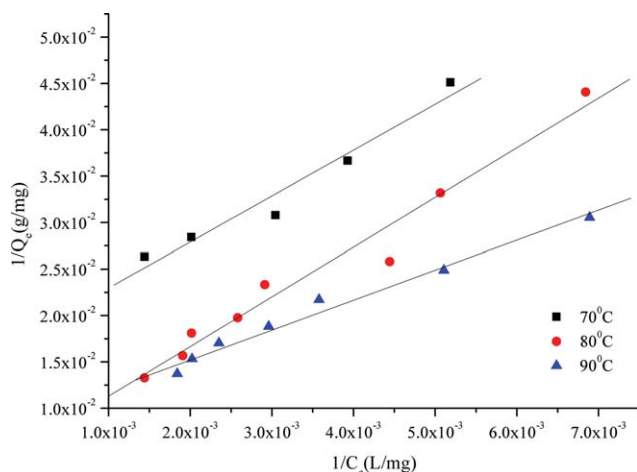


Figure 7 Langmuir plot of ZX-1 adsorption on the polyester fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

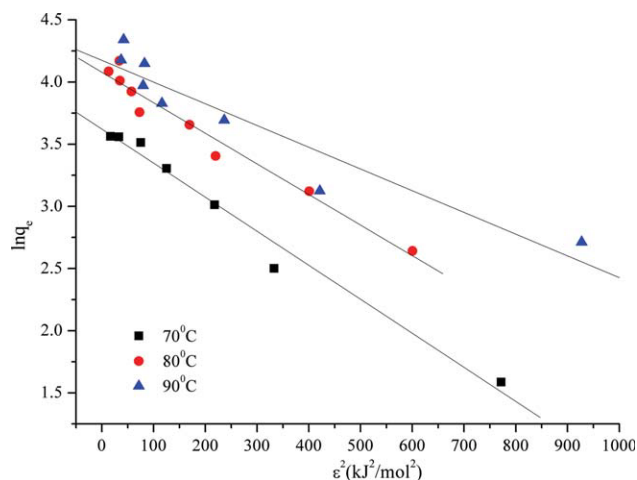


Figure 9 D-R plot of ZX-1 adsorption on the polyester fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Adsorption thermodynamics

In adsorption process, both energy and entropy (ΔS^0) must be taken into account to determine which processes will occur spontaneously. The values of the thermodynamic parameters are the actual indicators for practical applications of a process. The amount of ZX-1 adsorbed at equilibrium at different temperatures (70, 80, and 90°C) were examined to obtain thermodynamic parameters for the adsorption system. k_2 of ZX-1 adsorption is expressed as a function of temperature by the following Arrhenius-type relationship:

$$\ln K_2 = \ln A - \frac{E_a}{RT} \tag{13}$$

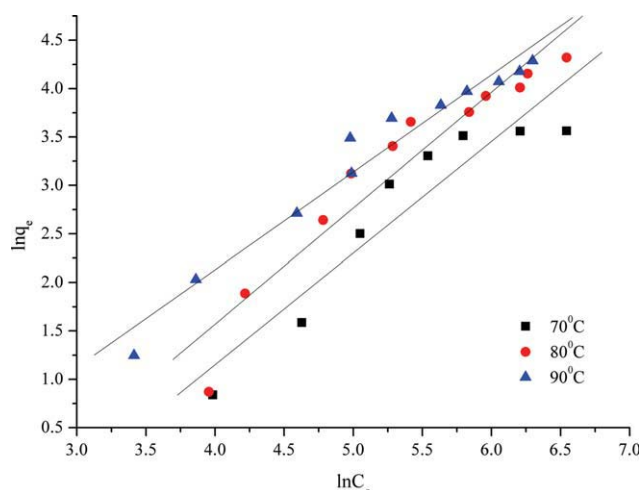


Figure 8 Freundlich plot of ZX-1 adsorption on the polyester fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where E_a is the Arrhenius activation energy of adsorption; A is the Arrhenius factor, R is equal to $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, and T is the operating temperature. When $\ln k_2$ was plotted versus $1/T$ (Fig. 10), a straight line with slope $-E_a/R$ was obtained. The magnitude of the activation energy provided an idea about the type of adsorption, which was mainly physical or chemical. Low activation energies (5–40 kJ/mol) are characteristics for physical sorption, whereas higher activation energies (40–800 kJ/mol) suggest chemisorption.^{39,40} The result obtained was 38.21 kJ/mol with a correlation coefficient (R^2) of 0.948 (Table III) for the adsorption of ZX-1 on the polyester fibers; this indicated that the adsorption had a low potential barrier, which corresponding to physical sorption.

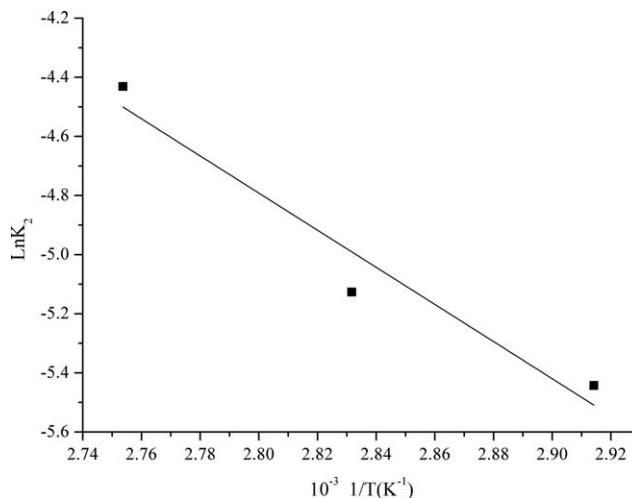


Figure 10 Activation energy of ZX-1 adsorption on the polyester fibers.

TABLE III
Thermodynamic Parameters Calculated According to the Pseudo-Second-Order Model for ZX-1 Adsorption on the Polyester Fibers

Temperature (°C)	E_a (kJ/mol)	K_C	R^2	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J K ⁻¹ mol ⁻¹)
70	+38.21	0.073	0.948	7.47	46.94	115.46
80		0.136		5.87		
90		0.180		5.18		

The other thermodynamic parameters,^{41,42} changes in (ΔG^0), enthalpy (ΔH^0), and (ΔS^0), were determined with eqs. (14)–(16), respectively:

$$K_C = \frac{C_A}{C_S} \quad (14)$$

$$\Delta G^0 = -RT \ln K_C \quad (15)$$

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (16)$$

where K_C is the equilibrium constant,⁴³ C_A is the amount of ZX-1 adsorbed on the adsorbent at equilibrium (mg/g), and C_S is the equilibrium concentration of ZX-1 in the solution (mg/L). q_2 of the pseudo-second-order model from Table I was used to obtain C_A and C_S . T is the solution temperature (K), and R is the gas constant. ΔH^0 and ΔS^0 were calculated from the slope and intercept of van't Hoff plot of $\ln K_C$ versus $1/T$ (Fig. 11). All of the thermodynamic parameters are given in Table III.

Generally, ΔG^0 for physical sorption is between -20 and 0 kJ/mol, but chemisorption is in the range -80 to -400 kJ/mol.⁴⁴ The results, shown in Table III, were 7.47 kJ/mol at 70°C to 5.18 kJ/mol at 90°C ; these values indicated that the adsorption reaction was not a spontaneous one and that the system gained energy from an external source.⁴⁵ The positive value of ΔH^0 indicated that the adsorption of ZX-1 on the polyester fiber was endothermic, so increasing

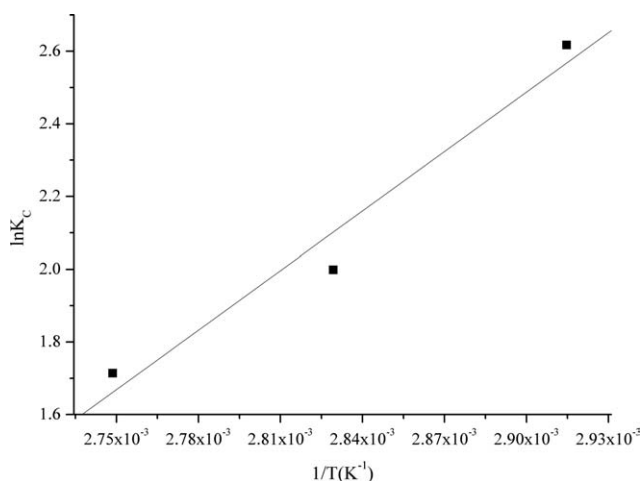


Figure 11 Plot of $\ln K_C$ versus $1/T$ for the estimation of thermodynamics.

the temperature led to a higher adsorption of ZX-1 at equilibrium.^{46,47}

CONCLUSIONS

The adsorption kinetics and thermodynamics of ZX-1 on the polyester fibers were investigated. The treatment temperature and time of ZX-1 on the polyester fibers were the main factors affecting the adsorption kinetics and equilibrium. A pseudo-second-order kinetic model agreed very well with the dynamic behavior of ZX-1 adsorption on the polyester fibers. The results fitted well with Langmuir adsorption isotherm. The activation energy of adsorption was evaluated with the k_2 values. The positive value of E_a confirmed the nature of physical adsorption of ZX-1 on polyester fiber. The positive ΔG^0 values showed that the adsorption process was not a spontaneous one and that the system gained energy from an external source, and the positive value of ΔH^0 indicated that the adsorption of the ZX-1 on the polyester fiber was endothermic, so increasing the temperature led to a higher adsorption of ZX-1 at equilibrium.

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