

Comparative Study on Adsorptive Characteristics of Diazinon in Water by Various Adsorbents

Keon Sang Ryoo,* Sun Young Jung, Hun Sim, and Jong-Ha Choi

Department of Applied Chemistry, Andong National University, Andong 760-749, Korea. *E-mail: ksr@andong.ac.kr
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The aim of the present study is to explore the possibility of utilizing fly ash and loess, as alternative to activated carbon, for the adsorption of diazinon in water. Batch adsorption experiment was performed to evaluate the influences of various factors like initial concentration, contact time and temperature on the adsorption of diazinon. The adsorption data shows that fly ash is not effective for the adsorption of diazinon. The equilibrium data for both activated carbon and loess were fitted well to the Freundlich isotherm model. The pseudo-second-order kinetic model appeared to be the better-fitting model because it has higher R^2 compared to the pseudo-first-order kinetic model. The thermodynamic parameters such as free energy (ΔG), the enthalpy (ΔH) and the entropy (ΔS) were calculated. Contrary to loess, the ΔG values of activated carbon were negative at the studied temperatures. It indicates that the adsorption of diazinon by activated carbon is a favorable and spontaneous process. The positive ΔH values of activated carbon and loess suggest that the diazinon adsorption process is endothermic in nature. In addition, the positive ΔS values show that increased randomness occurs at the solid/solution surface during the adsorption of diazinon.

Key Words : Diazinon, Activated carbon, Loess, Fly ash, Isotherm

Introduction

Organophosphate pesticides (OPPs) are one group of the most frequently encountered pesticides in the world to reduce the loss of crop yield. Diazinon ($C_{12}H_{21}N_2O_3PS$) is an organophosphate pesticide widely used for the control of insects in cereals, fruits, vines, vegetables, rice and other crops.¹⁻³ It kills insects by inhibiting the action of enzymes in the nervous system.⁴ Diazinon has been detected in the aquatic environment due to its high usage frequency in agriculture.⁵⁻⁷

Some techniques for removal of pesticides in water have been developed. Firstly, physical methods including activated carbon adsorption are very common for eliminating pesticides from water.⁸ Then, chemical methods performed by ozonation, gas charge plasma and Fenton treatment have been intensively investigated.^{9,10} More recent studies have focused on some new methods such as photocatalysis, biological methods and irradiation techniques through UV and so on.^{11,12}

Activated carbon has been known as an attractive technology for removing a variety of non-polar organic pollutants from wastewater. However, due to its high-cost, there is a necessity for developing and testing other adsorbents. Consequently, many investigators have studied the feasibility of using low cost substances for the treatment of wastewater.

Loess and fly ash may be used as alternative adsorbents replacing activated carbon for the removal of diazinon. Over several ten million years, Korean loess has been transported from arid areas in China and Mongolia by the wind and deposited at mountain regions near the coast. Especially, Gyeongju, Goseong, Sanchung and Hamyang are regions

that covered by thick loess stacks. The adsorptive capability of loess only or modified loess for organic compounds was reported by several literatures.¹³⁻¹⁵

Fly ash, a combustion by-product generated from a thermal power plant, has been widely used in a range of applications and particularly as filler for cement in concrete. However, large amounts are not still used and this requires disposal. Therefore, it is necessary to broad the use of fly ash for favorable environmental benefits. A lot of researcher studied on the adsorptive properties of fly ash and concluded that it has a significant adsorption capacity for the removal of organic compounds and dyes from aqueous solutions.¹⁶⁻¹⁸

The aim of the present study is to explore the possibility of utilizing loess and fly ash as well as activated carbon for the adsorptive removal of diazinon in water. Here, we investigated the effect of various factors such as temperature, contact time and concentration in details. The adsorption data were fitted to the Freundlich and the Langmuir isotherm equations. The adsorption kinetics of diazinon in water on each adsorbent were also analyzed by using pseudo-first-order and pseudo-second-order kinetic models. In addition, thermodynamic parameters such as the activation energy (E_a), the free energy (ΔG), the enthalpy (ΔH) and the entropy (ΔS) were estimated to study the feasibility of the adsorption process.

Experimental

Materials and Reagents. Fly ash was provided from an electrical power generating station in Pohang. Yellow sand was collected from Gyeongju. Activated carbon (20-40 mesh) was purchased from Aldrich Company, MO, USA.

All adsorbents were washed with distilled water for 24 h to remove dust and fine particulate matter. The washed adsorbents were dried overnight at 105 °C before use. Diazinon was obtained from Seongbo Chemical Company, Gyeonggi Do, Korea. All solvents supplied from J. T. Baker, Inc., NJ, USA were HPLC grade.

Adsorption and Kinetic Studies. Adsorption capacity and kinetics of adsorbents were determined by means of controlled experiments in a batch system. Adsorption studies were conducted by varying different parameters such as initial concentration, contact time and temperature. The adsorption and kinetic experiments were performed in the closed batch system prepared in 100 mL flasks, sealed with a cap. A series of flasks containing diazinon of known concentration in aqueous solution were kept in a thermostatic water bath placed on a shaker. A known amount of adsorbent was added into flasks and allowed to equilibrate. Contact time was ranged from 1 h to 1 day. At a given time interval, 1 mL of the aqueous solution was withdrawn by a syringe. Subsequently, the samples were centrifuged to separate aqueous and solid phases and then brought into a solid phase extraction (SPE) column. Diazinon was extracted using a cartridge (150 × 4.6 mm, Varian, USA) with a Bond Elut[®] C 18 (20 g of mass, 40 μm of particle size). Blank samples without adsorbent were also prepared to determine the potential losses of diazinon to flask walls and from processes other than adsorption.

Analysis. The compositions of adsorbents were analyzed with a X-ray Fluorescence Spectrometer (ZSX Primus II, Japan). The pH was measured by a pH meter (Radiometer PHM 250 ion analyser, USA). Particle size distribution was performed by a Particle Size Analyzer (Mastersizer 2000, England). Nitrogen adsorption-desorption isotherms of adsorbents at 77 K were determined using a Specific Surface Area Analyzer (ASAP-2010, Micromeritics, USA). The specific surface areas were obtained with reference to the Brunauer-Emmett-Teller (BET) method using the N₂ adsorption data. The pore volume were calculated using a BJH method. Concentration of diazinon was performed with a GC-TSD (CP 3800, Varian, USA). Separations were achieved using a fused silica capillary column (30 m × 0.320 mm I.D. × 0.25 μm film thickness, HP-5, USA). The extracted sample (1 μm) was injected with a split ratio of 1/10. The temperature was held for 1 min at 90 °C followed by a 8 °C/min ramp to the 220 °C for 5 min and then a 10 °C/min ramp to a final temperature of 250 °C. Response factors for diazinon was calculated from four concentration levels of external standards.

Table 1. Composition and property of fly ash, loess and activated carbon

Composition	Fly ash Loess Activated carbon		
	SiO ₂	60.68	50.5
Al ₂ O ₃	26.11	39.8	n.d.
Fe ₂ O ₃	4.29	5.73	n.d.
TiO ₂	1.42	0.50	n.d.
Na ₂ O	0.43	0.16	n.d.
CaO	3.52	0.91	n.d.
MgO	0.73	0.53	n.d.
K ₂ O	1.47	0.83	n.d.
SO ₃	0.24	0.08	n.d.
pH	9.8	7.2	5.6

^an.d.: not detected

Results and Discussion

Characterization of Adsorbent Materials. The adsorbent materials selected in this study were characterized through physicochemical analysis. The chemical composition and property of fly ash, loess and activated carbon is given in Table 1. As seen in Table 1, most of chemical compounds in fly ash are silica and alumina oxide together with some iron and calcium oxide as minor. Loess has also similar compositions. The pH of fly ash, loess and activated carbon shows different values. Fly ash exhibits weak basicity, while loess and activated carbon show neutral and weak acidic property, respectively.

The BET surface area and pore volumes of adsorbents obtained from N₂ are presented in Table 2. It is seen that fly ash has the lowest surface area and pore volume at 2.16 m²g⁻¹ and 0.003 cm³g⁻¹, respectively. The specific surface area of loess were determined as 41.69 m²g⁻¹ and its pore volume was found to be 0.125 cm³g⁻¹. Activated carbon exhibits higher surface area and pore volume than loess. It indicates that activated carbon has more accessible sites for adsorption. Fly ash and loess range mainly in particle size from 0.005 to 2.0 mm. On the other hand, activated carbon is composed of the particle size larger than 2 mm.

Equilibrium Time. The adsorption studies were carried out using different initial concentrations in the range of 10–100 mg L⁻¹ of diazinon for a dose of 1 g adsorbent, contact time (1–24 h) and temperature (298 K). Figures 1–4 represent the data from the adsorption studies of diazinon with various adsorbents for initial concentration plotted as a function of contact time. The time corresponding to the maximum

Table 2. Physicochemical properties of fly ash, loess and activated carbon

Adsorbent	Particle size distribution				Specific surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)
	(> 2 mm)	(2–0.005 mm)	(0.005–0.002 mm)	(< 0.002 mm)		
Fly ash	2.84	84.65	7.35	5.19	2.16	0.003
Loess	-	78.06	13.81	9.68	41.69	0.125
Activated carbon	100	-	-	-	678.03	0.753

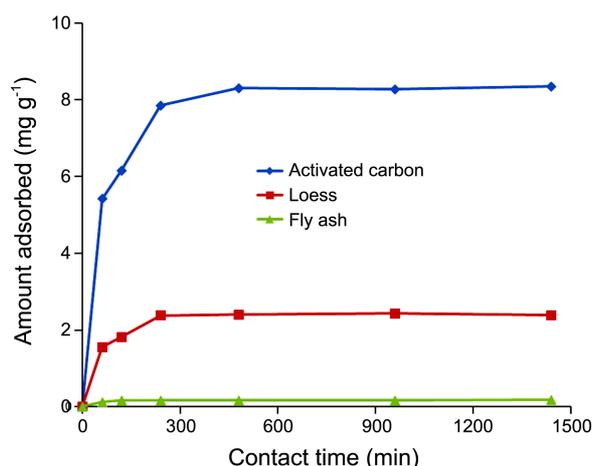


Figure 1. Adsorption of diazinon on various adsorbents (1 g L⁻¹) at 298 K for initial concentration (10 mg g⁻¹).

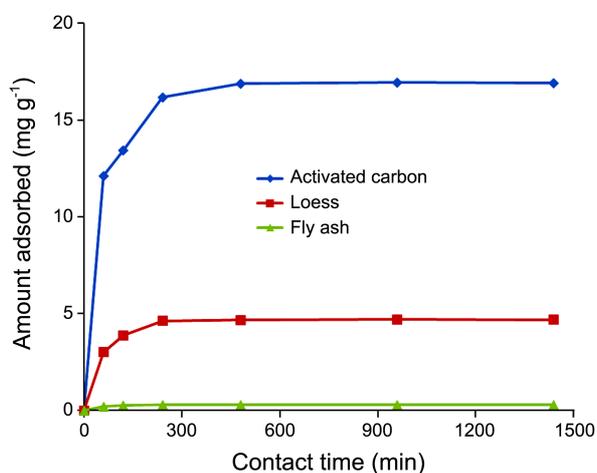


Figure 2. Adsorption of diazinon on various adsorbents (1 g L⁻¹) at 298 K for initial concentration (20 mg g⁻¹).

adsorption was considered as the equilibrium adsorption time.

As seen in Figures 1-4, the three adsorbents exhibited varying equilibrium time and adsorption behavior. The equilibrium adsorption times of diazinon by activated carbon and loess were found within 24 h of contact time. Whereas, in case of fly ash, the increasing adsorption of diazinon, regardless of initial concentrations, was not observed during the contact time. As a result, it indicates that fly ash can not play a crucial role as an adsorbent replacing activated carbon. It may be thought that this is because the surface area and the pore volume of fly ash have too much lower values, compared to other two adsorbents.

Contrary to fly ash, loess showed a little higher adsorption for diazinon. Loess reached equilibrium very quickly in about 4 h. After 4 h, the remaining concentration of diazinon in aqueous solution remained constant. Depending on the initial concentrations, a roughly 15-20% adsorption of diazinon at equilibrium was achieved by loess. Activated carbon took 8 h arriving at equilibrium. Since then, any additional adsorption of diazinon was not occurred. The percent

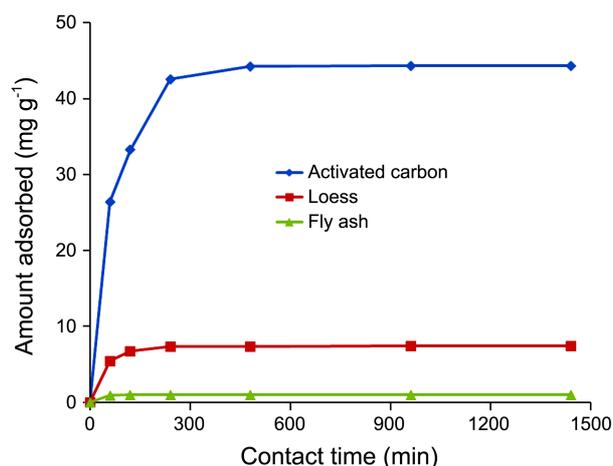


Figure 3. Adsorption of diazinon on various adsorbents (1 g L⁻¹) at 298 K for initial concentration (50 mg g⁻¹).

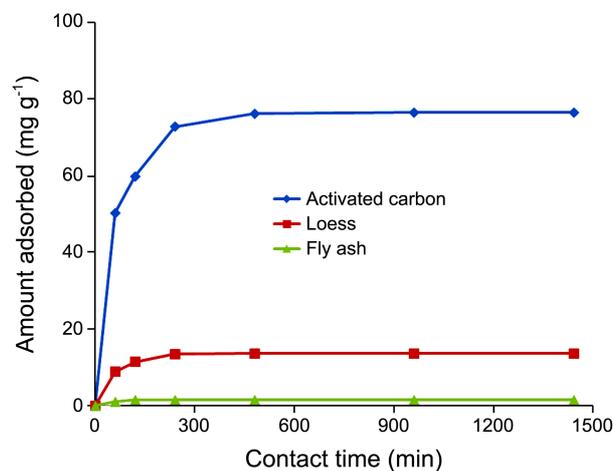


Figure 4. Adsorption of diazinon on various adsorbents (1 g L⁻¹) at 298 K for initial concentration (100 mg g⁻¹).

adsorption of diazinon on activated carbon was found to lie in the range of approximately 75-85%.

The Adsorption Isotherm. Two widely used isotherm models, Freundlich and Langmuir isotherms,^{19,20} were employed to investigate the adsorption behavior. The Freundlich isotherm, which is an empirical equation for multi-layer adsorption of adsorbate onto heterogeneous surfaces with a non-uniform distribution, can be expressed as follows:

$$q_e = k_f(c_e)^{1/n} \quad (1)$$

where, k_f and n are the Freundlich constants related to adsorption capacity and the adsorbent affinity for the adsorbate, respectively. For linearization of the data, the Freundlich equation is written in logarithmic form:

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \quad (2)$$

A linear plot of $\log q_e$ versus $\log c_e$, yields a slope $1/n$ and an intercept of $\log k_f$. The value of k_f is roughly an indicator of adsorption capacity. The value of $1/n$, ranging in between 0

and 1, is a measure of the adsorption intensity.

The Langmuir isotherm model describes mono-layer adsorption on homogeneous surface with no interaction between adjacent adsorbed solutes. The Langmuir isotherm is written as follows:

$$\frac{c_e}{q_e} = \frac{1}{Qb} + \frac{c_e}{Q} \quad (3)$$

where, q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}), c_e is equilibrium solute concentration in solution (mg L^{-1}). Q and b are empirical constants denoting mono-layer capacity and energy of adsorption, respectively, and can be evaluated from the slope and intercept of the linear plot of c_e/q_e against c_e .

The Freundlich and Langmuir isotherms of diazinon on loess and activated carbon are presented in Figures 5 and 6. It was observed that the experimental data deviates more in case of the Langmuir than Freundlich plot. This is further verified by the correlation coefficient (R^2) value, shown in Table 3, of the linear plots. It is evident that the Freundlich isotherm fits the experimental data better than the Langmuir

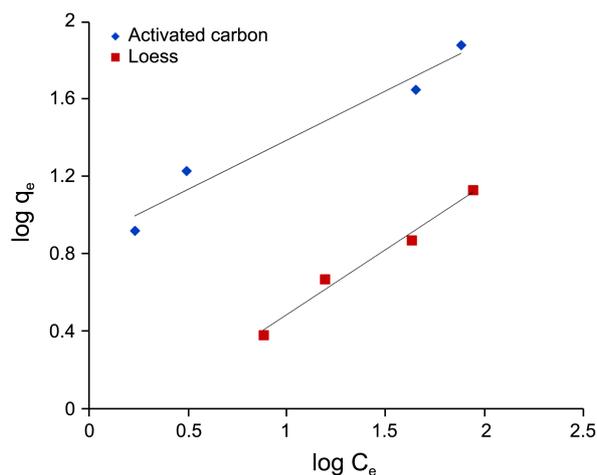


Figure 5. Freundlich isotherms of diazinon on activated carbon and loess at 298 K.

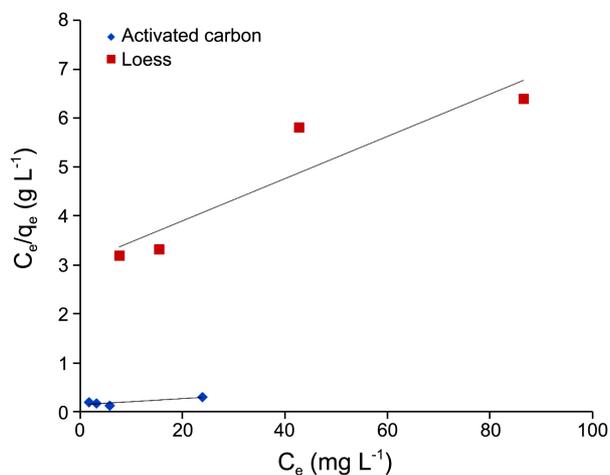


Figure 6. Langmuir isotherms of diazinon on activated carbon and loess at 298 K.

Table 3. Freundlich and Langmuir constants for adsorption of diazinon on loess and activated carbon at 298 K

Adsorbents	Langmuir constants			Freundlich constants		
	Q (mg g^{-1})	b (L mg^{-1})	R^2	$1/n$	k_F	R^2
Loess	24.69	0.014	0.8578	0.71	0.56	0.9817
Activated carbon	202.75	0.025	0.7162	0.84	5.37	0.9586

isotherm, as confirmed by the higher values of R^2 for both loess and activated carbon. This suggests that some heterogeneity in the surface or pores of activated carbon and loess will play a role in diazinon adsorption. Corresponding isotherm constants from the linear plots were also calculated and listed in Table 3. It was found that the Freundlich and Langmuir constant values, k_F and Q , for diazinon adsorption obtained by activated carbon are higher in comparison to the values obtained for loess.

Adsorption Kinetics. In order to investigate the adsorption processes of diazinon on loess and activated carbon, two well known models, pseudo-first-order and pseudo-second-order kinetic model,^{21,22} were employed to describe the adsorption process.

The pseudo-first-order kinetic model is given as:

$$\log \frac{q_e}{q_e - q_t} = \frac{k_1}{2.303} t \quad (4)$$

Eq. (4) can be rearranged to obtain a linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

The values of q_e and k_1 are determined from the slope and intercept of the straight line.

The pseudo-second-order kinetic model is presented as:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (6)$$

Eq. (6) can be linearized as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

The value of q_e and k_2 are determined from the slope and intercept of the straight line.

where, q_e and q_t refer to the amount of diazinon adsorbed (mg g^{-1}) at equilibrium and at any time, t (min), respectively. k_1 and k_2 are the equilibrium rate constants of the pseudo-first-order adsorption (min^{-1}) and the pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$), respectively.

Figures 7-10 show the pseudo-first-order and pseudo-second-order kinetic model fitting to the experimental data for activated carbon and loess at different initial concentrations. The experimental amount of adsorption equilibrium ($q_{e,\text{exp}}$), the rate constants of pseudo-first-order and pseudo-second-order kinetic (k_1 and k_2), the calculated amount of adsorption equilibrium ($q_{e,\text{cal}}$) and the correlation coefficients (R^2) are shown in Table 4.

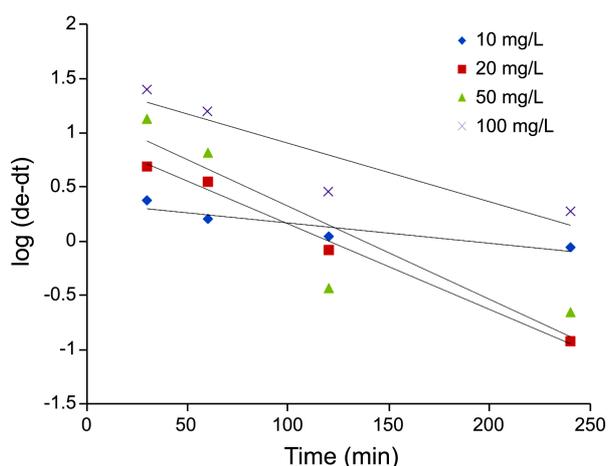


Figure 7. Pseudo-first-order kinetics of diazinon on activated carbon at different initial concentration.

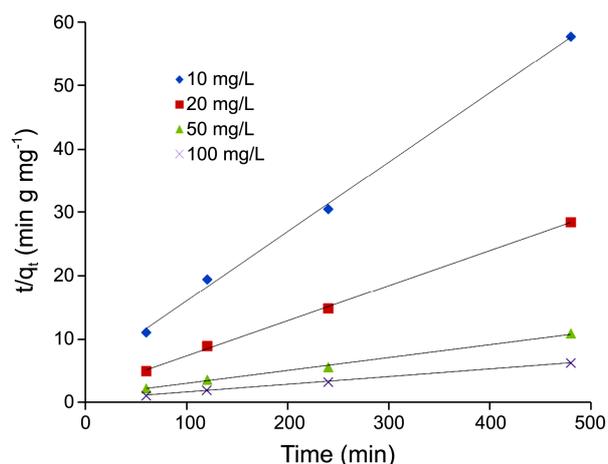


Figure 9. Pseudo-second-order kinetics of diazinon on activated carbon at different initial concentration.

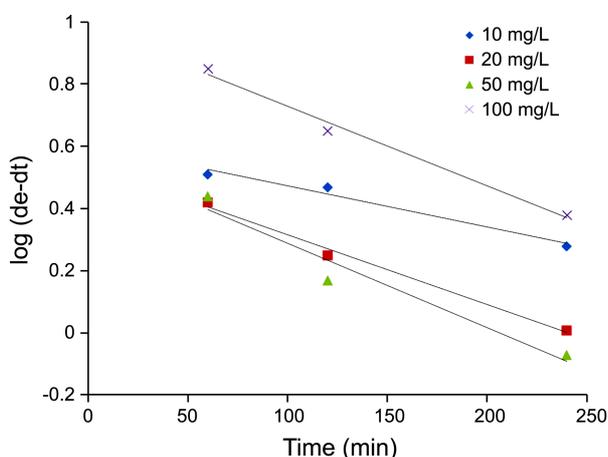


Figure 8. Pseudo-first-order kinetics of diazinon on loess at different initial concentration.

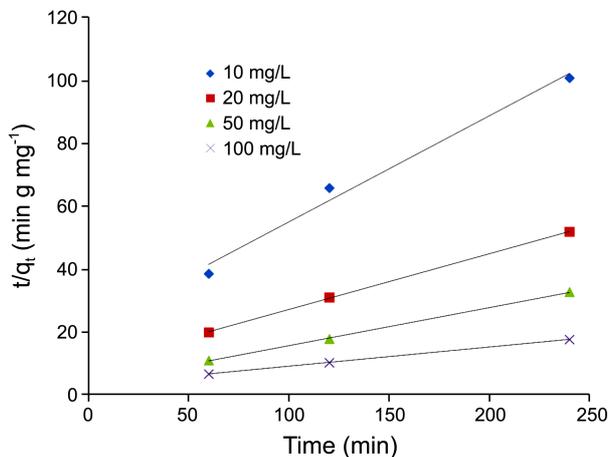


Figure 10. Pseudo-second-order kinetics of diazinon on loess at different initial concentration.

From Table 4, it was observed that the calculated amount of adsorption equilibrium ($q_{e,cal}$) from pseudo-first-order and pseudo-second-order kinetic model is relatively close to the experimental amount of adsorption equilibrium ($q_{e,exp}$). Meanwhile, the pseudo-second-order kinetic model, as shown clearly in Figures 7-10, appeared to be the better-

fitting model because it has higher R^2 than that of the pseudo-first-order kinetic model for both activated carbon and loess. This result suggests the diazinon adsorption can be approximated more appropriately by the pseudo-second-order kinetic model.

Estimation of Thermodynamic Parameters. To study

Table 4. Pseudo first and pseudo second order kinetic model parameters for different initial diazinon concentration at 298 K

Adsorbent	Initial concentration (mg L ⁻¹)	$q_{e,exp}$ (mg g ⁻¹)	Pseudo first order kinetic model			Pseudo second order kinetic model		
			$q_{e,cal}$ (mg g ⁻¹)	$k_1 \times 10^{-2}$ (min ⁻¹)	R^2	$q_{e,cal}$ (mg g ⁻¹)	$k_2 \times 10^{-3}$ (g mg ⁻¹ min ⁻¹)	R^2
Activated carbon	10	8.31	7.80	1.30	0.8494	10.82	1.02	0.9979
	20	16.89	17.01	1.30	0.9915	20.32	0.80	0.9990
	50	44.26	39.83	1.50	0.8072	59.11	0.18	0.9975
	100	76.21	75.68	1.30	0.8323	100.0	0.12	0.9991
Loess	10	2.38	4.77	0.65	0.9714	2.20	18.10	0.9860
	20	4.63	5.65	1.27	0.9919	5.45	3.77	0.9998
	50	7.34	8.19	1.82	0.9506	8.72	3.17	0.9997
	100	13.52	15.91	1.35	0.9892	16.24	1.22	0.9989

Table 5. Activation energy (E_a) values at different temperatures

Adsorbents	Temperature (K)	E_a (kJ mol ⁻¹)
Loess	278-298	3.79
	298-328	7.58
Activated carbon	278-298	3.21
	298-328	7.86

the effect of temperature on adsorption, adsorption kinetic experiments were further carried out using different temperatures (278, 298 and 328 K) with contact time at the selected diazinon concentration (100 mg L⁻¹). As the pseudo-second-order kinetic model is better in describing diazinon adsorption, the activation energy of adsorption, E_a , was obtained from the pseudo-second-order constant, k_2 , by using the following Arrhenius equation:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (8)$$

where A is the pre-exponential factor or the frequency factor and R is the gas constant (8.314 J mol⁻¹K⁻¹). T is the absolute temperature.

The corresponding plot of the values of $\ln k_2$ against $1/T$ at different temperatures was drawn and then the data were calculated to obtain the activation energy. The physisorption processes usually have low activation energies (5-40 kJ mol⁻¹), while higher activation energies (40-800 kJ mol⁻¹) suggest chemisorption.¹⁷ As given in Table 5, the values of E_a were found to be 3-8 kJ mol⁻¹. It can be suggested that the adsorption of diazinon may be physical in nature, considering that the values of E_a are in the typical range for physisorption.

In order to study the feasibility of the process and application of the present adsorbents, the thermodynamic parameters such as the free energy (ΔG), the enthalpy (ΔH) and the entropy (ΔS) were determined by using the following equations:

$$K_d = \frac{c_e}{q_e} \quad (7)$$

$$\Delta G = -RT \ln K_d \quad (8)$$

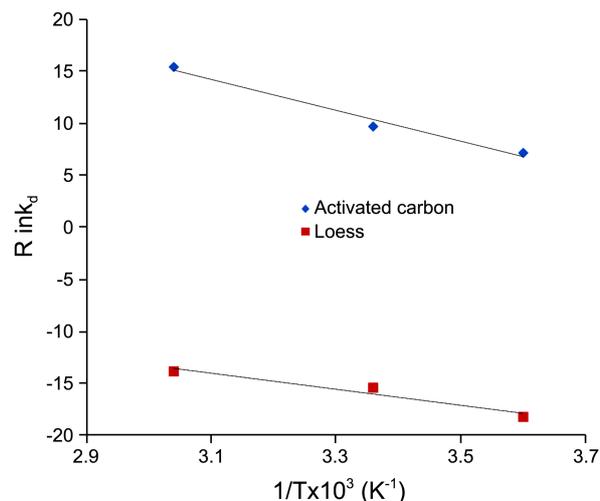
$$\Delta G = \Delta H - T\Delta S \quad (9)$$

where, K_d is the distribution coefficient (L g⁻¹) for the adsorption. The q_e and the c_e represent the equilibrium solute concentration on the adsorbent (mg g⁻¹) and in the solution (mg L⁻¹), respectively.

The enthalpy (ΔH) and entropy (ΔS) were evaluated by using the following equation:

$$R \ln k_d = \Delta S - \Delta H \frac{1}{T} \quad (10)$$

The plot of $R \ln k_d$ versus $1/T$ is presented in Figure 11. The H and the S values obtained from corresponding to the slope and the intercept of the derived straight line is presented in Table 6.

**Figure 11.** Plot of $\ln k_d$ vs. $1/T$ for estimation of thermodynamic parameters for adsorption of diazinon on activated carbon and loess.**Table 6.** Thermodynamic parameters for diazinon adsorption on loess and activated carbon

Adsorbent	ΔG (kJ mol ⁻¹)			ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
	278 K	298 K	328 K		
Activated carbon	-1.99	-2.88	-5.06	14.73	60.20
Loess	5.06	4.60	4.53	7.800	9.87

As shown in Table 6, contrary to loess, the ΔG of activated carbon shows the negative values at the studied temperatures. It indicates that the adsorption process of diazinon by activated carbon is of fairly favorable and spontaneous nature. The ΔG values decreased from -1.99 to -5.06 kJ mol⁻¹ with increasing temperature, which indicates that the adsorption was more spontaneous at higher temperatures. It is noted that the ΔG value, up to -20 kJ mol⁻¹ is indicative of physisorption, while more negative than -40 kJ mol⁻¹ indicates chemisorption.²³ Therefore, it is clear that the adsorption of diazinon on activated carbon follows the physisorption. Typically, the positive value of ΔH and ΔS confirms the endothermic nature and the increased randomness for the overall adsorption process, respectively. In this study, the ΔH and the ΔS were calculated as positive values for activated carbon and loess. These results imply that the adsorption of diazinon on loess and activated carbon is endothermic process and is aided by increased randomness at the solid/solution interface.

Conclusion

The ability of fly ash, loess and activated carbon in adsorption of diazinon from water was evaluated. The observed adsorption data show that fly ash is not an effective adsorbent replacing activated carbon. The adsorption isotherm study represents that the adsorption of diazinon by loess and activated carbon follows the Freundlich isotherm

model due to the higher R^2 values than the Langmuir isotherm model. The adsorption kinetics were more appropriately described by the pseudo-second-order model rather than pseudo-first-order model. The calculated values of E_a suggest that the adsorption of diazinon may be physical in nature. The ΔG values of activated carbon was negative at the studied temperatures. It indicates that the adsorption process of diazinon is favorable and spontaneous. Moreover, the positive ΔH and ΔS values confirm the endothermic nature of the adsorption and the increased randomness at solution-solute interface during the adsorption of diazinon.

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