Kinetics and thermodynamics of adsorption of azinphosmethyl from aqueous solution onto pyrolyzed (at 600 °C) ocean peat moss (*Sphagnum* sp.)

A.Z. Aroguz*

Chemistry Department, Engineering Faculty, Istanbul University, 34850 Avcilar, Istanbul, Turkey

Abstract

The removal of azinphosmethyl from aqueous solution onto pyrolyzed ocean peat moss (*Sphagnum* sp.), as a residue, from the Rhode Island coast (USA), has been investigated at different temperatures and initial concentrations. The ocean peat moss had been pyrolyzed at 600 °C in nitrogen atmosphere before the adsorption process. The kinetic data obtained from batch studies have been analyzed using pseudo-first order kinetic model. The rate constants were evaluated at different temperatures.

The thermodynamic parameters ($\Delta G°$, $\Delta H°$, $\Delta S°$) for the adsorption process were calculated and the results suggest that the nature of adsorption is endothermic and the process is spontaneous and favorable. The activation energy for adsorption process was estimated, about 18.3 kJ mol^{-1}. According to this value the adsorption of azinphosmethyl onto pyrolyzed ocean peat moss is in the range of physical adsorption.

The experimental data have been modeled using Langmuir, Freundlich and Temkin isotherms. It was found that Langmuir and Freundlich isotherms give the best correlation with the experimental data.
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1. Introduction

Pesticides have been extensively used in agriculture for many years to control pests in crops, vegetables, trees despite of their known toxic effects [1–3]. Therefore, many of them are environmental contaminants and found in surface and ground water. The number of studies of removal of pesticides from aqueous solution is increasing, because of the serious environmental problems and the contamination of waters. There are many techniques to remove pesticides from aqueous solution [3–5]. Among these, the adsorption process is generally considered to be the most effective method. Because of its high adsorption capacity, extraordinary surface area and microporous structure, activated carbon is widely used for pesticides removal from wastewater, for high removal efficiency [6–8]. But it is expensive and it has regeneration problems. Therefore, researchers con-

tinue their work to find out more economic and easily obtainable materials for adsorption [9]. A large number of natural materials such as bentonite [10], natural sediments [11], peat moss [12], fly ash [2], soil-fly ash [13], baggase fly ash [14], wood charcoal [15], hazelnut shell activated carbon [16], coconut shell [17] and natural substances [18,19] are considered effective adsorbents.

Azinphosmethyl is one of the most toxic organophosphorus pesticides and is widely used in agriculture where it causes environmental contamination [19]. There are many studies on azinphosmethyl [1,18–20].

In this study, the adsorption of azinphosmethyl has been extended to another adsorbent, ocean peat moss (*Sphagnum* sp.). The feasibility of using pyrolyzed (at 600 °C) peat moss (PMM600) for removal of azinphosmethyl was investigated and evaluated for its usefulness in simple pseudo-first order models. A kinetic study was carried out, using concentration, contact time, and temperature as parameters. The Thermodynamic parameters for the adsorption of azinphosmethyl were also calculated and discussed.

* Tel.: +90 212 473 70 33; fax: +90 212 473 71 80.
  E-mail address: aroguz@istanbul.edu.tr.

2. Methods

2.1. Reagents

Azinphosmethyl (phosporodithioic acid, *S*-(3,4-dihidro-4-oxobenzol-(1,2,3-*d*)-triazin-3-ylm-ethyl)*O*,*O*-dimethyl phosphorodithioate) was purchased from Hektas Company A.S., Gebze, Turkey. It is a solid compound with the melting point of 73 °C. The solubility of azinphosmethyl in water is 33 mg l^{-1}. Azinphosmethyl is highly toxic to aquatic vertebrates, fish, birds, small mammals and human beings.

2.2. Pyrolysis of adsorbent (PMM600)

The procedure of pyrolysis of adsorbent was described elsewhere [18]. Peat moss (*Sphagnum* sp.) was collected from Rhode Island cost in USA as a residue. It was placed in a sealed ceramic boat placed in the stainless steel tubular reactor of 220 mm in length and 75 mm internal diameter. The pyrolyzation of adsorbent was done at 600 °C with a heating rate of 15 °C min^{-1} using nitrogen gas under atmospheric pressure. The pyrolization time was 60 min at pyrolyzed temperatures. After the pyrolyzing process, the char was washed with hot distilled water and dried for 1 day, at 110 °C. Then, the pyrolyzed peat moss was ground and sieved through 200 mesh screen. The specific surface area of activated chars made from peat moss (S_{BET}) calculated by the BET method by using Micromeritics FlowSorb II-2300 is 206.7 (± 0.1) m^2 g^{-1} for 600 °C.

2.3. Batch adsorption experiments

In equilibrium experiments, 0.5 g of the adsorbent was weighed into flasks containing 50 ml of solution with different azinphosmethyl concentrations, 1×10^{-3}, 2.5×10^{-3}, 5×10^{-3}, 7.5×10^{-3} g l^{-1}. The flasks were immediately sealed with parafilm. Then they were mechanically shaken in a water bath at 30 °C and in each experiment the pH was held constant at 6.5 using dilute hydrochloric acid or sodium hydroxide solutions. Kinetic studies were also conducted in a temperature controlled shaker, at 30, 40, 50, 60 °C using constant azinphosmethyl concentration of 2.5×10^{-3} g l^{-1}. The samples were taken and centrifuged at different time intervals (between 0 and 360 min). The concentration of azinphosmethyl was determined during the adsorption process by UV–Vis Spectrometer (Jenway 6105) at a wavelength of 286 nm.

3. Results and discussion

3.1. Effect of initial concentration on azinphosmethyl removal

Removal of azinphosmethyl at different initial concentrations but constant pH and temperature is shown in Fig. 1. It is evident, that maximum adsorption was achieved for the initial azinphosmethyl concentration of 1×10^{-3} g l^{-1}. It is seen from this figure, that the uptake percent decreases from 51 to 34%,
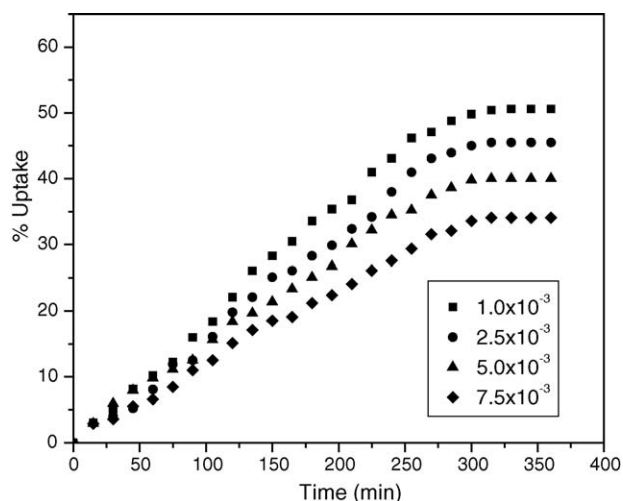

Fig. 1. The adsorption of azinphosmethyl on PMM600 for different initial concentrations at 30 °C, pH 6.5.

when the initial concentration value increases from 1×10^{-3} to 7.5×10^{-3} g l^{-1} for adsorbent dosage of 0.5 g/50 ml at pH 6.5 and 30 °C. Equilibrium was almost attained within 300 min, for all concentrations.

3.2. Effect of temperature

The adsorption of azinphosmethyl by PMM600 is not greatly affected by temperature (Fig. 2). As temperature varied from 30 to 60 °C, the uptake percent of azinphosmethyl increased from 50.6 to 62%. This indicates that the adsorption of azinphosmethyl onto PMM600 is an endothermic process.

3.3. Kinetic studies

Kinetic modelling of the adsorption of azinphosmethyl onto PMM600 was carried out by the pseudo-first order kinetic equa-
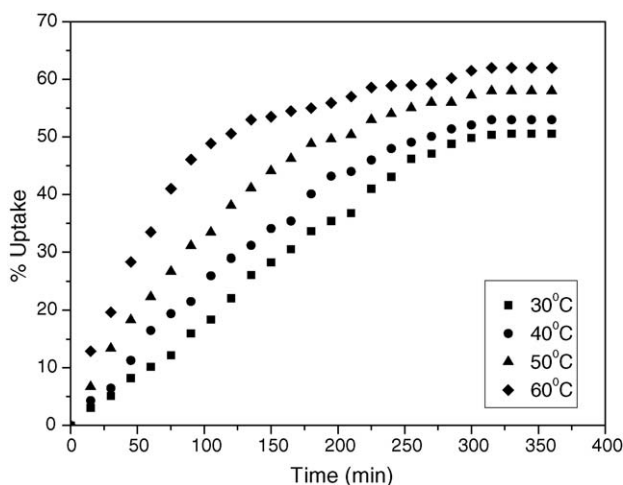

Fig. 2. The adsorption of azinphosmethyl on PMM600 at different temperature, initial concentration: 1×10^{-3}, pH 6.5.
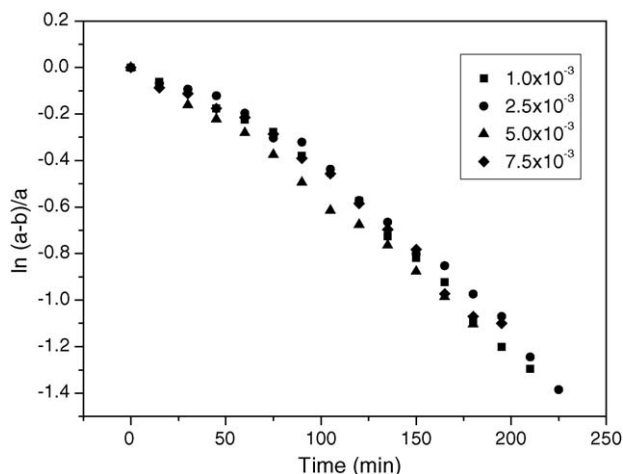
Fig. 3. Linear plots of the first order kinetic equation for azinphosmethyl adsorption, for different initial concentrations at 30 °C, pH 6.5.
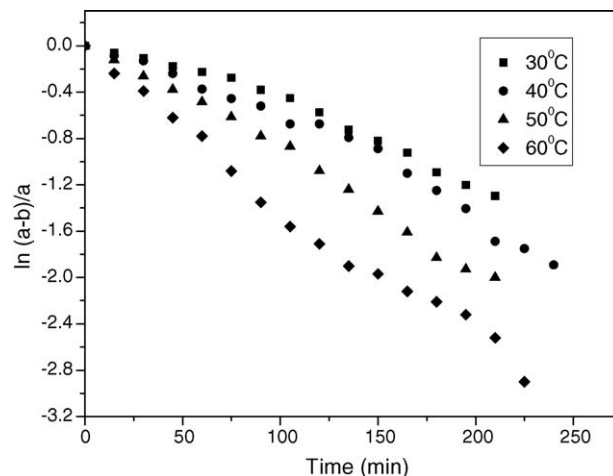

Fig. 4. Linear plots of the first order kinetic equation for azinphosmethyl adsorption, at different temperature, initial concentration: 1×10^{-3}, pH 6.5.

tion [21,22]

$$\ln \left(\frac{C_t - C_e}{C_0 - C_e} \right) = -k_{ads} t \tag{1}$$

where C_0, C_e, C_t (in mg l^{-1}) are the concentration of azinphosmethyl in solution at initial, equilibrium and time t, respectively. k_{ads} is the overall rate constant (in min^{-1}). The uptake percentage values of azinphosmethyl at equilibrium (a) and at any time (b) were applied to the Eq. (1) and the following equation was obtained for the first order kinetic model

$$\ln \left(\frac{a - b}{a} \right) = -k_{ads} t \tag{2}$$

The straight line plots of $\ln[(a - b)/a]$ versus t for different initial concentrations and different temperatures indicate the fitness of the model for the present system, as shown in Figs. 3 and 4, respectively. The overall rate constants, k_{ads}, of adsorption at different temperatures, were calculated from the slope of the respective plots obtained (Fig. 4) and the results are presented in Table 1. t-Test at 5% level of significance was applied to the results obtained from the kinetic studies. As seen from Table 1, t-stat values ($P < 0.05$) supported the results from least-square regression. When k_{ads} values and adsorbed amounts of azinphosmethyl were compared as a function of temperature, the adsorption rate increased with temperature. Since a rise in temperature increased the initial rate of adsorption, the time required to attain equilibrium did not change.

3.4. Thermodynamic parameters

The time dependence of the first order reaction can be fit to the Arrhenius equation

$$k_{ads} = A \, e^{-E_a/RT} \tag{3}$$

where A is the frequency factor (min^{-1}), E_a the activation energy (kJ mol^{-1}), T is the absolute temperature (K). The linear equation is obtained by taking logarithm of Eq. (3)

$$\ln k_{ads} = \ln A - \left(\frac{E_a}{RT} \right) \tag{4}$$

The activation energy for azinphosmethyl adsorption determined from the slope of the linear plot of $\ln k_{ads}$ versus $1/T$ is 18.3 kJ mol^{-1} (Fig. 5). The low activation energy (5–40 kJ mol^{-1}) is characteristic for physisorption, while higher energy (40–800 kJ mol^{-1}) suggest chemisorption [23]. Therefore, this value shows that azinphosmethyl adsorption is of a physical nature. Equilibrium constants, K_c, for the adsorption reaction of azinphosmethyl on adsorbent were calculated by the following equation:

$$K_c = \frac{M_{ads}}{C_e} \tag{5}$$

where K_c is the equilibrium constant, M_{ads} the adsorbed amount of adsorbate at equilibrium (mg l^{-1}) and C_e is the equilibrium concentration of adsorbate (mg l^{-1}). The changes in the Gibbs free energy (ΔG°) were evaluated by

$$\Delta G^\circ = -RT \ln K_c \tag{6}$$

Table 1
The rate constants of adsorption of azinphosmethyl onto PMM600 at various temperatures

Temperature (T) (°C)	K_c	k_{ads} ($\times 10^{-3}$ min^{-1})	k_1 ($\times 10^{-3}$ min^{-1})	k_2 ($\times 10^{-3}$ min^{-1})	R^2	t-stat
30	1.024	6.40	3.24	3.16	0.974	−22.13
40	1.128	8.60	4.35	4.25	0.972	−25.60
50	1.381	9.92	5.76	4.16	0.993	−35.98
60	1.632	12.2	7.56	4.64	0.984	−29.56
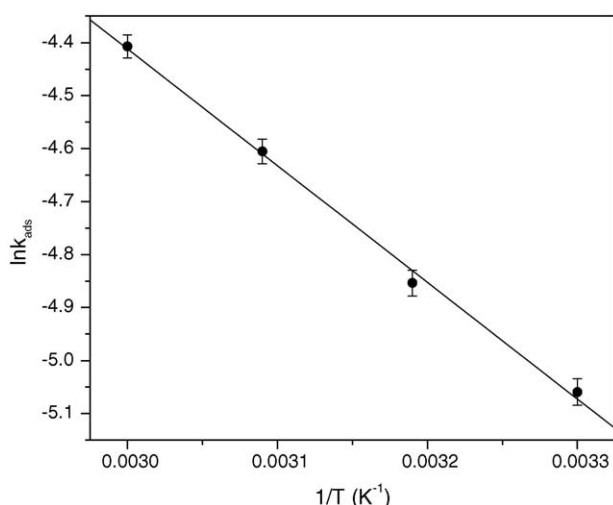
Fig. 5. Arrhenius plot for azinphosmethyl adsorption on PMM600 ($R^2 = 0.996$).
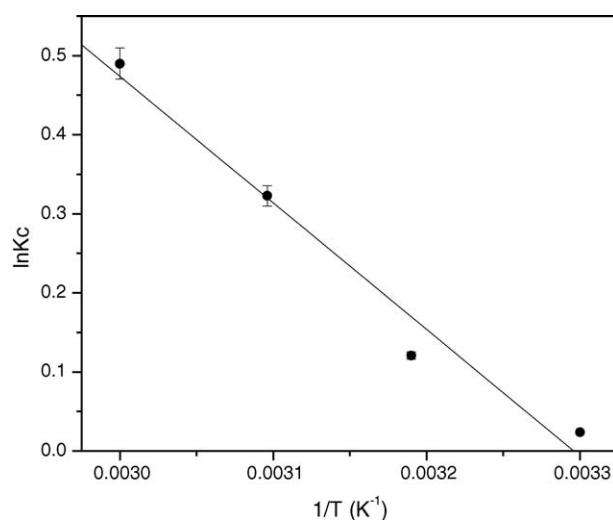
Fig. 6. Van't Hoff plot for the adsorption of azinphosmethyl removal ($R^2 = 0.972$).

The changes of the standard enthalpy (ΔH°) and entropy (ΔS°) were determined from the Van't Hoff equation

$$\ln K_c = -\left(\frac{\Delta H^\circ}{RT}\right) + \left(\frac{\Delta S^\circ}{R}\right) \tag{7}$$

ΔH° and ΔS° were obtained from the slope and intercept of the plot of $\ln K_c$ versus $1/T$ (Fig. 6). The values of the thermodynamics parameters of the adsorption of azinphosmethyl are listed in Table 2. The negative values of free energy changes (ΔG°) confirm that the adsorption of azinphosmethyl onto PMM600

Table 2
Thermodynamic data for adsorption of azinphosmethyl onto PMM600

Temperature (T) (°C)	ΔG° (J mol^{-1})	ΔH° (J mol^{-1})	ΔS° (J mol^{-1})
30	−60	13307	43.9
40	−313		
50	−867		
60	−1356		

is spontaneous and thermodynamically favorable. The decreasing value of ΔG° with temperature indicates more driving force and resulting in more adsorption capacity at higher temperature. The positive enthalpy changes indicate that the adsorption is an endothermic process and the enthalpy value (13.5 kJ mol^{-1}) due to the physisorption (<41.8 kJ mol^{-1}) is smaller than due to the chemisorption (41.8–125.4 kJ mol^{-1}) [24]. This result is good agreement with the activation energy value. The positive entropy value also suggests the increase randomness at the solid–solution interface during the adsorption of azinphosmethyl on PMM600.

3.5. Adsorption isotherm

The adsorption capacity of this system was investigated by the three-adsorption isotherms as Langmuir, Freundlich and Temkin isotherm. The isotherm parameters with the regression coefficients are listed in Table 3. To evaluate the applicability of each isotherm, t-test at 5% level of significance was also applied to the experimental results.

The Langmuir Model assumes monolayer uniform adsorption energies of adsorption surface and no immigration of adsorbate in the plane of surface. The linear form of Langmuir isotherm is given by the following equation:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \tag{8}$$

where q_e is the amount of adsorbed (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (mg l^{-1}), Q_0 and b are Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. Q_0 (mg g^{-1}) and b (l mg^{-1}) were obtained from the Langmuir adsorption curve (Fig. 7). The magnitude of the Langmuir constant b has small value (0.2531 mg^{-1}), and indicates a low heat of adsorption.

The Freundlich isotherm is based on the multilayer adsorption (heterogenous surface). The logarithmic form of the Freundlich Model is given as following equation:

$$\log q_e = \log k + \left(\frac{1}{n}\right) \log C_e \tag{9}$$

Table 3
The parameters for Langmuir, Freundlich and Temkin isotherms for adsorption of azinphosmethyl onto PMM600

Langmuir constants			
Q_0 (mg g^{-1})	b (l mg^{-1})	R^2	t-Stat
4.54	0.253	0.999	22.519

Freundlich constants			
n	k (mg g^{-1})	R^2	t-Stat
1.4031	1.738	0.993	23.475

Temkin constants			
A (l g^{-1})	B	R^2	t-Stat
3.184	0.895	0.981	11.627

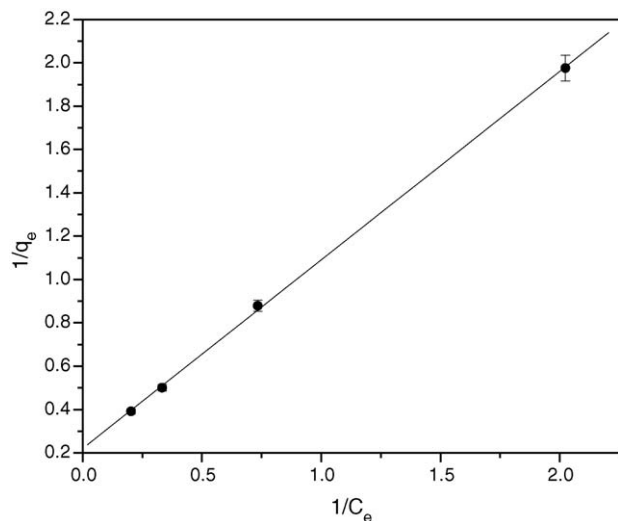Fig. 7. The Langmuir isotherm model for the adsorption of azinphosmethyl at 30 °C.

Fig. 9. The Temkin isotherm model for the adsorption of azinphosmethyl at 30 °C.

where k and $1/n$ are the Freundlich constants and show the adsorption capacity (mg g^{-1}) and sorbent affinity and have been determined from the intercept and slope of the straight line in Fig. 8, respectively. The value of $1/n$ is between 0 and 1 shows that the surface of the adsorbent is heterogenous in nature. Both Langmuir and Freundlich isotherm fitted well with the correlation coefficient greater than 0.99.

Temkin isotherm is given in the linearized form as follows

$$Q_e = B \ln A + B \ln C_e \qquad (10)$$

where B and A ($1\,g^{-1}$) are Temkin constants. Temkin isotherm shows a strong affinity for the adsorption capacity of azinphosmethyl on PMM600. Based on the correlation coefficient the results showed that good applicability was also obtained by Temkin isotherm (Fig. 9).

The adsorption capacity of azinphosmethyl onto peat moss was compared with the other adsorbent reported in literature
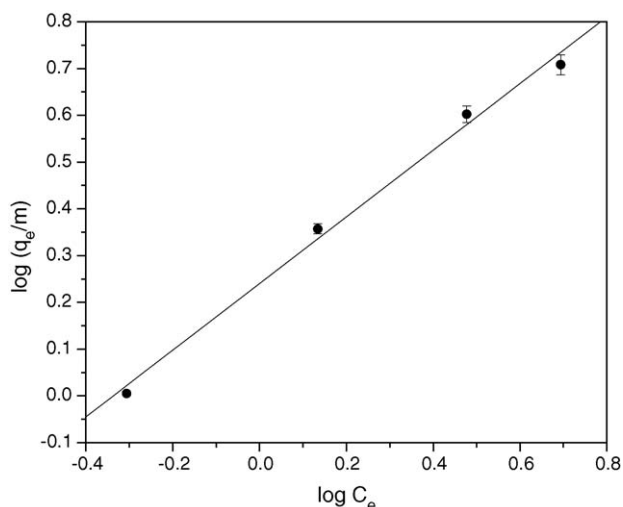
[18]. It can be observed that the adsorbent, pyrolyzed horseshoe sea crab (PHSC) exhibited high adsorption capacity but the correlation coefficients of the adsorption of azinphosmethyl onto (PMM600) were higher than the adsorption of azinphosmethyl onto (PHSC).

4. Conclusion

The pyrolyzed (600 °C) ocean peat moss was shown to be an economical and effective material for the adsorption of azinphosmethyl from aqueous solution. The first order kinetic reaction provides good correlation of the data for the adsorption of azinphosmethyl onto PMM600. The experiments in different temperature were also performed to investigate the thermodynamics aspects of adsorption. The positive enthalpy changes indicate that the adsorption is an endothermic process. Compared with the Langmuir and Freundlich isotherm, the Temkin isotherm was also tested to predict experimental data.

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Fig. 8. The Freundlich isotherm model for the adsorption of azinphosmethyl at 30 °C.

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