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Nonlinear Analysis of the Kinetics and Equilibrium for Adsorptive Removal of Methyl Parathion by Powdered Activated Carbon

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Abstract

The massive use of Methyl Parathion (MP) in the agriculture sector, has caused a setback to the environment and also has resulted in serious public health. In the present study, the nonlinear analysis method was used to evaluate the kinetics and equilibrium for MP adsorption on commercially available Powdered Activated Carbon (PAC) from an aqueous solution. The adsorption kinetic data were analyzed using the Pseudo First Order (PFO) and Pseudo Second Order (PSO) models. The experimental data were fitted using, two-parameter isotherms model (Langmuir, Freundlich, Temkin) and three parameters isotherms model (Sips, Redlich – Peterson, Toth). For the kinetic study, the adsorption process fitted the PSO model. Among two-parameter models, the Freundlich is better described for MP adsorption on PAC. From three-parameter isotherms, the Toth model was found to be the best representative for MP adsorption on the PAC. The results of the present study showed the efficiency of using PAC as an adsorbent for the removal of MP from an aqueous solution.

Keywords: Methyl parathion, Powdered activated carbon, Kinetics, Isotherms, Adsorption

1 Introduction

Pesticides have become essential for agriculture for protecting crops and livestock, which are vital to our food supply. However, the widespread use of pesticides has also resulted in serious public health [1]. Organophosphates have been widely used as pesticides in the agricultural industry and as chemical warfare agents [2]. Among the organophosphates, Methyl parathion (MP) is frequently used in cotton, wheat, rice, and sugar crops. However, the high trace levels of MP in aquatic environments might potentially harm both ecosystems and public health [3-5]. The toxic effects on reproductive, immune, and nervous systems were expected to occur in living organisms or vulnerable organisms during exposure to high concentrations of MP [6; 7]. These dangers resulted to unravel its actual transformation and fate in natural environments [8]. The World Health Organization classifies MP as class IA "extremely hazardous" pesticides [9].

For this reasons some treatment technologies are introduced to remove MP from aqueous medium, including as microbiological [10], coagulation /flocculation [11], photocatalytic [12], photolytic [13], electrochemical oxidation [14] and adsorption [15].

The adsorption of organophosphorus pesticides onto activated carbon has attracted the attention of many researchers. However, the forms PAC and GAC are the most used since they are considered as very capable, effective, and easy to use materials for the adsorption of a variety of pesticides [16]. The PAC adsorption process has been used as an effective method, in temporal and emergent practice, to remove residual pesticides and other hazardous chemicals in raw water during drinking water treatment [17]. PAC is commonly applied at water treatment plants, mainly for taste and odor control. It offers certain advantages over GAC, such as the low capital cost and flexibility of operation, as it can be applied only when needed. In the present study, we describe the kinetics and equilibrium of MP adsorption from aqueous solutions on commercial PAC using the nonlinear method.

2 Material and Methods

2.1 Adsorbent

The commercial PAC was provided by FLUKA. PAC was used without any treatment. Physical characteristics of PAC are shown in Table 1. The PAC characterization revealed the greatest content of acidic groups on the surface than the basic surface

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groups. The specific surface area for PAC was found to be 1002 m^2 g^{-1}. The particle sizes for PAC were found in the range 10–50 μm.

Table 1: Characteristics of the PAC

Parameters	Value
Total acidity (meq g^{-1})	0.704
Total basicity (meq g^{-1})	0.080
Specific surface (m^2 g^{-1})	1002
Particle size (μm)	10-50

2.2 Adsorbate

All chemicals used in this study were of analytical reagent grade. A stock solution containing 1000 mg L^{-1} of MP was prepared by dissolving 100 mg of MP in 100 mL of methanol. MP solutions were prepared by diluting the stock solution of MP to the desired concentrations in ultrapure water.

2.3 Batch experiments

To investigate the effect of contact time on MP removal by adsorption, 15 mg of PAC was added to 25 mL of MP at 5 mg L^{-1} stirring at 70 rpm at room temperature. Adsorption isotherms were obtained by varying the initial MP concentration from 5 to 100 mg L^{-1}. At the end of each experiment, the stirred solution mixture was microfiltered using a microfilter and the residual concentration of MP was determined by HPLC. The adsorption uptake at equilibrium time, q_e, and the percentage of the removal R (%) was expressed by equations (1) and (2), respectively:

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

$$\text{R (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

where q_e is the amount of MP adsorbed by PAC adsorbent (mg g^{-1}), C_i is the initial MP concentration (mg L^{-1}), C_e is the MP concentration at equilibrium (mg L^{-1}), V is the solution volume (L) and m is the mass of PAC adsorbent used (g). All batch experiments were conducted in triplicate and the mean values are reported.

2.4 Kinetics adsorption modeling

Several kinetic models have been described in an attempt to find a suitable mechanism explanation for solid-liquid adsorption systems, in which Lagergren's pseudo-first-order models (PFO) [18] and Ho's pseudo-second-order (PSO) model [18] are the two most widely applied to modeling the experimental data. The two kinetic models were used to describe the present data. The origin forms of the PFO equation [18] and PSO equation, [18] are expressed as:

$$q_t = q_e(1 - \exp^{-k_1 t}) \quad (3)$$

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

where q_t is the amount of MP adsorbed per unit mass of PAC (mg g^{-1}) at time t, k_1 is the PFO rate constant (L min^{-1}), k_2 (g$mg^{-1}min^{-1}$) is the PSO rate constant for adsorption, q_e (mg g^{-1}) and t is the contact time (min).

2.5 Equilibrium adsorption modeling

Several isotherm equations can explain solid-liquid adsorption systems, such as Langmuir, Freundlich, Temkin, Sips, Redlich-Peterson, and Toth. The Langmuir adsorption isotherm assumes that the adsorption takes place at specific homogeneous surface sites within the adsorbent [19]. The nonlinear Langmuir model has been defined by equation (5):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where q_e is the amount of MP adsorbed per unit mass of PAC (mg.g^{-1}), k_L is the Langmuir constant related to the adsorption capacity (L g^{-1}), C_e is the concentration of MP in the solution at equilibrium (mg L^{-1}), q_m is the maximum uptake per unit mass of PAC (mg.g^{-1}). The factor of separation of Langmuir, R_L, which is an essential factor characteristic of this isotherm is calculated by using the relation (6):

$$R_L = \frac{1}{(1 + k_L C_0)} \quad (6)$$

where C_0 is the higher initial concentration of MP, while K_L and q_m is the Langmuir constant and the maximum adsorption capacity, respectively. The parameters indicate the shape of the isotherm as follows: R_L values indicate the type of isotherm. The R_L value implies the adsorption to be favorable (R_L>1), linear (R_L=1), favorable (0<R_L<1), or irreversible (R_L=0). The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems [20]. The nonlinear representation of the Freundlich model is as in equation (7):

$$q_e = K_F C_e^{1/n} \quad (7)$$

where K_F (mg.g^{-1}) (L mg^{-1})^n and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic [21]. The Temkin isotherm has been applied in the following nonlinear form (8):

$$q_e = B_1 Ln K_T C_e \quad (8)$$

where B_1= RT/b is a constant related to the heat of adsorption and b shows the variation of adsorption energy (J mol^{-1}). K_T is a Temkin constant that takes into account the interactions adsorbate/adsorbent (dm^3 mg^{-1}). The Sips isotherm is a combination of the Langmuir and Freundlich isotherms, which represent systems for which one adsorbed molecule could occupy more than one adsorption site [22]. The nonlinear representation of the Sips model is as in equation (9):

$$q_e = q_m \frac{K_S C_e^n}{(1 + K_S C_e^n)} \quad (9)$$

where q_m the Sips maximum adsorption capacity (mg.g^{-1}), K_S the Sips equilibrium constant (L mg^{-1}), and n the Sips model exponent describing heterogeneity. The Redlich–Peterson isotherm model combines elements from both the Langmuir and Freundlich equation [23]. The nonlinear representation of the Redlich–Peterson model is as in equation (10):

$$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^n} \quad (10)$$

where K_{RP} (L g^{-1}) and α_{RP} (L mol^{-1}) are the Redlich-Peterson isotherm constants, while n is the exponent, which lies between 0 and 1. The Toth isotherm model combines the characteristics of both the Langmuir and Freundlich isotherm.[23]. The nonlinear representation of the Toth model is as in equation (11):

$$q_e = q_m \frac{C_e}{\left(1 + \alpha_T C_e\right)^{1/n}} \quad (11)$$

where q_m is the Toth maximum adsorption capacity (mg.g^{-1}), α_T is adsorptive potential constant (mg L^{-1}), and n Toth's heterogeneity factor. The relative parameters of each equation are obtained using the correlation coefficient R^2 between the calculated data and the experimental data by the nonlinear method. The correlation coefficient R^2 value is determined by the following equation (12):

$$R^2 = 100\left(1 - \frac{\left\|q_{exp} - q_{mod}\right\|^2}{\left\|q_{exp} - q_{avr}\right\|^2}\right) \quad (12)$$

where q_{exp} (mg.g^{-1}) is equilibrium capacity from the experimental data, q_{avr} (mg.g^{-1}) is equilibrium average capacity from the experimental data, and q_{mod} (mg.g^{-1}) is equilibrium from the model. So that $R^2 \leq 100$ – the closer the value is to 100, the more perfect is the fit.

3 Results and discussion

3.1 Kinetic study

The effect of contact time on the removal of MP (5 mg L^{-1}) is shown in Figure 1. The adsorption reaction is a fast process that at 10 min the removal yield of MP onto PAC was about 75%.

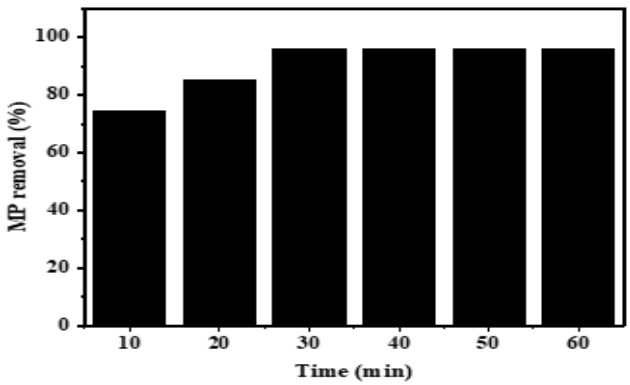

Figure 1: Removal percentage of MP by PAC

The MP removal efficiency increased from 74.4 % to 96 % when contact time increased from 10 to 30 min. The percentage removal efficiency of PAC increases with increasing the contact time and reached equilibrium within 30 min. The adsorption data kinetics was analyzed using the PFO, and PSO models. Figure 2 shows the experimental equilibrium data and the predicted theoretical kinetics for the adsorption of MP by PAC for 5 mg L^{-1}. The values of model parameters k_1, k_2, and R^2 are presented in Table 2.

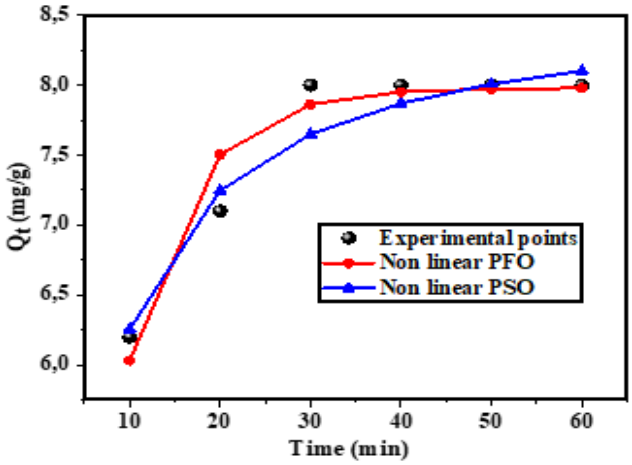

Figure 2: PFO and PSO nonlinear for PAC adsorbent

Table 2: PFO and PSO models constants for the adsorption of MP by PAC

Model	Parameters	Value
PFO	q_{exp}	8
	q_m	7.98
	K_1	0.140
	R^v (%)	98.5
PSO	q_e	8.61
	K_2	0.031
	R^v (%)	99.8

Based on the summary of kinetic models shown in Table 2, it was noticed that the correlation coefficient R^2 showed that the PSO model was the more suitable for adsorption MP behavior onto the PAC. It could be concluded that the mechanism of adsorption is the PSO reaction. A better fit to the PSO kinetic model suggested that the adsorption rate is dependent more on the availability of the adsorption sites rather than the MP concentration [15].

3.2 Adsorption isotherms

The isotherm of adsorption is employed to found the maximum capacity adsorption of MP onto PAC. The resulting curves and two-isotherm parameters are compared to the experimental data of PAC adsorbent for MP removal in Figure 3 and Table 4.

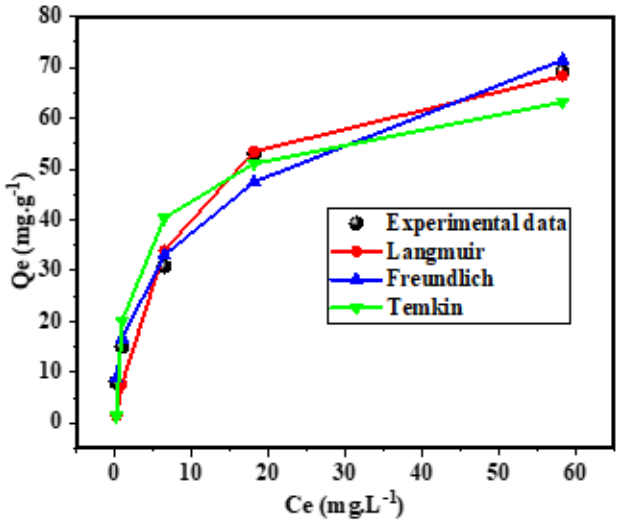

Figure 3: Non-linearized two-parameter isotherm models for MP adsorption by PAC

Table 3: Two- parameters isotherm models for MP retention on the PAC

	Parameters	Value
	q_m	78
	K_L	0.12
Langmuir	R_L	0.08
	R^2 (%)	98.73
	1/n	0.35
Freundlich	K_F	17.21
	R^2 (%)	99.51
	B_1	10.36
Temkin	K_T	7.69
	R^2 (%)	92.38

The results obtained in Table 3 indicate that the Freundlich model fitted very well to the experimental data, showing a high correlation coefficient R^2 value compared to Langmuir and Temkin isotherms. The abilities of the three-parameter equations, Sips, Redlich– Peterson, and Toth, to model the equilibrium adsorption data, were examined. The resulting curves and three-isotherm parameters are compared to the experimental data at PAC adsorbent for MP removal in Figure 4 and Table 4.

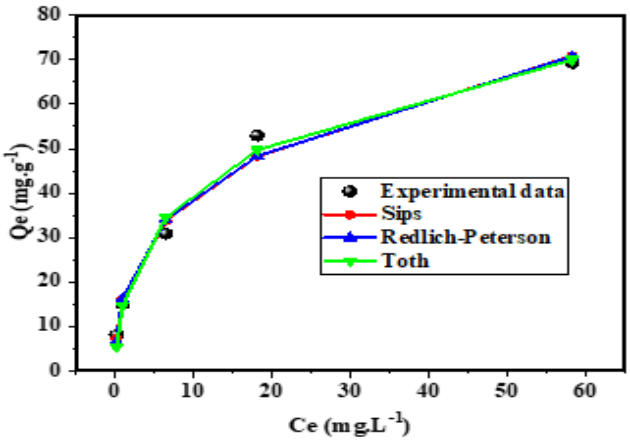

Figure 4: Non-linearized three-parameter isotherm models for MP adsorption by PAC

Table 4: Three-parameter isotherm models for MP retention on the PAC

Models	Parameters	Value
Sips	q_m	10.69
	K_S	12.70
	n	0.71
	R^2 (%)	99.60
Redlich-Peterson	K_{RP}	111.29
	α_{RP}	5.59
	n	0.68
	R^2 (%)	99.57
Toth	q_m	287.5
	α_T	1.04
	n	0.24
	R^2 (%)	99.63

The Toth isotherm showed a slightly high correlation coefficient R^2 value compared to Redlich-Peterson and Sips isotherms for the adsorption of MP onto PAC. The Toth isotherm exponent n is less than unity, indicating that the adsorption data were more of Freundlich form suggesting that the surface of PAC is heterogeneous for MP adsorption. Based on isotherm parameter determination, a PAC capacity of 78 mg g^{-1} was obtained. To compare the efficiency of PAC in removing aqueous MP, commercial granular activated carbon (GAC) has been used and showed a capacity removal of MP of 6.58 mg g^{-1}. From this value, the adsorption capacity q_m of PAC for MP is slightly 12 times higher than those of GAC, suggesting the higher effectiveness of PAC for the adsorption removal of MP. This finding is in agreement with reported by [24] and other organic molecules. The values of R_L, 1/n, and K_L are in between 0 and 1 give an indication of the favorability of the adsorption of MP onto PAC adsorbent.

4 Conclusions

A kinetic and equilibrium study is carried out using MP pesticide as adsorbate and PAC as an adsorbent. The PSO was the best kinetic model fitting the uptake of MP onto the PAC. The adsorption capacity of MP onto PAC using different two and three-parameter models is investigated. Among two-parameter isotherm models, Freundlich better described the isotherm data. In the case of three-parameter models, the Toth model was found to provide the closest fit to the equilibrium experimental data. This investigation showed the efficiency of using PAC as an adsorbent for the removal of MP from an aqueous solution.

Ethical issue

The authors are aware of and comply with, best practices in publication ethics specifically concerning authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that no conflict of interest would prejudice the impartiality of this scientific work.

Authors' contribution

Abdoulaye Demba N'diaye: Investigation, Writing – original draft, Methodology. Aoulad El hadj Ali Youssef: Writing - Review & Editing.

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