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Nonlinear Analysis of The Kinetics and Equilibrium for Adsorptive Removal of Paranitrophenol by Powdered Activated Carbon

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A B S T R A C T

Paranitrophenol (PNP) is one of the toxic chemicals, non-degradable, and bioaccumulative. In the present work, the nonlinear analysis method was used to assess the kinetics and equilibrium for PNP adsorption on commercially available Powdered Activated Carbon (PAC) from an aqueous solution. The adsorption kinetic data were analyzed using the Pseudo First Order (PFO), Pseudo Second Order (PSO), and Elovich models. The experimental data were fitted using two-parameter isotherms model (Langmuir, Freundlich and Temkin) and three parameters isotherms model (Sips, Redlich – Peterson and Toth). For the kinetic study, the adsorption process fitted the PSO model. Among two-parameter models, the Freundlich is better described for PNP adsorption on PAC. From three-parameter isotherms, the Sips model was found to be the best representative for PNP adsorption on the PAC. The results of the present study showed the efficiency of using PAC as an adsorbent for the removal of PNP from an aqueous solution.

A R T I C L E   I N F O

1. INTRODUCTION

Paranitrophenol (PNP), by the United States Environmental Protection Agency, is one of the toxic chemicals, non-degradable and bioaccumulative (Tang *et al.*, 2017). Its main sources vary such as the paint industry, pesticides, coal conversion, olive presses, in oil refining and it can also be found in the human and animal waste (Terzyk *et al.*, 2008).

Consequently, it is mandatory to remove phenolic compounds from wastewaters before their disposal in the environment (Al-Aoh *et al.*, 2013). Accordingly, some treatment technologies are introduced to remove PNP from aqueous media, including microbiological, reverse osmosis (Hidalgo *et al.*, 2015), photocatalytic, electrochemical oxidation (Zhang *et al.*, 2013) and adsorption (Cotoruelo *et al.*, 2012).

Adsorption is one of the most widely used methods for removing pollutants in tertiary treatments and activated carbons are most frequently employed. Activated carbons are important commercial adsorbents, with large specific surface area, high porosity, adequate pore size distributions, and high mechanical strength (Achari *et al.*, 2018).

The Powdered Activated Carbon (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 (Hu *et al.*, 1998). PAC is commonly applied at water treatment plants, mainly for taste and odor control. In the present study, we describe the kinetics and equilibrium of PNP adsorption from aqueous solutions on commercial PAC using the nonlinear method.

2. METHODS
2.1. Adsorbent and adsorbate

The commercial PAC was provided by FLUKA. PAC was used without any treatment. All chemicals used in this study were of analytical reagent grade. The stock solution is prepared by adding 1 g of the PNP to 1 L of ultrapure water. PNP solutions were prepared by diluting the stock solution of PNP to the desired concentrations in ultrapure water.

2.2. Batch experiments

To investigate the effect of contact time on PNP removal by adsorption, 15 mg of PAC was added to 25 mL of PNP at 5 mg L-1 stirring at 70 rpm at room temperature. Adsorption isotherms were obtained by varying the initial PNP 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 PNP was determined by High-Performance Liquid Chromatography (HPLC). The flow-rate used was kept at 0.5 mL min-1 and the mobile phase is composed of methanol- ultrapure water (80:20) (v/v). The adsorption uptake at equilibrium time, qe, and the percentage of the removal R (%) was expressed by equations (1) and (2), respectively:

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

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

where q_e is the amount of PNP adsorbed by PAC adsorbent (mg g^{-1}), C_i is the initial PNP concentration (mg L^{-1}), C_e is the PNP 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.

2.3. Kinetics adsorption modeling

The rate and mechanism of the adsorption process were evaluated using three different kinetic models, namely the pseudo-first-order model (PFO), pseudo-second-order model (PSO), and Elovich model (Guo *et al.*, 2012). The non-linear kinetics PFO, PSO, and Elovich model may be expressed by equations (3), (4), and (5), respectively:

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

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{4}$$

$$q_t = \left(\frac{1}{\beta}\right) Ln(1 + \alpha\beta t) \tag{5}$$

Where q_t is the amount of PNP 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 rate constant for adsorption, q_e (mg g^{-1}), t is the contact time (min), α and β, known as the Elovich coefficients. The α represents the initial adsorption rate (mg g^{-1}min^{-1}) and the β is related to the extent of surface coverage and activation energy for chemisorption (g mg^{-1}).

2.4. 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 (Langmuir, 1918). The nonlinear Langmuir model has been defined by equation (6):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

where q_e is the amount of PNP 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 PNP 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 (7):

$$R_L = \frac{1}{(1 + k_L C_0)} \tag{7}$$

where C_0 is the higher initial concentration of PNP, while K_L and q_m are 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 (Freundlich, 1906). The nonlinear representation of the Freundlich model is as in equation (8):

$$q_e = K_F C_e^{1/n} \tag{8}$$

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 (Oyelude *et al.,* 2015). The Temkin isotherm has been applied in the following nonlinear form in equation (9):

$$q_e = B_1 Ln K_T C_e \tag{9}$$

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 between adsorbate/adsorbent (L 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 (Sreńscek-Nazzal *et al.,* 2015). The nonlinear representation of the Sips model is as in equation (10):

$$q_e = q_m \frac{K_S C_e^n}{(1 + K_S C_e^n)} \tag{10}$$

where q_m is the Sips maximum adsorption capacity (mg.g^{-1}), K_S the Sips equilibrium constant (L mg^{-1}), and n the Sips model exponent describes heterogeneity.

The Redlich–Peterson isotherm model combines elements from both the Langmuir and Freundlich equation (Dhaouadi & M'Henni, 2009). The nonlinear representation of the Redlich–Peterson model is as in equation (11):

$$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^n} \tag{11}$$

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 (Dhaouadi & M'Henni, 2009). The nonlinear representation of the Toth model is as in equation (12):

$$q_e = q_m \frac{C_e}{\left(1 + \alpha_T C_e\right)^{1/n}} \tag{12}$$

Where q_m is the Toth maximum adsorption capacity (mg.g^{-1}), α_T is the adsorptive potential constant (mg L^{-1}), and n Toth's heterogeneity factor.

The relative parameters of each equation are obtained using the Sum of the Squares of the Errors (SSE) and the coefficient of determination R^2 between the calculated data and the experimental data by nonlinear regressive analysis using the solver Excel. The *SSE* and *R^2* values are determined respectively by the following equations (13) and (14):

$$SSE = \left(q_{exp} - q_{mod}\right)^2 \tag{13}$$

$$R^2 = 100 \left(1 - \frac{\left\|q_{exp} - q_{mod}\right\|^2}{\left\|q_{exp} - q_{avr}\right\|^2} \right) \tag{14}$$

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. Thus, $R^2 \leq 100$ is the closer the value is to 100, resulting in a more perfect fit.

3. RESULTS AND DISCUSSION
3.1. Kinetic study

The effect of contact time on the removal of PNP (5 mg L^{-1}) is shown in **Figure 1**. The adsorption reaction is a fast process that at 10 min the removal yield of PNP onto PAC was about 46.82 %. The PNP removal efficiency increased from 46.82 % to 81.63 % when contact time increased from 10 to 90 min. The percentage removal efficiency of PAC increases with increasing the contact time and reached equilibrium within 90 min.
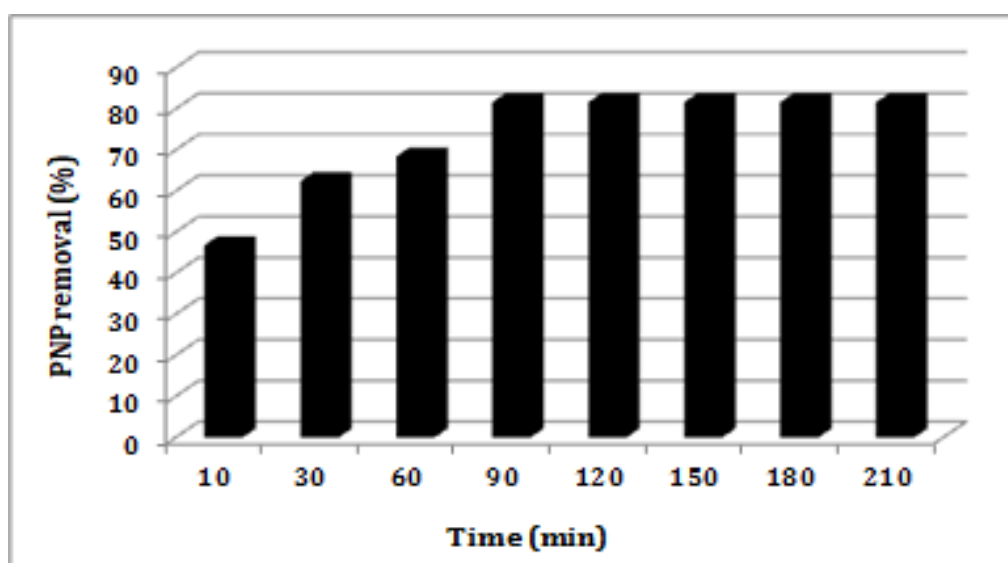

Figure 1. Removal percentage of PNP by PAC.

The adsorption data kinetics were analyzed using the PFO, PSO, and Elovich models. **Figure 2** shows the experimental equilibrium data and the predicted theoretical kinetics for the adsorption of PNP by PAC for 5 mg L^{-1}. The values of model parameters k_1, k_2, α, β, SSE, and R^2 are presented in **Table 1**.

Based on the summary of kinetic models shown in **Table 1**, it was noticed that the three kinetics models are found to be suitable for fitting the present adsorption kinetics data in the following subsequent order: PSO > Elovich > PFO. The best fit of PSO and Elovich kinetic models to the experimental data indicates the chemisorption of PNP on the PAC surface. Similar results are reported by (Deokar & Mandavgane, 2015).

3.2. Adsorption isotherms

The isotherm of adsorption is employed to find the maximum capacity adsorption of PNP onto PAC. The resulting curves and two-isotherm parameters are compared to the experimental data of PAC adsorbent for PNP removal in **Figure 3** and **Table 2**.
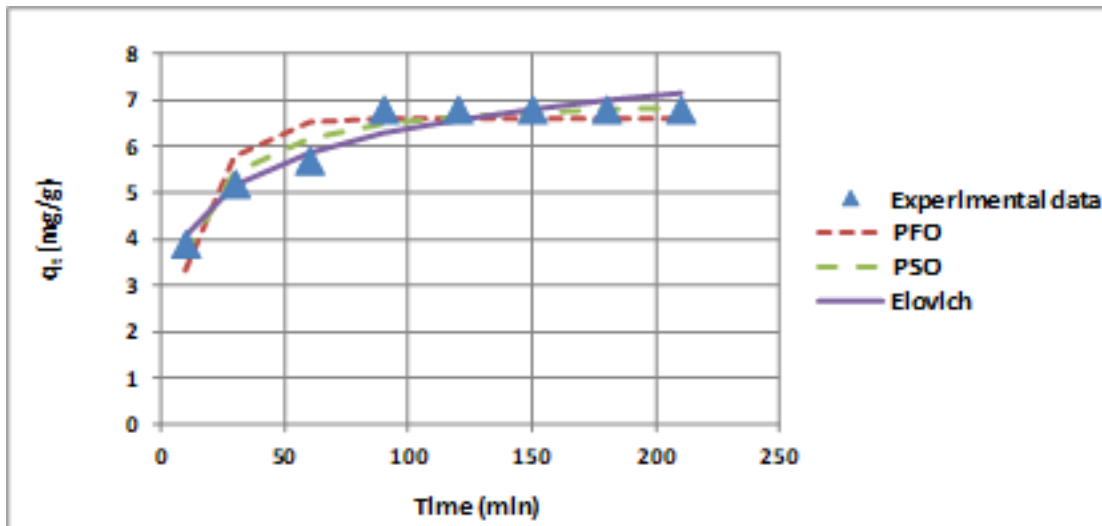
Figure 2. PFO, PSO, and Elovich nonlinear for PAC adsorbent.

Table 1. PFO, PSO, and Elovich models constants for the adsorption of PNP by PAC.

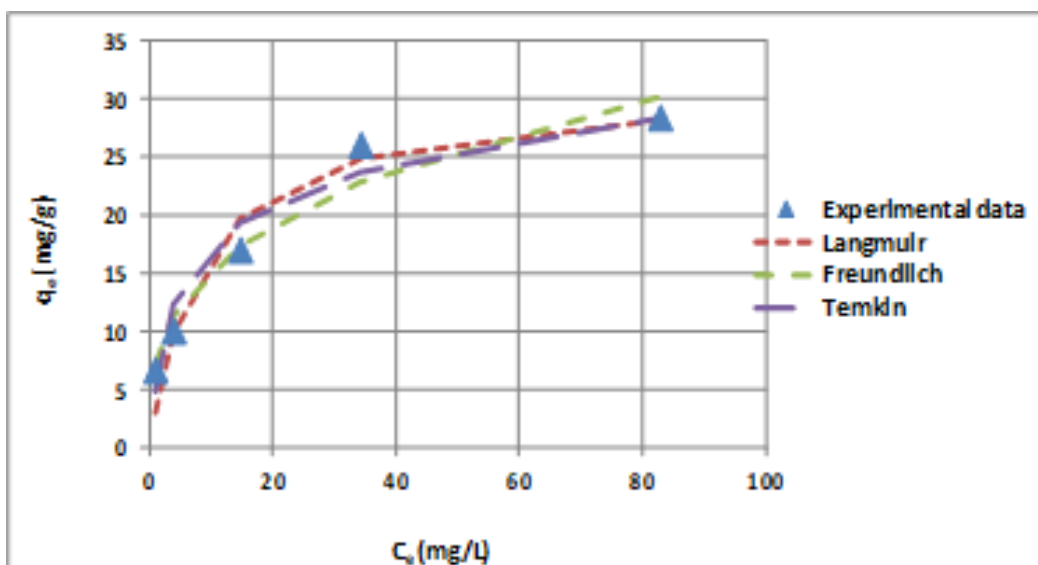| Model	Parameters	Value
PFO	q_{exp}	6.800
	q_e	6.590
	K_1	0.070
	SSE	1.530
	R^2 (%)	81.470
PSO	q_e	7.160
	K_2	0.015
	SSE	0.480
	R^2 (%)	94.200
Elovich	α	5.330
	β	0.980
	SSE	0.530
	R^2 (%)	93.620

Figure 3. Non-linearized two-parameter isotherm models for PNP adsorption by PAC.

Table 2. Two- parameters isotherm models for PNP retention on the PAC.

	Parameters	Value
	q_m	31.000
	K_L	0.120
Langmuir	R_L	0.080
	SSE	22.400
	R^2 (%)	99.940
	n	3.125
	K_F	7.190
Freundlich	SSE	15.960
	R^2 (%)	99.960
	B_1	5.210
	K_T	2.760
Temkin	SSE	19.330
	R^2 (%)	94.680

From **Table 2**, the values of R_L and K_L are between 0 and 1 indicating the favorability of the adsorption of MP onto PAC adsorbent.

The results obtained in **Table 2** indicate that the Freundlich model fitted very well with the experimental data, showing slightly a high correlation coefficient R^2 value and a low SSE value compared to Langmuir and Temkin isotherms. The magnitude of the exponent n indicates the favorability of adsorption. It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics. The studied PAC is a good adsorbent for PNP (n =3.125) (**Table 2**). It should be noted that most of the isotherm adsorption studies of PNP on various adsorbents follow the Freundlich isotherm model (Adekola & Azeez, 2016).

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 PNP removal in **Figure 4** and **Table 3**.
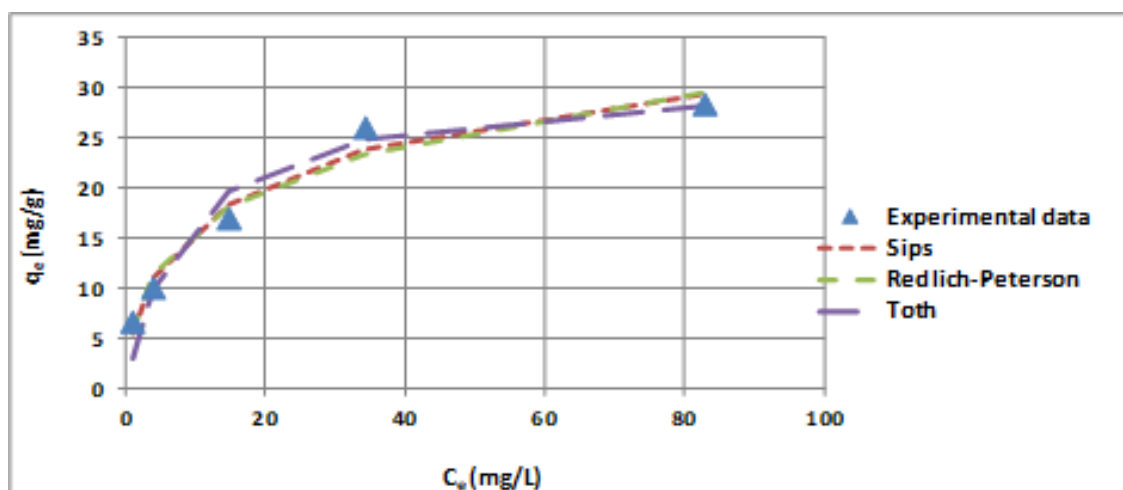
Figure 4: Non-linearized three-parameter isotherm models for PNP adsorption by PAC.

The Sips isotherm showed a slightly high correlation coefficient R2 value and low SSE value compared to Redlich-Peterson and Toth isotherms for the adsorption of PNP onto PAC.

The Sips 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 PNP

adsorption. The multilayer adsorption capacity, qm, was found to be 4.38 mg g-1. Values of the adsorption capacity of other adsorbents for PNP from the literature are given in Table 4 for comparison. The result clearly showed that the PAC adsorbent developed is much more effective and comparable for the removal of PNP from an aqueous solution compared to some adsorbents previously reported.

Table 3. Three-parameter isotherm models for PNP retention on the PAC.

Models	Parameters	Value
Sips	q_m	45.22
	K_S	0.15
	n	0.57
	SSE	9.87
	R^2 (%)	97.29
Redlich-Peterson	K_{RP}	13.44
	α_{RP}	1.27
	n	0.76
	SSE	13.16
	R^2 (%)	96.58
Toth	q_m	0/71
	α_T	0.12
	n	0.20
	SSE	22.40
	R^2 (%)	93.80

Table 4. Comparison of q_m of PAC with other adsorbents for PNP adsorption.

Adsorbents	q_m (mg g^{-1})	References
Bentonite	0.290	Moussou *et al.,* (2014)
char ash	7.384	Magdy *et al.,* (2018)
Graphene Oxide	35.100	Yanga and Wang, (2018)
Partially reduced Graphene Oxide	29.940	Yanga and Wang, (2018)
PAC	31.000	Present study

4. CONCLUSION

A kinetic and equilibrium study is carried out using PNP as an adsorbate and PAC as an adsorbent. The PSO was the best kinetic model fitting the uptake of PNP onto the PAC. The adsorption capacity of PNP 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 Sips 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 PNP from an aqueous solution.

5. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the paper was free of plagiarism.

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