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Application of a Mixed Order Model to Determine the Rate Adsorption of 1-Nitronaphthalene onto Activated Carbon

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Abstract

This study investigated the adsorption kinetics of 1-nitronaphthalene solution (a polycyclic aromatic hydrocarbon, PAH) onto seven different masses of activated carbon. The coefficient of determination (r^2) was used to determine the best-fit kinetic model and to confirm agreement between experimental data and the kinetic rate equations. The results indicated that adsorption could be defined with masses of 0.0200 g and 0.0501 g when fitted using a second order rate equation. Adsorption on to masses of 0.1003 g, 0.1203, 0.1501 g, and 0.2001 g was best defined when data were fitted to a pseudo second order rate equation. However, adsorption onto a mass of 0.0701 g did not fit with any simple rate law. Consequently, a new mathematical mixed order equation was developed to determine the rates of adsorption and the rate constants by combining two orders of equations: the pseudo first order and pseudo second order, to achieve a better fit with the same data.

Keywords: Polycyclic aromatic hydrocarbon (PAHs); Pseudo first order; Pseudo second; Adsorption kinetic; Mixed order

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Introduction

Polycyclic aromatic hydrocarbons (PAHs), sometimes called polynuclear aromatic hydrocarbon (PAHs) or polyarenes, are a group of ubiquitous environmental contaminants [1-2]. PAHs are characterized by the presence of two or more fused benzene rings in linear, angular or cluster arrangements. They can be found as both particles and gases [3]. PAHs tend to accumulate in marine sediments and are a source of significant environmental concern due to their toxicity, mutagenicity, and carcinogenicity [4]. PAHs are one of the main components of crude oil [5]. They occur as colorless, white/pale yellow solids with low solubility in water, high melting and boiling points, and low vapor pressure. PAHs with higher molecular weight have decreased solubility in water, higher melting and boiling point. PAHs cannot be easily destroyed by biological treatment and many of them can inhibit biological processes. [6-7]. Long term effects on humans may include: decreased immune function, increased incidence of cataracts, kidney and liver damage, breathing problems, and reduced lung function [8].

In this study, 1-nitronaphthalene was used as a representative of PAHs. 1-nitronaphthalene is formed by the reaction between naphthalene and dinitrogen pentoxide (N_2O_5 is formed by the reaction between ozone and nitrogen dioxide) [9]. The 1-nitronaphthalene interacts with cytochrome P450 (CTP) in the lung and liver [10] causing abnormal tissue. It affects the respiratory system by destroying ciliated cells in the airway, for example when receiving 1-nitronaphthalene at a concentration of 100 to 150 mg kg^{-1} in 24 h [11-12]. Although 1-nitronaphthalene is a harmful compound, it is extensively used as an essential compound in the manufacture of some dyes, pharmaceuticals, perfumes, and plastics. Wastewater from these processes may therefore be contaminated with 1-nitronaphthalene [13].

Adsorption onto activated carbon [ACs] is a waste water treatment method sometimes used in practical situations. It is recognized by the U.S. Occupational Safety and Health Administration (OSHA) as an effective and efficient system for treatment or removal of pollutants and carcinogenic compounds [14]. Activated carbon has been widely used as an effective adsorbent for more than 200 years and is recognized as a low-energy process for product purification [15], pollution control, wastewater treatment, industrial purification processes and for removal of taste, odor and micropollutants [16-17]. Activated carbon has a complex structure and consists of amorphous carbon and graphite crystalline units, giving activated carbon a greater adsorption surface area than other absorbents of the same mass, thus increasing its efficiency as an adsorbent.

The objective of this study was to describe possible adsorption kinetic models for adsorption of a 1-nitronaphthalene solution (PAH) onto the surface of activated carbon by varying the mass of the adsorbent [ACs]. A coefficient of determination (r^2) was used to determine the best-fit for different model of the adsorption kinetics.

Materials and methods

The research was carried out in the laboratory of the Department of Applied Chemistry, RMIT University, Australia. The adsorbent [ACs] was commercial granular activated carbon and the adsorbate chemical was 1-nitronaphthalene [B] (see below). It was purified before use in the experiments as outlined below. Differential pulse polarography was used for measuring the concentration of the various 1-nitronaphthalene solutions.

Reagents and solutions

The commercial activated carbon was provided by PICA Activated Carbon Company, Australia (coconut fiber-based granular activated carbon, Picatif TE 70). The selected activated carbon was sieved prior to use using standard copper test sieves [Endecotts (Test Sieves) Ltd., London, England], to a particle size range of 1.0 - 1.4 mm. Removal of unwanted compounds that may have interfered with the effectiveness of the activated carbon was achieved using Soxhlet extraction into ultra-pure water. The extraction time was at least 120 hours and the process was repeated until UV-spectra produced less than 1 % impurity. Treated activated carbon was then left to dry for three days at room temperature before use as an adsorbent [ACs].

The specific surface area of ACs was characterized via adsorption of nitrogen at 77 K using the Brunauer-Emmet-Teller (BET) method (a Micromeritics model ASAP 2000). The total surface area of ACs was 1,588±63 $m^2 g^{-1}$, micropore surface area 1,230±45 $m^2 g^{-1}$ and external surface area 358±48 $m^2 g^{-1}$.

The 1-nitronaphthalene was purchased from Merck Pty, Ltd. (CAS number [86-57-7], $C_{10}H_7NO_2$). The 1-nitronaphthalene compound used in this study was dissolved in $0.51\pm 0.03\cdot10^{-3}$ mol L^{-1} 5 % aqueous methanol (BDH Laboratory Supplies Poole, BH151TD, England, HyperSolv CAT number 15250, HPLC grade) and quality was assessed using UV-spectrophotometer over the range of 200 - 300 nm. It was necessary to purify the initial solution by recrystallizing it using absolute methanol as the solvent and repeating the process until UV-spectra produced less than 1 % impurity. A stock solution of 1-nitronaphthalene at concentration of $1.02\pm0.03\cdot10^{-3}$ mol L^{-1} in absolute methanol was prepared for use as the adsorbate [B] in all experiments.

Adsorption analysis

Adsorption analysis was carried out using the differential pulse polarography measurements technique (Model E 505, Metrohm Herisau, Switzerland). Experiments that evaluated the adsorption onto the surface area of the adsorbent [B] used the same concentration of $0.51\pm 0.03\cdot10^{-5}$ mol L^{-1} (as the initial concentration) but different masses of adsorbents were studied across a range from about 0.02 g to 0.20 g, at a constant temperature of 25.5±1.0 °C.

Adsorption kinetics experiment

A known mass of purified activated carbon (adsorbent; [ACs]) was placed in ultra-pure water (70 mL) in a glass jacketed beaker at constant temperature of 25.5±1.0 °C. It was stirred with a Telfon coated stirring bar for 2 h, and 25 ml of pH 7 buffer was added (pH 7.0 buffer was prepared by dissolving 1.4 g of potassium dihydrogen orthophosphate (KH_2PO_4) and 1.4 g disodium hydrogen orthophosphate (Na_2HPO_4) per 1 L of ultra-pure water). Timing began at the moment 5 mL of the stock solution of 1-nitronaphthalene was added (starting concentration was $0.51\pm0.03\cdot10^{-5}$ mol L^{-1}). The adsorption kinetics in the solution were determined by recording the change in voltage with a dropping mercury electrode. The dropping mercury was the working electrode and saturated calomel was used as the reference. Platinum wire was used as the auxiliary electrode. A schematic diagram representing the adsorption kinetics technique is shown in Figure 1.

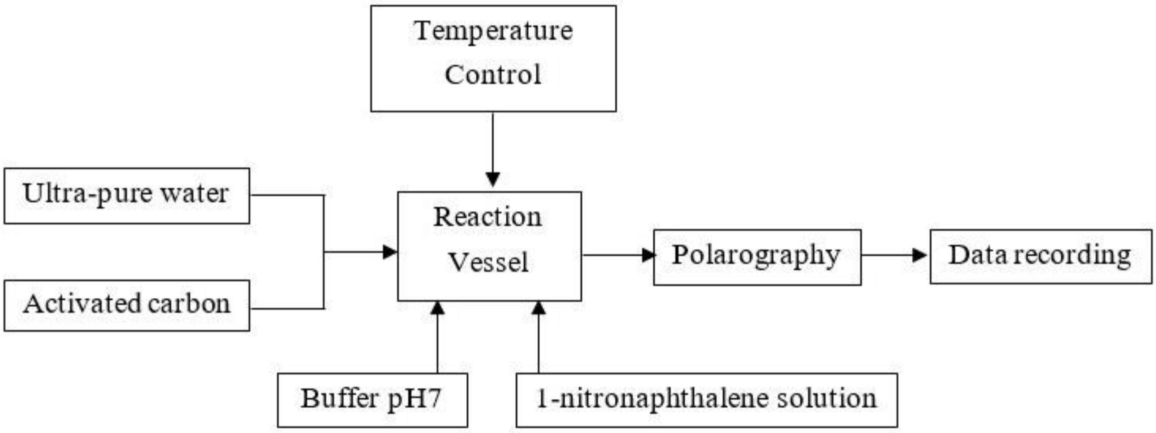

Figure 1 Schematic diagram of the adsorption kinetics experiment.

Adsorption processes

The nature of interactions between the activated carbon surface and the adsorbate determines the behavior of the adsorbate's diffusion into the activated carbon, including its adsorption rate.

The adsorption processes of PAHs on ACs have been described as three consecutive steps as: (1) migration of adsorbate (PAHs) from the solution to the outer surface of the adsorbent (ACs) by molecular diffusion (bulk layer to the external surface of the adsorbent (film diffusion); and (3) diffusion through the interior (micropore area) of the adsorbent. This is divided into diffusion steps (intraparticle diffusion). When adsorbates are transported by diffusion into the porous region, this is referred to as pore diffusion, while transport over the outer surface of the adsorbent is referred to as surface diffusion. In adsorption processes, both pore and surface diffusion occur simultaneously [18-20].

In order to interpret experimental data, it is necessary to identify the slowest (rate limiting) step in the adsorption kinetic models [21-22].

The plot of concentration versus time showed two distinct regions. In the initial first few minutes of adsorption, the first stage region of each plot (i.e. for each mass) was curved, approximating to a straight line in the final stage. The initial process could be explained primarily by boundary layer diffusion, whereas the final linear region reflected an intraparticle diffusion effect and was found to be the rate limiting step in adsorption processes [19, 21-24].

Adsorption kinetic models

A convenient method for characterization of the rate of adsorption is to determine the rate order kinetics. The rate law of adsorption can be measured by determining the change in concentration of adsorbates that are removed from solution as a function of time. The general chemical adsorption process is described by Eq. 1. The rate law of adsorption is expressed in the form of a differential rate expression according to Eq. 2.

$$ACs + B \rightarrow ACs - B \qquad \text{(Eq. 1)}$$

The rate law of adsorption as expressed in the form of a differential rate expression is shown as

$$Rate = k_x[ACs]^{a'}[B]^{b'} \qquad \text{(Eq. 2)}$$

Where; [B] = concentration of adsorbate, [ACs] = concentration of adsorbent surface sites, a', b' = orders of the concentration terms of adsorbent and adsorbate and k_x = rate constant

The second order rate law

In the simplest case the adsorption rate depends on both the concentration of adsorbent surface sites [ACs] and the concentration of adsorbate [B] in the first order in [ACs] and first order in [B] (a'=b'=1). The overall order of reaction is the sum of the orders of all reactants which becomes is second order overall (Atkin 2018). The second order rate law is in the form of

$$Rate = k_2[ACs][B] \qquad \text{(Eq. 3)}$$

Where: k_2 = second-order rate constant, b = initial concentration of the adsorbent surface sites [ACs], $(b - x)$ = concentration of the adsorbent surface sites [ACs] at time t and x = concentration adsorbed

The second-order differential rate law has the form

$$-\frac{dx}{dt} = k_2(b - x)(a - x) \qquad \text{(Eq. 4)}$$

Integrating in terms of the partial fractions, gives

$$k_2t = \frac{1}{a-b}ln\frac{b(a-x)}{a(b-x)} \qquad \text{(Eq. 5)}$$

The pseudo first order rate law

When the concentration of adsorbent surface sites [ACs] is in large excess, the rate of adsorption will depend only on the concentration of the adsorbate [B]. The pseudo first order rate law is in the form of;

$$Rate = k_2'[B] \qquad \text{(Eq. 6)}$$

Where: k_2' = the pseudo first-order rate constant: $k_2' = k_2[ACs]$, a = initial concentration of the adsorbate [B], $(a-x)$ = concentration of the adsorbate [B] at time t.

The pseudo first-order differential rate law is in the form of;

$$-\frac{dx}{dt} = k_2'(a-x) \qquad \text{(Eq. 7)}$$

Integrating both sides gives;

$$k_2't = ln(a) - ln(a-x) \qquad \text{(Eq. 8)}$$

The pseudo second order rate law

When the concentration of adsorbent surface sites [ACs] is in excess, and the rate of adsorption is second order in [B]. The pseudo second order rate law is in the form of

$$Rate = k_3'[B]^2 \qquad \text{(Eq. 9)}$$

Where: k_3' = the pseudo second-order rate constant: $k_3' = k_3[ACs]$

The pseudo second-order differential rate law has the form

$$-\frac{dx}{dt} = k_3'(a-x)^2 \qquad \text{(Eq. 10)}$$

Integrating both sides gives;

$$k_3't = \frac{1}{(a-x)} - \frac{1}{(a)} \qquad \text{(Eq. 11)}$$

Fitting the experimental data to the kinetic adsorption model

The order of the reaction is determined by the best straight line as shown by the graph [25-26]. The coefficient of determination or the root mean square error (r^2) is used as the measure of how well the straight line is fitted to the data. The coefficient of determination (r^2) can have a value between $0 \geq r^2 \leq 1$. A good model is indicated by a value that is closer to 1 [26] and can be calculated by

$$r^2 = 1 - \frac{SS_{res}}{SS_{tot}} \qquad \text{(Eq. 12)}$$

Where SSres is the residual sum of square

$$SS_{res} = \sum_{i=1}^{n}\left(Q_{exp} - Q_{calc}\right)^2 \qquad \text{(Eq. 13)}$$

Where SS_{tot} is the total sum of square

$$SS_{tot} = \sum_{i=1}^{n}\left(Q_{exp} - Q_{mean}\right)^2 \qquad \text{(Eq. 14)}$$

Results and discussion

All experiments were conducted at a constant temperature of 25.5±1.0°C using the same initial concentration of 1-nitronaphthalene solution ($0.51\pm0.03\cdot10^{-5}$ mol L^{-1}).

The results of the adsorption kinetics on 0.0701 g activated carbon indicated that the adsorption process did not follow simple kinetics. Applying a pseudo first order model showed that the experimental data did not fit with this model, indicating that the rate of adsorption was not dependent on the concentration of the adsorbate [B] (Figure 2). The results also did not fit with a second order model (Figure 3). This indicates that the adsorption rate was not dependent on either concentration of adsorbent surface sites [ACs] or concentration of adsorbate [B] in the first order (a'=b'=1). In such a situation, it is reasonable to apply a higher order model with a pseudo second order model. Such results can be described as an s-curve (Figure 4). This fit indicated that the adsorption rate was not a second order in respect of [B].

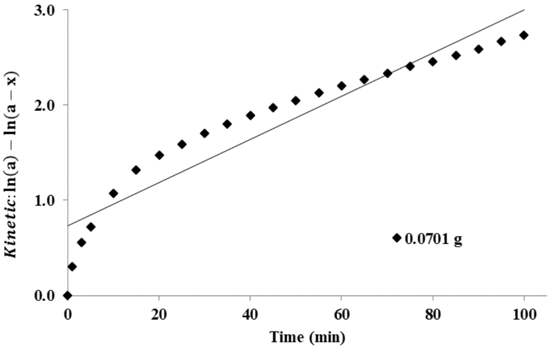

Figure 2 Pseudo first order kinetics for adsorption of 1-Nitronaphthalene by 0.0701 g activated carbon at 25.5 °C.

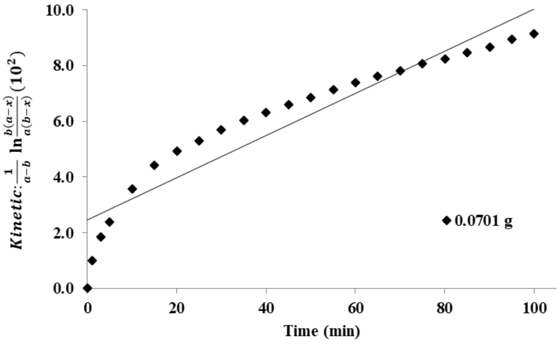

Figure 3 Second order kinetics for adsorption of 1-Nitronaphthalene by 0.0701 g activated carbon at 25.5 °C.

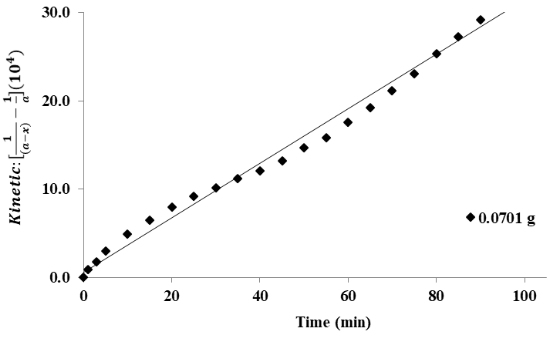

Figure 4 Pseudo second order kinetics for adsorption of 1-Nitronaphthalene by 0.0701 g activated carbon at 25.5 °C.

A new mathematical model was necessary to determine the rate of adsorption and the rate constants where 0.0701 g of activated carbon was used. It is possible to combine two orders together to achieve a better result with the same data. The mixed order model (Eq. 15) is a combination of the pseudo first order equation with the pseudo second order equation. The mixed order rate law follows the form of;

$$-\frac{d(a-x)}{dt} = 2k_2(a-x)^2 + k_1(a-x) \quad \text{(Eq. 15)}$$

Where k_1 = the pseudo first order rate constant, k_2 = the pseudo second order rate constant, a = initial concentration of the adsorbate [B] and $(a-x)$ = concentration of the adsorbate [B] at time t.

The data for adsorption with 0.0701 g adsorbent fits well with the mixed order model (Eq. 16). The result was practically linear (Figure 5) with a high coefficient of determination (r^2) value of 0.9986, a low sum of error square (SSE) value of 0.3077, and the gradient is the rate constant (k) which is equal to 0.2753 (Table 1).

The best fit for the results of the adsorption kinetics onto activated carbons masses of 0.0200 g and 0.0501 g was the second order rate law (Figure 6). It indicates that the adsorption rate was dependent on both the concentration of adsorbent surface sites [ACs] and the concentration of adsorbate [B] in the first order (a'=b'=1), which had regression coefficients (r^2) of 0.9981 and 0.9919 respectively (Table1). The rate constants for adsorption with 0.0200 g and 0.0501 g of adsorbent [ACs] were 8.4016 and 6.7491, respectively (Table 1).

Integrating both sides and using partial fractions,

Let $u = (a - x)$

$$-\frac{du}{dt} = 2k_2u^2 + k_1u, -\frac{du}{dt} = \frac{1}{2k_2u^2+k_1u}$$

$$-\frac{dt}{du} = \left(\frac{1}{k_1}\right)\left(\frac{1}{u}\right) - \left(\frac{2k_2}{k_1}\right)\left(\frac{1}{2k_2u+k_1}\right)$$

$$-\int dt = \left(\frac{1}{k_1}\int\frac{du}{u}\right) - \left(\frac{2k_2}{k_1}\right)\left(\frac{du}{2k_2u+k_1}\right)$$

Let $v = 2k_2u + k_1, dv = 2k_2du, du = \frac{1}{2k_2}dv$

$$-t = \frac{1}{k_1}\ln u - \frac{1}{k_1}\ln v + c$$

$$-t = \frac{1}{k_1}\ln(a - x) - \frac{1}{k_1}\ln[2k_2(a - x) + k_1] + c$$

At $t = 0, (a - x) = a$

$$-t = \frac{1}{k_1}\ln a - \frac{1}{k_1}\ln(2k_2a + k_1) + c$$

$$c = -\frac{1}{k_1}\ln a + \frac{1}{k_1}ln(2k_2a + k_1)$$

$$-t = \frac{1}{k_1}ln(a - x) - \frac{1}{k_1}\ln a - \frac{1}{k_1}ln[2k_2(a - x) + k_1] + \frac{1}{k_1}ln(2k_2a + k_1)$$

$$k_1t = -ln(a - x) + \ln a + ln[2k_2(a - x) + k_1] - ln(2k_2a + k_1)$$

$$k_1t = \ln\left[\left(\frac{a}{a-x}\right)\left(\frac{2k_2(a-x)+k_1}{2k_2a+k_1}\right)\right] \quad \text{(Eq. 16)}$$

The results of the adsorption kinetics on activated carbon masses of 0.1003 g, 0.1203 g, 0.1501 g, and 0.2001 g followed and had the best fit with the pseudo second order rate law (Figure 7) with high regression coefficients (r^2) of 0.998, 0.994, 0.997 and 0.996, respectively (Table 1). Therefore, the concentrations of the adsorbent surface sites [ACs] was in excess in these cases. The rates of adsorption were second order in [B], and the pseudo second order rate law explained the response well. The values of the rate constants are shown in Table 1.

Comparison with other studies

The kinetic models for 0.3 g granular activated carbon for adsorption of naphthalene, acenaphthene, fluorene, anthracene, pyrene solutions, were fitted best to the pseudo second order rate law except for fluranthene which was fitted best to the pseudo first order rate law [27]. The granular activated carbon was provided by Aguas de Levante (Spain) with a BET surface area 1,000 m^2 g^{-1}, macroporous volume 1.5 cm^3 g^{-1}. Experimental results were reported by Cabal [28] on the commercial activated carbon (Sinoharm Chemical Reagent Co., Ltd., China). The BET surface area has 718.2 m^2 g^{-1}, pore volume 0.845 cm^3 g^{-1}. The kinetic models for the adsorption onto 0.1 g of adsorbent [ACs] with different adsorbate solutions such as phenanthrene, fluoranthene, Benzo(a) anthracen were fitted best to the pseudo second order rate law, which agree with the best adsorption kinetic model as this work in activated carbon mass 0.1003 g.

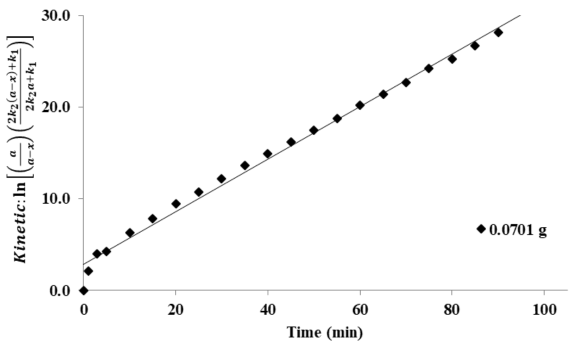

Figure 5 Mixed order kinetics between pseudo first order and pseudo second order for adsorption of 1-Nitronaphthalene by 0.0701g activated carbon at 25.5 °C.

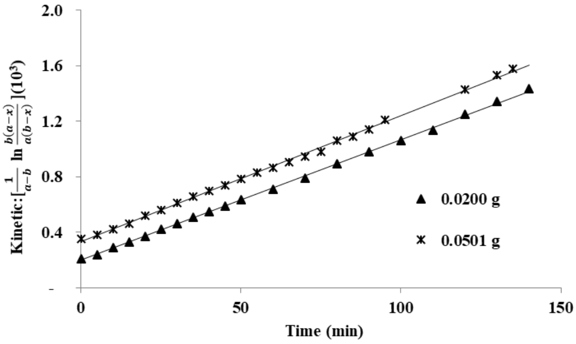

Figure 6 Second order kinetics for adsorption of 1-Nitronaphthalene by 0.0200g and 0.0501g activated carbon at 25.5 °C.

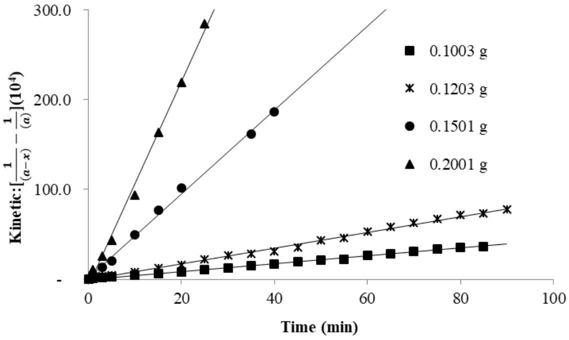

Figure 7 Adsorption by 0.1003 g, 0.1203, 0.1501 g, and 0.2001 g. activated carbon $[ACs]$ at 25.5 ^{o}C. The best fit line of the pseudo second order.

Table 1 Parameters of pseudo first order, second order, mixed order, pseudo second order and rate constant (Stage 2) of adsorbent (ACs) masses of 0.0200 g, 0.0501g, 0.0701g, 0.1003 g, 0.1203 g, 0.1501 g and 0.2001 g

Model	Rate constant (Stage 2)	Coefficient of Determination (r^2)	Sum of error square (SSE)
Activated carbon mass: 0.0200g			
Pseudo first order	0.0070	0.9961	36.7526
Second order	***8.4016***	***0.9981***	***0.0443***
Mixed order	1.0000	0.9961	6.3045
Pseudo second order	518.6112	0.9403	13228.6800
Activated carbon mass: 0.0501g			
Pseudo first order	0.0202	0.9232	22.8225
second order	***6.7491***	***0.9919***	***0.1904***
mixed order	0.4721	0.9845	1.9355
pseudo second order	2034.1174	0.9694	15329.6477
Activated carbon mass: 0.0701g			
Pseudo first order	0.0207	0.2685	0.9018
Second order	6.9356	89.6302	0.9027
Mixed order	**0.2753**	**0.3077**	**0.9986**
Pseudo second order	3087.9143	13256.5980	0.9804
Activated carbon mass: 0.1003g			
Pseudo first order	0.0170	0.9050	0.2542
Second order	4.6421	0.8543	98.0080
Mixed order	0.2924	0.9604	1.6334
Pseudo second order	***4320.7834***	***0.9981***	***1.8000***
Activated carbon mass: 0.1203g			
Pseudo first order	0.0235	0.8226	0.4944
Second order	4.5817	0.8232	96.2542
Mixed order	0.2913	0.9873	1.4981
Pseudo second order	***8835.0109***	***0.9954***	***1.7403***

Table 1 Parameters of pseudo first order, second order, mixed order, pseudo second order and rate constant (Stage 2) of adsorbent (ACs) masses of 0.0200 g, 0.0501g, 0.0701g, 0.1003 g, 0.1203 g, 0.1501 g and 0.2001 g *(Continued)*

Activated carbon mass: 0.1501g			
Pseudo first order	0.0745	0.7598	0.7526
Second order	11.5986	0.7600	117.0481
Mixed order	0.3016	0.9740	0.7764
Pseudo second order	***46777.2911***	***0.9969***	***4.0794***
Activated carbon mass: 0.2001g			
Pseudo first order	0.1205	0.9111	0.3738
Second order	14.0598	0.9112	43.6067
Mixed order	0.2514	0.9638	0.6531
Pseudo second order	***115588.1855***	***0.9958***	***7.4915***

Conclusion

The kinetic models for the adsorption of 1-Nitronaphthalene solution (PAH) onto the surface of 0.0200 g and 0.0501 g of adsorbent [ACs] were fitted best to the second order rate law (Table 1), and for 0.1003 g, 0.1203 g, 0.1501 g, and 0.2001 g were fitted best to the pseudo second order rate law (Table 1). The mass of 0.0701 g adsorbent [ACs] could not be fitted to any simple rate law, but did fit well to a mixed order model, that combination of pseudo first order and pseudo second order models.

The advantages of this finding are:

1. The study of adsorption kinetic models is important, being able to pin-point the adsorption process using activated carbon for removed of 1-Nitronaphthalene from wastewater.

2. This study indicated that the adsorption kinetic models from both experimental and theoretical is significant. It illustrates a new problem-solving procedure by combining the two order rate laws together to achieve better results with the same data.

The findings of this study will help in predicting the rate at which adsorption takes place and improve design systems.

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