Adsorption of 4-nitrophenol on palm oil fuel ash activated by amino silane coupling agent

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ABSTRACT

Adsorption of 4-nitrophenol on palm oil fuel ash activated by amino silane coupling agent was investigated. Experiments were carried out at 30°C as function of contact time, initial concentration (2500–4500 mgl^{-1}) and pH (1–7.4). The equilibrium adsorption data of 4-nitrophenol on activated palm ash were analyzed by Langmuir Freundlich and Temkin models. The results indicated that the Langmuir model provides the best correlation of the experimental data. The maximum adsorption capacity of the activated palm oil fuel ash was determined with the Langmuir equation and found to be 1000 mg g^{-1} adsorbent at 30°C. Adsorption kinetics data were modeled using the pseudo-first-order, pseudo-second-order and intra-particle diffusion equations. It was shown that pseudo-second-order kinetic equation could best describe the adsorption kinetics. The results obtained in this work indicate that activated palm oil fuel ash is suitable as adsorbent material for adsorption of 4-nitrophenol from aqueous solutions.

Keywords: 4-Nitrophenol; Activated palm oil fuel ash; Adsorption isotherm; Kinetics

1. Introduction

According to previous studies, 4-nitrophenol is an ordinary pollutant found especially in the effluents generated from petroleum refineries, coke oven, steel foundry, pesticides, preservatives, disinfectants, pulp processing, pharmaceuticals, petrochemicals and other industries [1,2]. It is not only introduced into the environment by the above mentioned industries but also formed naturally from the decomposition of leaves or wood. Stability of 4-nitrophenol and its resistance to microbiological degradation enable this compound to remain for many years in the environment [3]. 4-Nitrophenol is carcinogenic and toxic in nature and it poses danger to the human, flora and fauna in the biosphere and hence it has been included in the both of USA and EU Environmental Protection Agency (EPA) list of priority pollutants [2,4]. As a consequence, it is required to remove this compound from industrial wastewaters before safe disposal into the environment. Possible methods of removal of 4-nitrophenol from waste water include biological degradation, chemical oxidation, solvent extraction and adsorption have been used [5–7]. The literature analysis indicated that adsorption is the best and the most extensively technique used for the removal of 4-nitrophenol from aqueous solutions, as it is efficient for low to medium levels of 4-nitrophenol concentration and for its simplicity and flexibility of design [1,8,9]. Activated carbon is the most commonly used adsorbent in this technique, as it is a carbonaceous material with

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a large surface area and high porosity [10,11]. Nevertheless, the relatively high cost of activated carbon has induced the employment of low cost, naturally occurring adsorbents to remove trace organic contaminants from waste water, especially phenolic compounds [12]. Among them, anion-cation modified palygorskite [1], triton-x-100 [13], water-compatible hypercrosslinked polymeric adsorbent [14], Victorian low rank coal-based [15], pyrophyllite modified by amino silane coupling agent [16], kaolinite [17], antimony, cadmium and zirconium ferrocyanides [18], palm shell based activated carbon [19] and HDTMA+ pillared montmorillonites [20] have been used. South East Asia is known as major producer and exporter of palm oil especially Malaysia and Indonesia. Additionally, Malaysia has extensive agricultural and industrial activities involving palm oil, where the total oil palm planted areas have increased to 4.3 million hectares in 2007, a growth of 3.4% compared to 2006 [21]. In 2007 there were approximately 406 palm oil mills in Malaysia [22]. Therefore, this important economic activity generates a huge amount of effluent which could pollute the environment if not properly treated. For example, it was estimated that for each ton of crude palm oil produced, about 2.5–3.5 tons of palm oil mill effluent are generated. Thus, it is possible to expect that 26.80–39.12 million tons in the form of shell and fibers are produced yearly. This waste is usually used as boiler fuel for the steam generation for palm oil mill consumption. As a result, thousands of tons of ash will be produced after combustion of this solid waste. Understanding the gravity of environmental effects arising from waste disposal, rapid mitigation programme can be taken in such a way that this waste can be optionally used to produce eco-friendly and cheap adsorbent for the removal of pollutant from wastewater. Therefore, palm oil fuel ash has been used for the removal of SO_2 [23,24], acid green 25 dye [25], direct dye [26] and trivalent chromium on Cr (VI) [27]. Cross-linked chitosan/OPA beads have been also used to remove reactive dye [28]. Pyrophyllite modified by amino silane coupling has been used to remove 4-nitrophenol from aqueous solution [29]. Therefore, the purpose of this work was to evaluate the adsorption potential of activated palm oil fuel ash toward 4-nitrophenol. The equilibrium and kinetic data of the adsorption process were then studied to understand the adsorption mechanism of 4-nitrophenol molecules onto the palm oil fuel ash activated by amino silane coupling agent.

2. Materials and methods

2.1. 4-Nitrophenol and adsorbent preparation

4-Nitrophenol, with the molecular formula $C_6H_5NO_3$ and molecular weight 139.11, was chosen as adsorbate. The aqueous solutions were prepared by dissolving the solute in deionizedwater to the required concentrations. The palm oil fuel ash used in this work was obtained from East Oil Mill, Golden Hope Plantation Sdn. Bhd., Pulau Carey, Selangor. It was sieved using a sieve machine (Omron, Japan) to get samples of particle size between 200 and 150 μm and washed several times with distilled water and oven dried overnight at 118°C. The amino silane coupling agent, N-(3-(trimethoxysilyl) propyl) ethylenediamine, 97% with the chemical formula $H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$ was purchased from Sigma-Aldrich, USA. It was first hydrolyzed before being used for the activation of the palm oil fuel ash. This step was referred to Sayilkan et al. [16] and Sener et al. [30] used 10 g of distilled water was added drop wise into a round-bottom flask containing 40 g of amino silane coupling agent without using any solvent and catalyst. The reaction was allowed to stand at room temperature for 30 min until a clear and homogeneous solution was obtained. The hydrolyzation reaction of amino silane coupling agent and water occurs according to the following reaction:

$$H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3 + 3/2\ H_2O \rightarrow H_2N(CH_2)_2NH(CH_2)_3Si(OH)_{3/2}(OCH_3)_{3/2} + 3/2\ CH_3OH$$
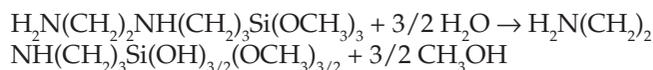
Both un-reacted water and alcohol were vacuum extracted for 45 min. The viscous solution obtained was diluted with 40 g of dry methanol, then 20 g of palm oil fuel ash was activated by refluxing with 80 g of this diluted solution at room temperature for 20 h and the solid paste was finally filtered and dried under vacuum for 3 h at 80°C before use.

The FT-IR (Perkin Elmer-2000 FT-IR) technique was used to find out the functional groups present in both the raw palm oil fuel ash and activated by amino silane coupling agent. The type and percentage of each chemical element in palm oil fuel ash and activated samples were determined using X-Ray Fluorescence Spectrometry (XRF) model Bruker S4-Explorer X-ray Fluorescence (Germany).

2.2. Batch equilibrium and kinetic studies

The factors affecting the adsorption capacity of 4-nitrophenol on the surface of palm oil fuel ash activated adsorbent including pollutant initial concentration, agitation contact time and solution pH were examined. Initial concentration and time effects on activated palm ash adsorption performances were investigated by adding a fixed amount (0.5 g) of this adsorbent to five 250 ml glass bottles filled with 100 ml of diluted 4-nitrophenol solutions with initial concentrations of 2500–4500 mg l^{-1}. Those bottles with other five bottles filled with 100 ml of (2500–4500 mg l^{-1}) 4-NP solution were then sealed and placed in a shaker at 150 rpm and at room temperature (30 ± 1°C) for different contact

times (2, 5, 10, 30, 60, 120, 180 and 1440 min). The initial pH of the solutions was recorded to be 7.4. The bottles were then removed from the shaker and the solutions were filtered using qualitative filter paper 102 (Double Rings, China). The absorbances of the filtrates (after diluting 100 times) were measured at 316.8 nm using a UV-vis spectrophotometer (Shimadzu, Japan). The amount of 4-NP adsorbed on activated palm oil fuel ash at equilibrium, q_e and at any time t, q_t (mg g^{-1}) was calculated from Eqs. (1) and (2):

$$q_e = \frac{(C_o - C_e)\,V}{W} \tag{1}$$

$$q_t = \frac{(C_o - C_t)\,V}{W} \tag{2}$$

where C_o, C_e and C_t are the liquid phase concentrations of 4-nitrophenol at initial, equilibrium and any time t, respectively, V (l) the volume of the solution and W(g) is the mass of adsorbent.

To investigate the effect of pH solution on the adsorption uptake, five equal amounts (0.5 g) of the adsorbent were added to five 250 ml glass bottles, each containing 100 ml of a 4500 mg l^{-1} 4-nitrophenol solution, at different initial pH values ranging from 2 to 7. The solutions were shaken at 150 rpm and room temperature (30 ± 1°C) until equilibrium time was reached (3 h). pH adjustments were done using solutions of 0.5 M HCl and 0.1M NaOH and the pH values were measured using pH meter Mettles Toledo (Model: Ross FE 20, U S A).
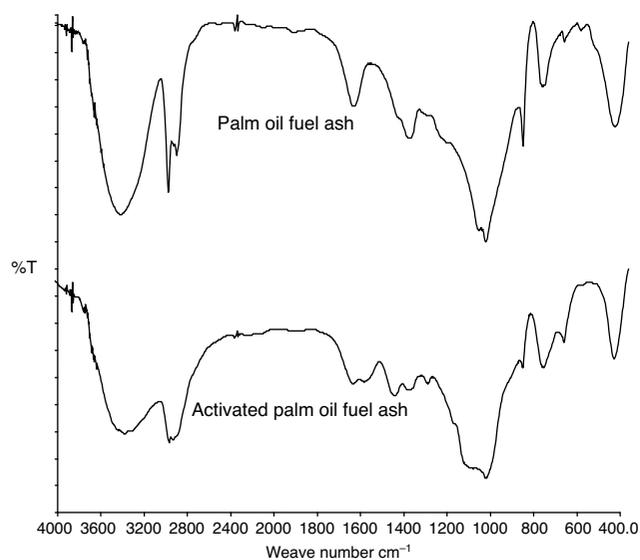
Fig. 1. FT-IR spectra recorded for palm oil fuel ash and activation by amino silane coupling agent.

3. Results and discussion

3.1. Characterization of the adsorbents

The results of FT-IR spectra of raw palm oil fuel ash and activated by amino silane agent were presented in Fig. 1 and Table 1. Fig. 1 shows that the absorption peaks appearing in the region 3449–3354 cm^{-1} represent OH stretching vibration in the case of palm oil fuel ash samples before and after modification by amino silane chemical agent. The band recorded in the range of 2978 cm^{-1} to 2924 cm^{-1} corresponds to aliphatic CH$_2$ – bending vibration in both raw and activated palm oil fuel ash. There are two main groups of absorption peaks recorded for each one of the two palm oil fuel ash samples in the regions between 800.68 cm^{-1} and 777.31 cm^{-1} and 478.30 cm^{-1} and 461.09 cm^{-1} corresponding to the

Table 1
FT-IR vibration band positions and their assignments for palm oil fuel ash and activation by amino silane coupling agent

Adsorbent	Band position (cm^{-1})	Assignments
Palm oil fuel ash	3406	O–H stretching vibration of OH bonded to the adsorbent surface
	2975	Aliphatic CH-stretching vibration
	1647	C=C stretching vibration
	1393	CH$_3$ deformation
	1047	Si–O stretching vibration
	879	Si–H deformation
	793	CH out-of-plane deformation
	462	Bending of Si–O groups
Activated palm oil fuel ash	3366	O–H stretching vibration of OH bonded to the adsorbent surface
	2967	Aliphatic CH-stretching vibration
	1650	C–NH–C bending vibration
	1586	Amide Π band: dil soln
	1465	CH$_2$ deformation
	1384	CH$_3$ deformation
	1311	Assignment uncertain
	1119	Si–O stretching vibration
	1046	Si–O–Si stretching vibration
	787	CH out-of-plane deformation
	467	Bending of Si–O groups

bending of CH out-of-plane deformation and Si-O groups respectively. It was also observed from Fig. 1 and Table 1 that the raw and activated palm oil fuel ashes differ together in the following:

1) Absence of C=C stretching vibration in the region 1650–1580 cm^{-1} for activated sample.

2) Appearing absorption peak in the region of 1650 cm^{-1} corresponding to the C$^-$NH–C bending vibration in the case of modified one.

3) Disappeared of the Si-based functional groups from the adsorbent sample after modification.

4) Reduction of intensity of OH stretching peaks for the activated sample. These results are in agreement with the finding reported by Sener et al. [30].

The results of X-ray fluorescence spectrometric analysis obtained for the chemical composition of the samples of raw and activated palm oil fuel ash are listed in the Table 2. The results indicate the existence of silica and potassium oxides as the major components and different percentage of other oxides.

3.2. Effect of silane modification on the adsorbent adsorptive properties

It can be suggested that the modification of oil palm ash by prehydrolyzed agent lead to chemical reaction between the OH groups of this compound molecules $H_2N(CH_2)_2NH(CH_2)_3Si(OH)_{3/2}(OCH_3)_{3/2}$ and the OH groups and/or oxygen atoms on the oil palm fuel ash surface. The chemical equation of this reaction can be represented as the follows:

Oil palm fuel ash surface after modification

Oil palm fuel ash surface before modification
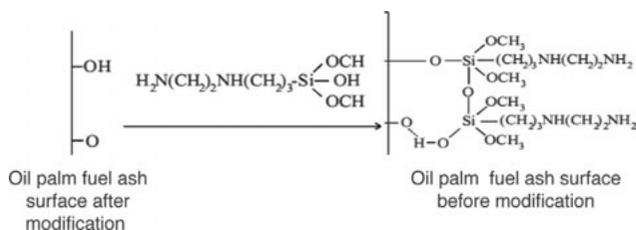
Moreover, it can also be suggested from this equation that the 4-nitrophenol as a weak acid react with

amino functional groups presented on the oil palm fuel ash after modification as a weak base. This indicates that the treatment of oil palm fuel ash created a new active adsorption sites.

3.3. Effects of contact time and initial concentration

The effects of contact time and initial concentration on the amount of 4-nitrophenol adsorption onto the surface of palm oil fuel ash activated by amino silane coupling agent are given in Fig. 2. It was observed from the Fig. 2 that, the amount of 4-nitrophenol adsorbed (q) increases with increasing agitation time and the time required to attain the equilibrium was about 60 min for each investigated concentration. However, the experimental data were measured at 180 min to make sure that full equilibrium was attained. The removal of 4-nitrophenol (mg g^{-1}) increased with increase in agitation time and concentration and remained nearly constant after equilibrium time. The time required to attain this state of equilibrium is termed equilibrium time, and the amount of 4-nitrophenol adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operation conditions. In the q_t versus t graphic a greater initial slope (initial adsorption rate) was observed for higher 4-nitrophenol initial concentrations due to the a greater driving force of the adsorption process that makes it faster for lower
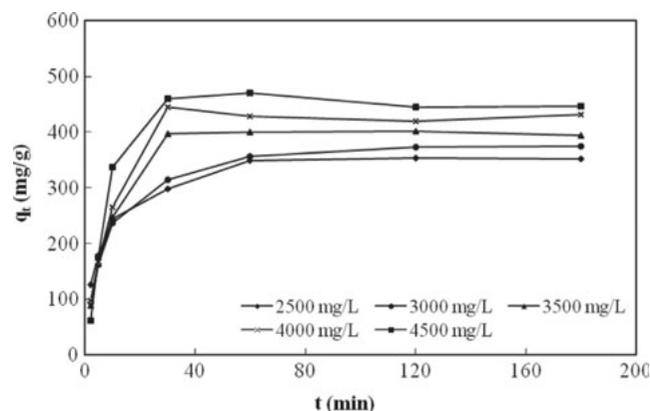
Fig. 2. Effects of initial concentration and contact time on the 4-nitrophenol adsorption onto activated palm oil fuel ash.

Table 2
Chemical composition of palm oil fuel ash and activation by amino silane coupling agent, using X-RF

Adsorbents	Weight percent (%) of components								
	SiO$_2$	K$_2$O	CaO	P$_2$O$_5$	MgO	Al$_2$O$_3$	SO$_3$	Fe$_2$O$_3$	Others
Palm oil fuel ash	74.67	9.33	4.05	3.51	2.71	1.83	0.28	3.07	0.55
Activated palm oil fuel ash	75.52	8.54	4.38	3.97	2.41	1.58	0.20	2.82	0.58

adsorption times at which the pollutant transport on the sorbent surface is the prevailing mechanism. These results are in agreement with the finding reported by Huang et al. for the adsorption of 4-nitrophenol on the XAD-4 resin and HJ-1 resin [11].

3.4. Effect solution pH

As shown in Fig. 3, the adsorption of 4-nitrophenol on activated palm oil fuel ash is not affected by changing the solution pH from 2 to 5 but the adsorption increased at pH above 5. 4-Nitrophenol as a weak acid exists in solution either as a 4-nitrophenolate ion when the solution pH is greater than its pK_a which is equal to 7.12 or as a neutral 4-nitrophenol molecule in the opposite case [18]. The 4-nitrophenolate ions adsorb on the surface of adsorbents by electrostatic attraction mechanism. However, the neutral 4-nitrophenol molecules can be adsorbed on the adsorbents surface by several mechanisms such as Van der Waals forces, complex donor–acceptor mechanism and chemical reaction between 4-nitrophenol molecules as a weak acids and amino functional groups on the adsorbents surface as a weak abases. In this study it was expected that the 4-nitrophenol is adsorbed on the surface of activated palm oil fuel ash in the pH range of 1–5 by hydrogen bonding. This mechanism is not affected by changing the pH value, thus justifying a constant 4-nitrophenol adsorption capacity in this range. However, in the pH range 5–7 most of 4-nitrophenol molecules could be adsorbed by both the chemical reaction between 4-nitrophenl and amino functional groups and some of them adsorbed by electrostatic attraction between the negative phenolate ions and the positive sites on the surface of the adsorbent, so the adsorption capacity of 4-nitrophenol increased sharply in this pH range. At solution pH greater than 7, the activated palm oil fuel ash

is negatively charged and the 4-nitrophenol molecule dissociates to the anionic form [31]. This will generate repulsion between sorbate and adsorbent and the amount of 4-nitrophenol adsorbed will be very small. As solution pH decreases, the magnitude of negative charge on the activated palm oil fuel ash and 4-nitropheonol reduces, reducing the repulsion between sorbate and adsorbent and the amount of 4-nitrophenol adsorbed from solution begins to increase [32]. This observed behavior of the adsorption of 4-nitropheonl with varying solution pH has been reported by several authors [31,33].

3.5. Adsorption isotherms

In adsorption systems, it is necessary to study the adsorption isotherms to understand the interactions between the adsorbate and adsorbent and optimize the adsorbent dose to use [1]. The essential of practical design and operation of the adsorption technique is the correlation of the equilibrium data by either theoretical or empirical equation. Several models are available to describe the experimental data of adsorption. Langmuir and Freundlich are the most frequently employed models. In this work, Langmuir, Freundlich and Temkin models were used to describe the equilibrium experimental data of 4-nitrophenol adsorption on the activated palm oil fuel ash. The linear form of the Langmuir, Freundlich and Temkin models are represented in Eqs. 3, 4 and 5 respectively [24,34].

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \tag{3}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{5}$$

where q_e is the amount of a substance adsorbed at equilibrium (mg g^{-1}), q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg g^{-1}), C_e is the concentration of the adsorbate at equilibrium (mg l^{-1}). K_L (l mg^{-1}), K_F (mg g^{-1})(l mg^{-1})$^{1/n}$ and K_T (l mg^{-1}) are the Langmuir, Freundlich and Temkin constants, respectively. B_1 (J/mol) and n are other constants related to the heat of adsorption and adsorption intensity of the adsorbent, respectively. The value of n indicates a favorable adsorption when $1 < n < 10$, it is more favorable as $1/n < 1$ [19]. The dimensionless separation factor, R_L which is expresses the essential characteristic of the Langmuir equation was also calculated by the following equation [35]:
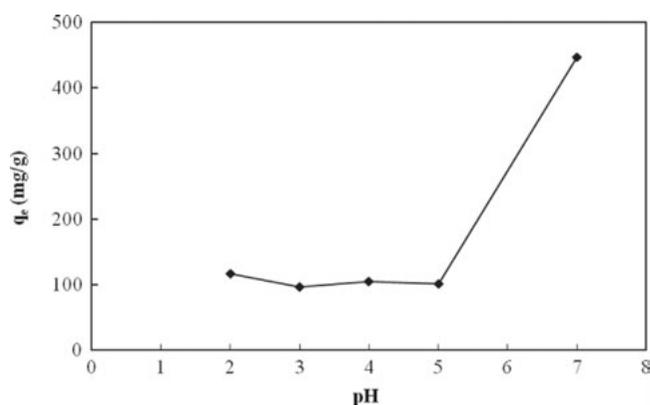
Fig. 3. Effect of PH on 4-NP adsorption by activated POFA Conditions: 4000mg l^{-1} initial 4-nitrophenol concentration, $T = 30°C$, $W = 0.5$ g, $V = 100$ ml.

$$R_L = \frac{1}{1 + K_L \, C_0} \tag{6}$$

Where K_L is the Langmuir constant and C_o is the 4-NP highest initial concentration. R_L value implies the adsorption to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The linear plots of C_e/q_e versus C_e (Fig. 4), $\ln q_e$ against $\ln C_e$ (Fig. 5) and q_e against $\ln C_e$ (Fig. 6) were obtained from the Langmuir, Freundlich and Temkin isotherm models respectively, for the adsorption of 4-nitrophenol on the palm oil fuel ash modified by amino silane coupling agent. Parameters of these models were determined from the slopes and intercepts of the above mentioned linear plots. Values of
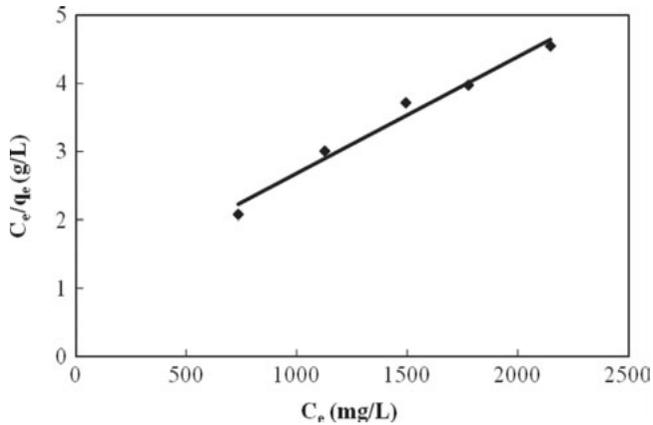
Fig. 4. Linearized Laongmuir isotherm for the adsorption of 4-nitrophenol onto activated palm oil fuel ash.
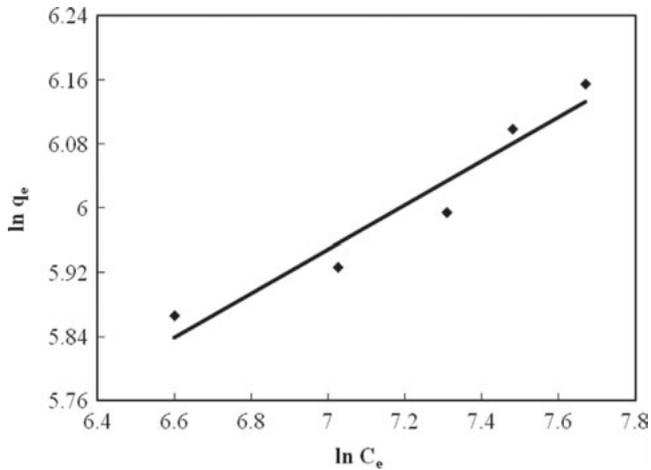
Fig. 5. Linearized Freundlich isotherm for the adsorption of 4-nitrophenol onto activated palm oil fuel ash.
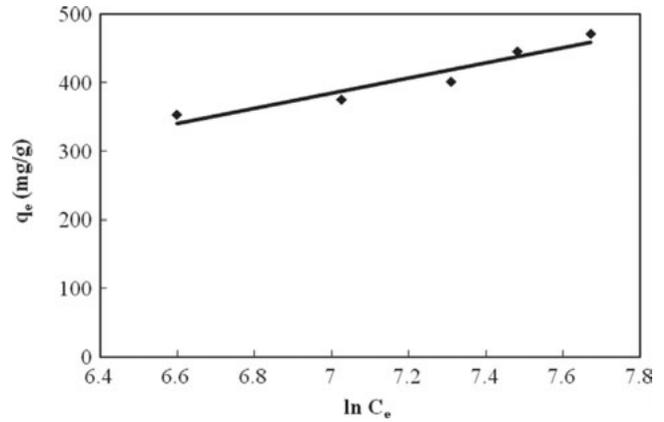
Fig. 6. Linearized Temkin isotherm for the adsorption of 4-nitrophenol onto activated palm oil fuel ash.

these parameters, their corresponding correlation coefficients (R^2) and a dimensionless adsorption factor (R_L) are listed in Table 3. It was observed from Table 3 that the palm oil fuel ash has a high adsorption capacity ($q_{max} = 1000$ mg g^{-1}) and intensity {$K_F = 56.14$ (mg g^{-1})(l mg^{-1})$^{1/n}$} toward 4-nitrophenol. The value of R_L ($1 > R_L > 0$) and Freundlich exponent n ($n > 1$) suggest that the adsorption conditions were constructive for the adsorption of 4-nitrophenol on palm oil fuel ash modified by amino silane coupling agent. The correlation coefficient R^2 values were 0.97, 0.93 and 0.91 for Langmuir, Freundlich and Temkin, respectively, indicating that all of these models used in this work fit the equilibrium experimental data and that Langmuir model gave the best fit. This indicates the homogeneous nature of palm oil fuel ash surface. This means that the active adsorption sites on the modified adsorbent surface have the same affinity toward 4-nitorphenol because the mechanism of this adsorption was the chemical reaction between 4-nitrophenol as acid and amino functional groups as base. The results also implied the formation of monolayer coverage of 4-nitrophenol molecules to the external surface of this adsorbent. Similar results were reported for the adsorption of 4-nitrophenol on the functional chitosan [31] and palm shell based activated carbon [19].

Table 4 lists the comparison of maximum monolayer adsorption capacity of 4-nitrophenol using various adsorbents. The oil fuel ash activated by amino silane coupling agent prepared in this work had a relatively

Table 3
Langmuir, Freundlich, and Temkin parameters for adsorption of 4-nitrophenol onto activated palm oil fuel ash

Langmuir isotherm			Freundlich isotherm				Temkin isotherm		
q_{max} (mg g^{-1})	K_L (l mg^{-1})	R^2	K_F (mg g^{-1})(l mg^{-1})$^{1/n}$	$1/n$	n	R^2	K_T (l mg^{-1})	$B1$ (J mol^{-1})	R^2
1000	0.001	0.978	56.14	0.274	3.64	0.93	0.028	111.40	0.912

Table 4
Comparison of the maximum monolayer adsorption of 4-NP on various adsorbents

Adsorbent	Maximum monolayer adsorption capacity (mg g⁻¹)	References
Bagasse fly ash	8.3	[36]
Zeolite	1.02	[37]
Fly ash	7.80–9.68	[38]
Rice husk	15.31	[39]
Sugar fly ash	0.76–1.15	[36]
Granular activated carbon	206.30	[40]
Acid activated jute stick char	39.38	[41]
Mansonia wood sawdust	21.28	[42]
Oil fuel ash activated by amino silane coupling agent	1000	[Present study]

large adsorption capacity of 1000 mg g⁻¹ if compared to some data obtained from the literature. Oil fuel ash activated by amino silane coupling agent is suitable for 4-nitrophenol removal from aqueous solution since it has relatively high adsorption capacity and the cost of the adsorbent is also low as the precursor and as oil fuel ash itself is easily available as solid waste. The comparison of adsorption capacities of various low-cost adsorbents with oil fuel ash activated by amino silane coupling agent shows that it is effective for the removal of 4-nitrophenol.

3.6. Adsorption kinetics

The kinetic experimental data obtained for the adsorption of 4-nitrophenol on activated palm oil fuel ash were interpreted by means of pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models. The linear form of the pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models are represented by Eqs. (7)–(9):

$$\log(q_e - q_t) = \log q_e - K_1 \frac{t}{2.303} \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

$$q_t = K_{dif} \sqrt{t} + C \tag{9}$$

Where K_1 (min⁻¹), K_2 (g mg⁻¹ min⁻¹) and K_{dif} (mg g⁻¹ min⁻¹/²) are the rate constants for the pseudo-first

order, pseudo-second order and intra-particle diffusion kinetic models, respectively; q_t (mg g⁻¹) and q_e (mg g⁻¹) are the amount of 4-nitrophenol adsorbed at any time t and equilibrium. The linear plots of these models are shown in Figs. 7, 8 and 9 for pseudo-first order,
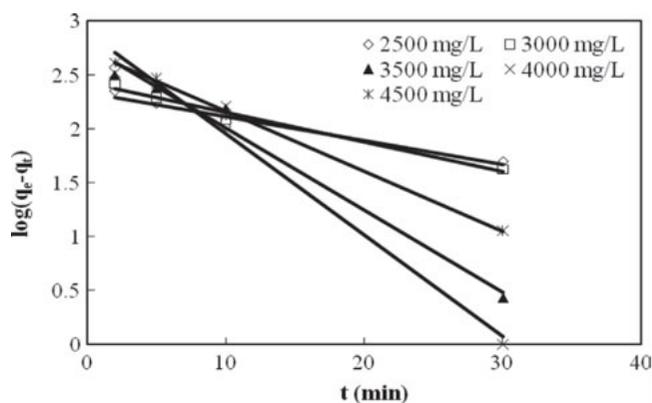
Fig. 7. Pseudo-first-order kinetics of 4-nitrophenol adsorption onto activated palm oil fuel ash at various initial concentrations.
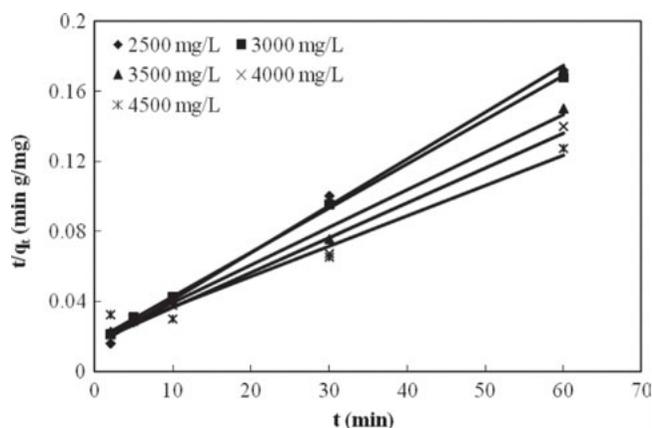
Fig. 8. Pseudo-second-order kinetics of 4-nitrophenol adsorption onto activated palm oil fuel ash at various initial concentrations.
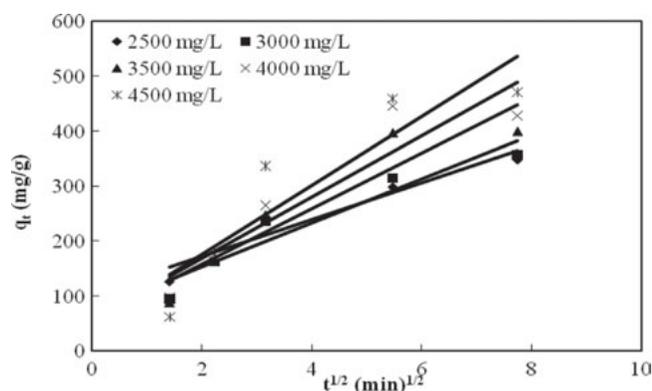
Fig. 9. Intra-particle-diffusion kinetics of 4-nitrophenol adsorption onto activated palm oil fuel ash at 30°C.

Table 5
 Kinetic parameters of 4-nitrphenol adsorption onto activated palm oil fuel ash at various initial concentrations

C_o (mg l^{-1})	$q_{e,exp}$ (mg g^{-1})	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Intra-particle diffusion		
		$q_{e,cal}$ (mg g^{-1})	K_1 (min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2	K_{dif} (mg g^{-1} min$^{-1/2}$)	C	R^2
2500	348.34	214.87	0.051	0.947	500.02	0.00028	0.996	33.43	105.00	0.933
3000	356.8	266.16	0.062	0.979	500.32	0.00024	0.999	39.84	73.36	0.918
3500	399.92	582.14	0.175	0.982	500.38	0.00024	0.994	50.58	56.61	0.883
4000	428.26	776.22	0.214	0.975	500.65	0.00025	0.988	55.58	57.75	0.861
4500	470.78	526.53	0.127	0.998	1000.71	0.00005	0.973	62.80	49.36	0.824

pseudo-second order and intra-particle diffusion respectively. The kinetic parameters including $(K_1, q_{e,cal})$, $(K_2, q_{e,cal})$ and (K_{dif}, C) were calculated from slopes and intercepts of the linearized plots of the above mentioned kinetic models. The values of these parameters with the correlation coefficient, R^2, were listed in Table 5. The values of the R^2 were in the ranges of 0.947–0.998, 0.973–0.999 and 0.824–0.933 for pseudo-first order, pseudo-second order and intra-particle diffusion, respectively. Nevertheless, the R^2 values obtained indicated that the pseudo-first order kinetic model was suitable to describe the experimental data but the pseudo-second order model gave the best fitting. This indicates that most of the 4-nitrophenol molecules are adsorbed onto the surface of palm oil fuel ash by chemisorption mechanism, although some of them may also be adsorbed by physisorption mechanism. Moreover, it was observed from Table 5 a big difference between $q_{e,exp}$ values and $q_{e,cal}$ values for both models. This big difference conforms that the 4-nitrophenol adsorbed on the modified oil palm fuel ash by chemiphysisorption mechanisms [16]. Similar results were observed in the adsorption of 4-nitrophenol from aqueous solution by HDTMA$^+$ pillared montmorillonite [20]. According to the correlation coefficient values, it was concluded that the intra-particle diffusion mechanism was involved in the adsorption of 4-nitrophenol on modified palm oil fuel ash, but this was not the rate controlling step because the lines were straight but did not pass through the origin. Zhou et al. [20] also found that the intra-particle diffusion was involved in the sorption process, but it was not the controlling step [20].

4. Conclusions

Activated palm oil fuel ash was used as an adsorbent for the removal of 4-nitrophenol from an aqueous solution. The Fourier transform infrared spectroscopy (FTIR) measurements showed that the most of surface chemistry of the activated palm oil fuel ash was influenced by the acidic treatment. The adsorption capacities were affected by the initial 4-nitrophenol concentration. The uptake increased with the increase in initial 4-nitrophenol concentration. Solution pH has a negligible effect in the range of 1–5 and active effect above 5. The Langmuir model agrees very well with the equilibrium isotherm. The R_L values showed that activated palm oil fuel ash was favorable for the adsorption of 4-nitrophenol. According to the values of correlation coefficients, the pseudo-second order kinetic model fits very well with the dynamical adsorption behavior of 4-nitrophenol. On the other hand, there is a big difference between $q_{e,exp}$ values and $q_{e,cal}$ values for both models which indicated that the adsorption of 4-nitrophenol on the modified oil palm ash surface occurred by chemisorptions and physisorption mechanisms. The present investigation showed that activated palm oil fuel ash was a promising low-cost adsorbent to be used in the removal of 4-nitrophenol from aqueous solutions over a wide range of concentrations.

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