Removal of nitrobenzene from aqueous solution by a novel lipoid adsorption material (LAM)

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ABSTRACT

In this study, a novel adsorbent referred to as a lipoid adsorption material (LAM) was synthesized with a hydrophobic nucleolus (triolein) and hydrophilic membrane structure (polyamide). The LAM was applied to the adsorption and removal of nitrobenzene from aqueous systems. Experiments were carried out to investigate the adsorption behavior of nitrobenzene on LAM, including the development of adsorption isotherms, the determination of adsorption kinetics, and to explore the influence of adsorbent dosage, contact time, temperature and the initial concentration of nitrobenzene on adsorption. The performance of LAM was compared with equal amounts of granular activated carbon (GAC) for adsorption. The adsorption isotherms for LAM were found to be described by the Linear equation, while the adsorption isotherms for granular activated carbon (GAC) were described by the Freundlich equation. Results indicated that the adsorption of nitrobenzene by LAM occurred mainly due to the partition function caused by the triolein nucleolus. Two kinetics models, pseudo-first-order and pseudo-second-order models were used to fit the experimental data for LAM adsorption. By comparing the correlation coefficients, it was found that the pseudo-first-order model was most suitable to describe the adsorption of nitrobenzene on LAM. The results also indicated that the factors that affect the adsorption rate would be either the nitrobenzene concentration or the character of the adsorbent. Thermodynamic calculations indicated that the adsorption of nitrobenzene on LAM was spontaneous and was an exothermic reaction. With an initial nitrobenzene concentration of $200 \, \mu g \, l^{-1}$, an equilibrium concentration was reached within 8 h using LAM as an adsorbent and the average removal efficiency was 94.3%. For GAC, the adsorption equilibrium was achieved after 12 h with a 91.9% nitrobenzene removal efficiency.

1. Introduction

Persistent organic pollutants (POPs) are compounds of great concern due to their characteristics of toxicity, persistency and bioaccumulation within ecosystems [1–3]. Many of these compounds can present high risks to ecological and human health even at low concentrations [4,5]. Nitrobenzene is a type of POP which is widely used in the production of different types of products including dyes, explosives and pesticides [6]. After use, nitrobenzene in solution is generally discharged into wastewater treatment plants where a large proportion of it cannot be removed by conventional treatment processes and is discharged into the surrounding aquatic environment [7]. Methods to remove residual POPs from the environment have been subject to increasing research in recent years, focusing on removal mechanisms such as adsorption, ozonation,

and advanced oxidation processes [8–10]. However, hazardous POPs like nitrobenzene, with low water solubility, are especially difficult to remove from wastewater. Activated carbon, with a high porosity and an extensive surface area, has been widely used as an effective adsorbent for several organic compounds of concern in water and wastewater treatment [11,12]. Adsorption with granular activated carbon (GAC) material is considered to be one of the most efficient methods for controlling the nitrobenzene in water [13]. However, the high cost of both activated carbon materials and their regeneration presents difficulties which limit their application. Therefore, the search for low-cost and easily acquired adsorbents has led many researchers to explore more economical and efficient techniques of using the natural and synthetic materials as adsorbents. These include bagasse fly ash [14–17], red mud [18,19] and bottom ash [20,21]. New agents are also being developed, including a biomimetic fat cell (BFC) for removal of lindane from aqueous solution [22,23] and a triolein-embedded activated carbon composite adsorbent (CA-T) for removal of dieldrin from aqueous solution [24].

Previous researchers have shown that the fatty tissue of organisms can accumulate hydrophobic chemicals and that the level of

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accumulation has a positive correlation with the quantity of fat [25–27]. Based on this bioaccumulation as a function of the quantity of fat tissue, an innovative lipoid adsorption material (LAM), with a hydrophobic nucleolus (triolein) and hydrophilic membrane structure (polyamide), was synthesized and used for atrazine removal [28]. Similar material, such as BFC [22,23], have been synthesized and applied in previous studies. However, lindane was the only target pollutant used in BFC research and no research has been conducted into the adsorption kinetics. To completely characterize the adsorption performance of this innovative adsorbent, the adsorption behavior of other typical pollutants in the environment should be examined. This research was conducted to investigate the adsorption behavior of nitrobenzene as a model POP contaminant onto LAM compared to the adsorption onto a commercially used granular activated carbon (GAC). Batch adsorption experiments were carried out to study the adsorption isotherms and adsorption kinetics.

2. Materials and methods

2.1. Reagents and chemicals

For the preparation of LAM, terephthaloyldichloride, 1,6-hexanediamine, triolein and 4′-aminoacetophenone were purchased from Shanghai Guoyao Chemical Co. Ltd. (China). Tween 20 was purchased from Shanghai Jierun Chemical Co. Ltd. (China). Sodium hydroxide, hydrochloric acid, pyridine, cyclohexane and methanol were purchased from Tianjin Basifu Chemical Co. Ltd. (China). All chemicals were analytical grade.

Nitrobenzene (98%, without further purification) was purchased from Shanghai Lingfeng Chemical Co. Ltd. (China). GAC with a specific surface area of $850 \, m^2 \, g^{-1}$ was obtained from Tianjin Third Chemical Factory (China). The GAC was boiled in distilled water for 2 h to remove impurities and subsequently dried for 24 h at a temperature of $105 \, °C$.

2.2. LAM preparation

An interface polymerization reaction was employed for preparation of LAM [29]. The preparation was described in previous research [28] and is briefly described here. Triolein, terephthaloyldichloride and Tween 20 were dissolved into quantitative cyclohexane to form the oil phase of the reaction. 1,6-Hexanediamine and sodium hydroxide were then mixed with distilled water to form the water phase. The water phase was slowly added to the oil phase in a drop-by-drop manner to control the interfacial polymerization speed. The oil phase which contained no triolein and the same water phase were used to prepare LAM prepolymer. The synthesized material was thoroughly rinsed with deionized water then dried for 24 h at a temperature of $105 \, °C$.

2.3. Adsorption equilibrium

Preliminary kinetic tests were carried out to determine the equilibrium time and adsorption capacity of the sorbents. It was assumed that equilibrium was attained when no further changes in nitrobenzene concentration were observed after a 24 h contact time.

The adsorption of nitrobenzene from aqueous solution by LAM (with 3% triolein content) and by GAC was compared in the experiment. Adsorption isotherms were obtained by mixing 30 mg LAM or GAC with 150 ml nitrobenzene solution of different concentrations (50, 100, 200 and $300 \, \mu g \, l^{-1}$). The suspensions were agitated using a mechanical shaker at $150 \, r \, min^{-1}$ and at a temperature of

$30 \, °C$ for 24 h. Liquid samples were taken throughout the reaction period until equilibrium was achieved.

2.4. Adsorption kinetics

Batch adsorption experiments were conducted to investigate the effects of various parameters including adsorbent dose, the initial concentration of nitrobenzene, temperature, on the sorption kinetics of nitrobenzene on LAM and GAC. To determine the adsorbent dose, five different quantities of adsorbents (10, 20, 30, 40 and 50 mg LAM and GAC) were mixed with a nitrobenzene solution of $200 \, \mu g \, l^{-1}$. To explore the effect of initial pollutant concentration, initial nitrobenzene concentrations of 50, 100, 200 and $300 \, \mu g \, l^{-1}$ were applied with 30 mg LAM or GAC. The above experiments were carried at $30 \, °C$. Temperature ranged between 20 and $40 \, °C$ with 30 mg LAM or GAC and with a nitrobenzene solution of $200 \, \mu g \, l^{-1}$ in the temperature experiment. A liquid volume of 150 ml in 500 ml sealed conical flask was used for all tests and the suspensions were agitated using a mechanical shaker at $150 \, r \, min^{-1}$. Samples were withdrawn at regular intervals to analyze the residual nitrobenzene. Blank experimental runs were conducted simultaneously under the same conditions which contained the adsorbent in 150 ml of distilled water. The stability of the nitrobenzene solution was verified by agitating a nitrobenzene solution without any adsorbent. There was no change in the concentration of nitrobenzene in this control solution during the experiment.

The removal efficiency of nitrobenzene was calculated using Eq. (1):

$$\%\text{removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

The adsorption capacity of nitrobenzene was calculated using the mass balance in Eq. (2):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where q_e ($\mu g \, mg^{-1}$) is the equilibrium adsorption capacity; C_0 and C_e ($\mu g \, l^{-1}$) are the initial and equilibrium concentrations of nitrobenzene in solution, respectively; V (l) is the volume of aqueous solution containing nitrobenzene; and m (mg) is the weight of the adsorbent. The experiments were performed in triplicate and average values were taken into account. The relative deviations between results were less than 5%.

2.5. Adsorption kinetic theory

Adsorption rate constants for the nitrobenzene were calculated by using pseudo-first-order and pseudo-second-order models. The conformity between the experimental data and the model-predicted values was expressed by the correlation coefficients (R^2). A relatively high R^2 value indicates that the model successfully describes the kinetics of the nitrobenzene adsorption.

2.5.1. Pseudo-first-order-and pseudo-second-order-model

The pseudo-first-order equation is given by Srivastava et al. [30] and presented in Eq. (3).

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

The equation can be expressed in a linear form as shown in Eq. (4):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

where q_t ($\mu g \, mg^{-1}$) is the amount of nitrobenzene adsorbed at time t (min); q_e ($\mu g \, mg^{-1}$) is the amount of the nitrobenzene adsorbed on the adsorbent at time under equilibrium conditions; k_1 is the pseudo-first-order rate constant (min^{-1}).
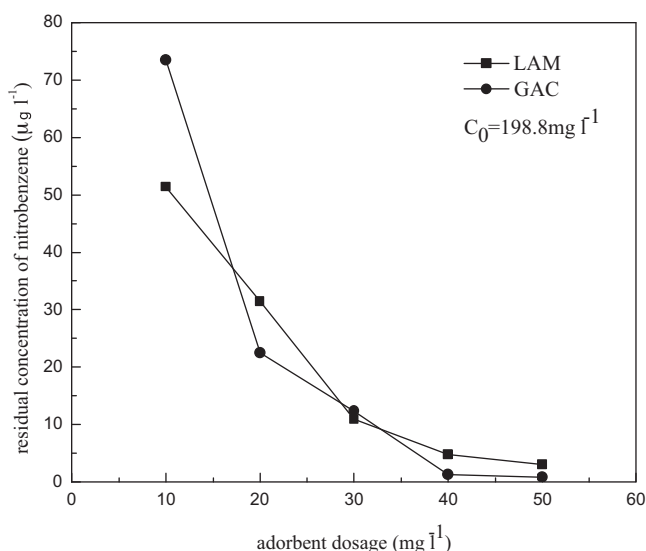
Fig. 1. Effect of adsorbent dose on the adsorption of nitrobenzene by LAM and GAC; T = 303 K, t = 8 h and C_0 = 200 mg l^{-1}.

The pseudo-second-order model is given by Ho and Kay [31] and shown in Eq. (5).

$$q_t = \frac{t k_2 q_e^2}{1 + t k_2 q_e} \tag{5}$$

which can be rewritten as Eq. (6).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where k_2 is the pseudo-second order rate constant (min^{-1}).

2.5.2. Adsorption isotherms

In order to describe the adsorption isotherm, three important isotherms were selected in this study, the Linear isotherm (Eq. (7)), the Langmuir isotherm (Eq. (8)) and the Freundlich isotherms (Eq. (9)).

Linear isotherm

$$q_e = k_{Li} C_e + b \tag{7}$$

Langumuir isotherm

$$q_e = \frac{Q_m k_L C_e}{1 + k_L C_e} \tag{8}$$

Freundlich isotherm

$$q_e = k_F C_e^{1/n} \tag{9}$$

where q_e (μg mg^{-1}) is the amount of nitrobenzene absorbed per milligram of adsorbent at equilibrium; C_e (μg l^{-1}) is the equilibrium concentration of nitrobenzene in solution; k_{Li}, k_L and k_F (l mg^{-1}) are the constants related to the Linear, Langumuir and Freundlich isotherms respectively; Q_m (μg mg^{-1}) is the maximum monolayer adsorption capacity; $1/n$ the slope in Freundlich isotherm, ranging between 0 and 1, indicative of the degree of nonlinearity between solution concentration and adsorption; b is a constant.

2.5.3. Thermodynamic parameters

The thermodynamic parameters of the adsorption process were obtained from experiments at various temperatures using Eq. (10) [7,32,33].

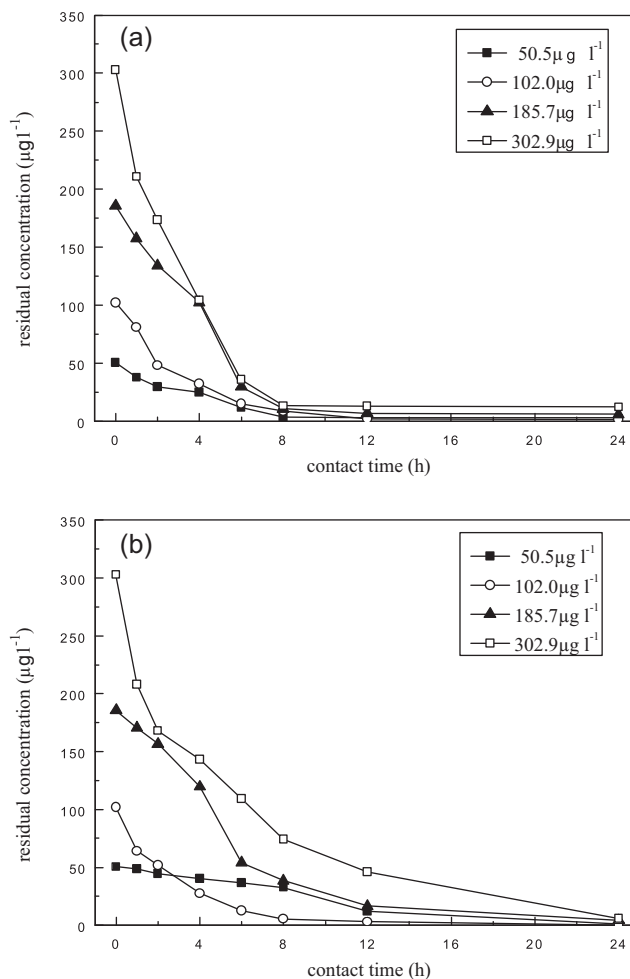$$\ln(k) = \ln(k_0) - \frac{E}{R}\left(\frac{1}{T}\right) \tag{10}$$

Fig. 2. Effect of contact time on the adsorption of nitrobenzene by (a) LAM and (b) GAC; T = 303 K, m = 30 mg l^{-1} and C_0 = 200 mg l^{-1}.

where k_0 is the pre-exponential factor; k is the rate constant for the model; E (KJ mol^{-1}) is the adsorption free energy; R (8.314 J (mol K)$^{-1}$) is the universal gas law constant and T (K) is the absolute temperature of solution.

Standard free energy changes ($\Delta G°$, KJ mol^{-1}) and the average standard enthalpy change ($\Delta H°$, KJ mol^{-1}) for interactions were calculated from the relationships in Eq. (11) and (12) [24]:

$$\Delta G° = -RT \ln K_{Li} \tag{11}$$

$$\ln K_0(T_3) - \ln K_0(T_1) = \frac{-\Delta H°(T_1 - T_3)}{R}\left(\frac{1}{T_3} - \frac{1}{T_1}\right) \tag{12}$$

Standard entropy changes ($\Delta S°$) were calculated using Eq. (13):

$$\Delta G° = \Delta H° - T\Delta S° \tag{13}$$

2.6. Analytical procedure

The concentration of nitrobenzene was determined using a gas chromatograph (GC). A GC (GC4890N/ECD, Agilent, United States) with an HP-5 column (30 m length, 320 μm internal diameter, 0.25 μm film thickness) was used. Column temperature was programmed at 110 °C initially, and increased to 300 °C within 1 min. The injector temperature was set at 240 °C and the detector at 280 °C, respectively. Nitrogen gas of extra purity (>99.999%) was used as the carrier gas at a flow rate of 2.2 ml min^{-1}. The retention time for nitrobenzene was 3 min.
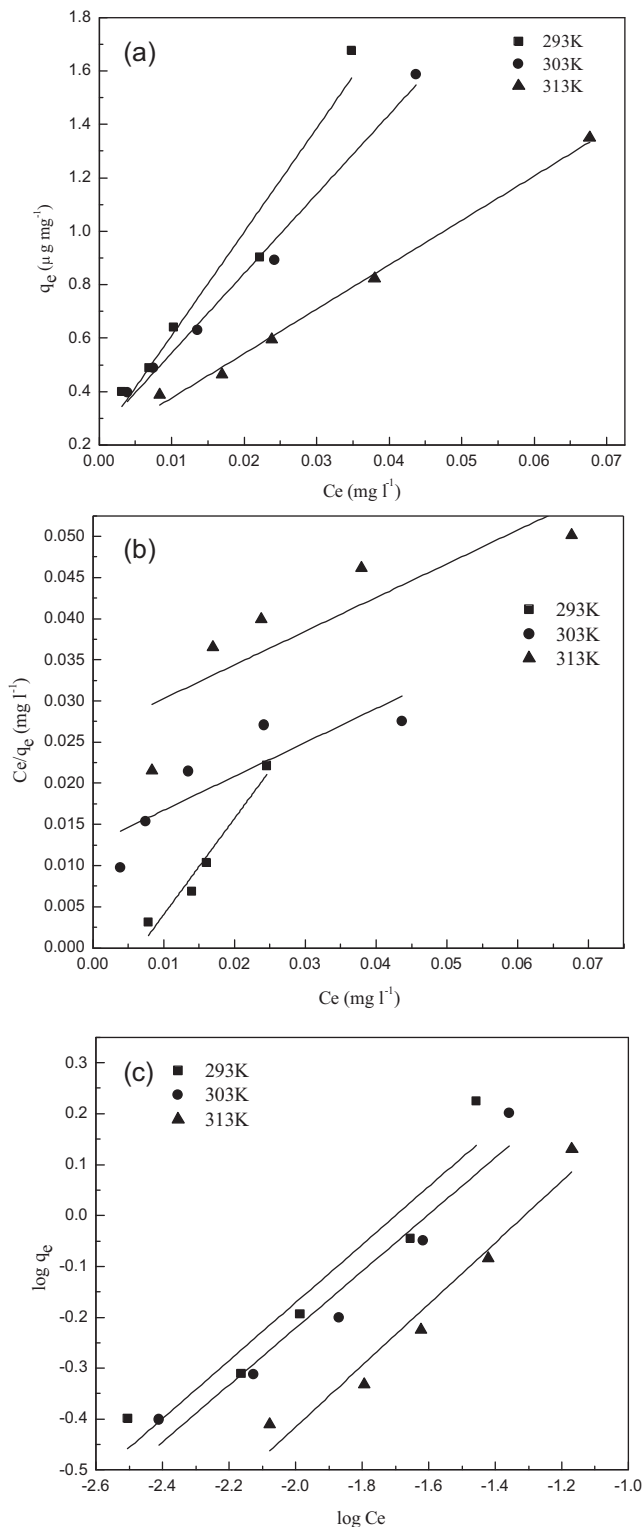
Fig. 3. The adsorption isotherms plot for nitrobenzene adsorption on LAM at different temperature ($m = 30\,mg\,l^{-1}$, $C_0 = 200\,mg\,l^{-1}$): (a) linear model, (b) Langmuir model, and (c) Freundlich model.

3. Results and discussion

3.1. Characterization of LAM

A series of LAM adsorbents with 1%, 3%, 5% and 10% triolein content were synthesized and characterized in the previous research [28]. The average particle size of LAM with 3% triolein, which was used in this experiment, was 59.17 μm. The median particle diameters of the material were 44.02 μm. The specific area and the average pore size of the LAM with 3% triolein content was 20.27 ($m^2\,g^{-1}$) and 47.18 (nm), respectively, with specific pore capacity of 0.0489 ($ml\,g^{-1}$). The thermal gravimetric (TG) analysis results showed that LAM was thermally stable under temperature lower than 400 °C, as indicated by the T_{max} of triolein (470 °C).

3.2. Effect of adsorbent dosage on nitrobenzene adsorption

The effect of adsorbent dosage on the removal of nitrobenzene by LAM and GAC at $C_0 = 200\,\mu g\,l^{-1}$ is shown in Fig. 1. With the increase in LAM dosage from 10 to 30 mg l^{-1}, the nitrobenzene removal efficiency increased rapidly from 63% to 95%. This was attributed to an increase in the adsorbent concentration, which increased the available surface area and adsorption sites [34]. With a further increase in LAM dosage to 50 mg l^{-1}, the nitrobenzene removal efficiency increased slightly to 98%. It is readily understood that the number of available adsorption sites increases with the increase of the adsorbent dosage, consequently leads to the increase in the amount of adsorbed nitrobenzene molecular. Moreover, as the LAM dose was increased from 10 to 50 mg l^{-1}, the adsorption capacity for nitrobenzene decreased from 12.6 to 3.92 mg μg^{-1}. The decrease in adsorption capacity with the increase in the adsorbent dosage was mainly attributed to the unsaturation of adsorption sites during the adsorption process [35]. Therefore, in this study, the optimum adsorbent dosage for both LAM and GAC was found to be 30 mg l^{-1} for further experiments. Under this dosage, the residual concentration of nitrobenzene at the adsorption equilibrium was lower than 17 μg l^{-1}. This value is the maximum concentration allowed in the standards for drinking water quality (GB5749-2006) in China, the removal efficiency arrived 95% for both of the adsorbent.

3.3. Effect of contact time (t) on nitrobenzene adsorption

Fig. 2 shows the effect of contact time on the removal of nitrobenzene by LAM and GAC at $C_0 = 50$–300 μg l^{-1}. In all cases, the adsorbent dosage was 30 mg l^{-1}. As shown in Fig. 2, when the initial nitrobenzene concentration increased from 50 to 300 μg l^{-1}, q_e for both LAM and GAC increased. For LAM, an adsorption equilibrium was generally obtained within 8 h for all the initial concentrations. No obvious concentration changes occur after adsorption equilibrium and the average removal efficiency of nitrobenzene reached 93.2, 91.4, 94.3 and 95.6% when the initial concentrations of nitrobenzene were 50, 100, 200 and 300 μg l^{-1}, respectively. For GAC, an adsorption equilibrium was generally obtained within 12 h for all the initial concentrations, which was longer than that determined for LAM. This may be due to the granular shape of GAC, which made it difficult for GAC to be dispersed equally throughout the reaction system, which therefore reduced contact surface area that exposed to the adsorbate. More important, the pollutant removal mechanism of LAM was revealed to be through both the physical adsorption of LAM membrane and the bioaccumulation of LAM nucleous-triolein [28], which results in a faster adsorption of pollutants, especially those with low water solubility. The average removal efficiency of nitrobenzene for GAC reached 75.9, 97, 91.1 and 84.8% when the initial concentrations of nitrobenzene were 50, 100, 200 and 300 μg l^{-1}, respectively.

Similar materials, BFC and CA-T, have been used to remove different organic chemicals from aqueous solution, including lindane, dieldrin and hydrophobic organic chemicals (HOCs) from treated landfill leachate [22–24,36]. The researches showed that BFC had a good lindane removal ability, which was close to that by powder active carbon (PAC) [22,23]. And when BFC was used for HOCs

Table 1
Parameters of adsorption isotherms of nitrobenzene onto LAM at different temperatures.

Temperature (K)	Linear model			Langmuir model			Freundlich model		
	k_{Li} (l mg^{-1})	b	R^2	Q_m (µg mg^{-1})	k_L (l mg^{-1})	R^2	k_F (l mg^{-1})	$1/n$	R^2
LAM									
293	38.795	0.2216	0.9565	1.22	119.17	0.9603	9.29	0.5696	0.9711
303	29.733	0.2474	0.9902	2.43	32.66	0.7422	7.86	0.5585	0.9483
313	16.613	0.21	0.9951	2.38	16.38	0.7661	6.18	0.6032	0.9565
GAC									
293	21.768	0.3838	0.9869	1.94	56.09	0.9519	5.92	0.4782	0.9915
303	15.499	0.3746	0.9828	1.77	44.42	0.9507	4.55	0.4587	0.9802
313	6.502	0.4368	0.9504	1.15	72.23	0.9852	2.15	0.3161	0.9988

removal in treated landfill leachate, it also showed a better adsorption performance than GAC [36]. In the study of using CA-T to remove dieldrin from aqueous solution, the equilibrium adsorption capacity of CA-T for dieldrin was found to be larger than that of GAC. All these studies have proved that this kind of adsorbents, that with triolein embedded, is promising for removing hydrophobic organic chemicals from aqueous solution.

3.4. Nitrobenzene adsorption isotherms

The correlation of equilibrium data using either theoretical or empirical equations is essential for the design of adsorption systems. The adsorption isotherms of nitrobenzene onto LAM at temperatures of 293, 303 and 313 K, fitted with the Linear, Langmuir and Freundlich adsorption isotherms, are shown in Fig. 3. The adsorption isotherms on GAC are not shown.

The isotherm parameters and linear regression statistics obtained from the fitting of the sorption data to the Linear, Langmuir and Freundlich isotherms for both LAM and GAC are given in Table 1. Most R^2 values for LAM exceed 0.95 for both the Linear and the Freundlich models, suggesting that both models closely describe the experimental results. However, the Linear model was more suitable than Freundlich model to describe the adsorption isotherm, as reflected by the correlation coefficients. The R^2 values for GAC exceed 0.95 for all the Linear, Langmuir and Freundlich models. However, the most suitable model to describe the adsorption isotherm for GAC was Freundlich isotherm.

The values of k_{Li} for LAM were 38.795, 29.733 and 16.613 L mg^{-1} at 293, 303 and 313 K, respectively. Based on these results, k_{Li} decreased with the increase in the temperatures, as did the k_F values for GAC. This reveals that the adsorption capacity of nitrobenzene on LAM and GAC decreased with increasing temperatures. These results indicate that the rise in temperature and excess energy supply promotes desorption, which is in accordance with previous studies [6,7]. There is virtually universal accord that sorption processes play an important role in the fate and transport of organic chemicals, and the sorption partitioning model has been widely accepted. Two types of adsorption, i.e., linear and nonlinear, have been defined to describe the nature of the function which predominantly controls the adsorption process. The sorption of the non-polar organic chemicals by soil/sediment occurs essentially by partition [37], and the linear sorption isotherms are associated with this model. The sorption of the polar organic chemicals by soil/sediment occurs mainly by sorption, and non-linear isotherms are associated with this model. Non-linear isotherms are typically described by the Freundlich isotherms. The Freundlich sorption coefficients k_F and n are empirical constants, representing the extent of sorption and the degree of non-linearity of sorption respectively. If the constant n has a value of 1, the Freundlich isotherm is identical to the linear isotherm [37]. If the n is below one, the adsorption is a chemical process; otherwise, the adsorption is physical process [34]. The values of n in this experiment suggest that the adsorption of nitrobenzene on both LAM and GAC

was a physical process. The study also showed that the adsorption of nitrobenzene on the LAM was correlated well with the Linear isotherm, indicating that the sorption of nitrobenzene by LAM resulted mainly from the partition function, which may be attributed to the existence of the triolein nucleolus. Linear constants were used in Eqs. (10)–(13) to calculate thermodynamic parameters.

3.5. Adsorption kinetic study

3.5.1. Pseudo-first-order kinetic model

The values of $\ln(q_e - q_t)$ at different C_0 for LAM were calculated from the experimental data. The plots of $\ln(q_e - q_t)$ against t at 303 K are shown in Fig. 4. The kinetics parameters of nitrobenzene adsorption onto LAM according to the pseudo-first-order model (Eq. (4)) at different C_0 are tabulated in Table 2. The results showed that the pseudo-first-order model fits the experimental data quite well, as most of the R^2 values were greater than 0.94 (except for the one at $C_0 = 200 \, \mu g \, l^{-1}$, which is 0.8548). This indicates the applicability of the first-order kinetic model to describe the adsorption process of nitrobenzene onto LAM.

3.5.2. Pseudo-second-order kinetic model

The values of t/q_t at different C_0 for LAM at 303 K are plotted against t in Fig. 5. Fitting kinetics parameters of adsorption of nitrobenzene on LAM according to the pseudo-second-order model (Eq. (6)) at different C_0 are tabulated in Table 2. The rather low R^2 and notable variances between the experimental and theoretical uptakes shown in Table 2 reveal clearly the poor fitting of the
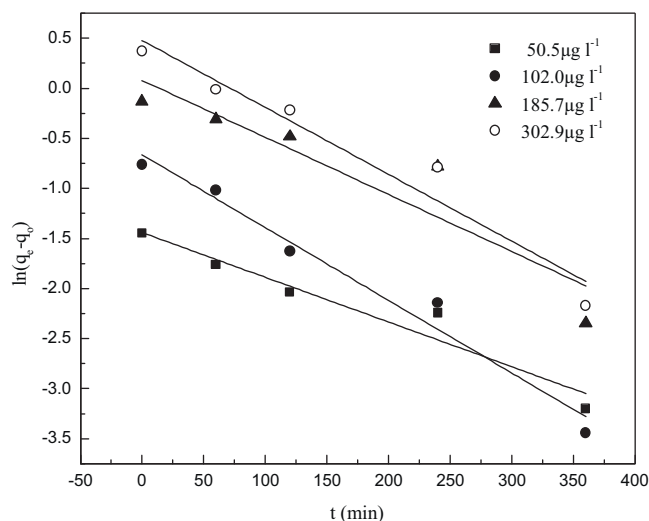

Fig. 4. Plots of $\ln(q_e - q_t)$ versus time (min) for adsorption of nitrobenzene onto LAM at 303 K. The solid points belong to experimental data while the line is calculated from nonlinear least square regression of the data according to pseudo-first-order rate expression (Eq. (4)).

Table 2
Fitting kinetics parameters of adsorption of nitrobenzene onto LAM according to pseudo-first-order (Eq. (4)), pseudo-second-order (Eq. (6)) at 303 K.

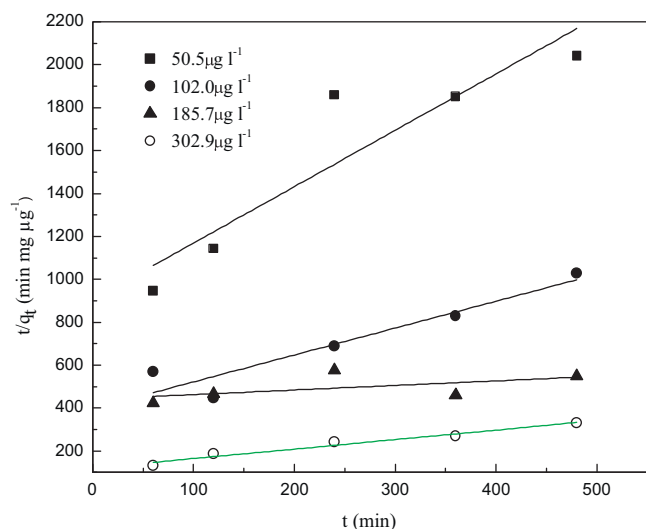| C_0 (μg l^{-1})	$q_{e,exp}$ (μg mg^{-1})	Pseudo-first-order model			Pseudo-second-order model		
		$q_{e,cal}$ (μg mg^{-1})	k_1 (min^{-1})	R^2	$q_{e,cal}$ (μg mg^{-1})	k_2 (min^{-1})	R^2
50.5	0.2352	0.2366	0.0045	0.9421	0.3804	2.629	0.8533
102.0	0.4662	0.5141	0.0073	0.9732	0.6368	1.2531	0.8976
185.7	0.8755	1.0830	0.0057	0.8548	4.7037	0.2126	0.3248
302.9	1.4481	1.6128	0.0067	0.9477	2.2589	0.4427	0.9687

Fig. 5. Plots of t/q_t versus time (min) for adsorption of nitrobenzene onto LAM at 303 K. The solid points belong to experimental data while the line is calculated from nonlinear least square regression of the data according to pseudo-second-order rate expression (Eq. (6)).

Table 3
Thermodynamic parameters of nitrobenzene adsorption on LAM.

T (K)	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ (mol K)$^{-1}$)	E (kJ mol^{-1})
293	−8.87	−31.50	−0.077	−31.50
303	−8.55		−0.076	
313	−7.31		−0.077	

pseudo-second-order model. Thus the adsorption of nitrobenzene on LAM is not considered to be a second-order reaction.

3.6. Thermodynamic analysis of nitrobenzene adsorption on LAM

The thermodynamic analysis of nitrobenzene adsorption on LAM was conducted according to Eqs. (10)–(13). The values obtained are shown in Table 3.

The free energy changes ($\Delta G°$) were negative, indicating that the reactions were spontaneous. A negative value of the standard enthalpy change ($\Delta H°$) indicated that the adsorption of nitrobenzene on LAM was an exothermic reaction. This finding was also supported by the decreasing adsorption of nitrobenzene with the increasing in temperature. The negative entropy changes ($\Delta S°$) indicated that the activity of the solute in solution decreased after adsorption of LAM.

4. Conclusions

A novel adsorbent, LAM, with a hydrophobic nucleolus (triolein) and hydrophilic membrane structure (polyamide) was synthesized and found to be effective for the removal of nitrobenzene from aqueous solution. The adsorption capacity and removal efficiency of LAM was higher than that of GAC. The average removal efficiency of

nitrobenzene for LAM reached 94.3% at 303 K after 8 h contact time when the initial concentrations of nitrobenzene were 200 μg l^{-1}. The adsorption isotherm data of nitrobenzene on LAM fitted the Linear equation, which indicated that the adsorption of nitrobenzene by LAM resulted mainly from the partition function due to the existence of the triolein nucleolus. The adsorption data was well described by the pseudo-first-order kinetics model, which showed that the factors which affected the adsorption rate would be either the nitrobenzene concentration or the character of the adsorbent. Based on the negative free energy changes accompanied by a negative entropy changes, the adsorption of nitrobenzene on LAM was spontaneous and was an exothermic reaction.

References

[1] R.J. Norstrom, M. Simon, C.G. Derek, R.E. Schweinsburg, Organochlorine contaminants in arctic marine food chains: identification, geographical distribution, and temporal trends in polar bears, Environ. Sci. Technol. 22 (1988) 1063–1071.
[2] H. Iwata, S. Tanabe, N. Sakai, A. Nishimura, R. Tatsukawa, Distribution of persistent organochlorines in the oceanic air and surface sea water and the role of ocean on their global transport and fate, Environ. Pollut. 85 (1994) 15–33.
[3] K.S. Guruge, S. Tanabe, Contamination by persistent organochlorines and butyltin compounds in the west coast or Sri Lanka, Mar. Pollut. Bull. 42 (2001) 179–186.
[4] S.B. Haderlein, R.P. Schwarzenbach, Adsorption of substituted nitrobenzenes and nitrophenols to mineral surfaces, Environ. Sci. Technol. 27 (1993) 316–326.
[5] X.K. Zhao, G.P. Yang, X.C. Gao, Studies on the sorption behaviors of nitrobenzene on marine sediments, Chemosphere 52 (2003) 917–925.
[6] W. Wei, R. Sun, J. Cui, Z.G. Wei, Removal of nitrobenzene from aqueous solution by adsorption on nanocrystalline hydroxyapatite, Desalination 263 (2010) 89–96.
[7] Q.D. Qin, J. Ma, K. Liu, Adsorption of nitrobenzene from aqueous solution by MCM-41, J. Colloid Interface Sci. 315 (2007) 80–86.
[8] U. von Gunten, Ozonation of drinking water. Part I. Oxidation kinetics and product formation, Water Res. 37 (2003) 1443–1467.
[9] M. Sievers, Advanced oxidation processes, in: P.A. Wilderer (Ed.), Treatise on Water Science, IWA Publishing, London, 2011, pp. 377–408.
[10] M.L. Soto, A. Moure, H. Domínguez, J.C. Parajó, Recovery, concentration and purification of phenolic compounds by adsorption: a review, J. Food Eng. 105 (2011) 1–27.
[11] L. Li, P.A. Quinlivan, D.R.U. Knappe, Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution, Carbon 40 (2002) 2085–2100.
[12] P.A.M. Mourão, P.J.M. Carrott, M.M.L. Ribeiro Carrott, Application of different equations to adsorption isotherms of phenolic compounds on activated carbons prepared from cork, Carbon 44 (2006) 2422–2429.
[13] M. Chen, L. Cui, C.H. Li, G.W. Diao, Adsorption, desorption and condensation of nitrobenzene solution from active carbon: a comparison of two cyclodextrins and two surfactants, J. Hazard. Mater. 162 (2009) 23–28.
[14] V.K. Gupta, I. Ali, Removal of DDD and DDE from wastewater using bagasse fly ash, a sugar industry waste, Water Res. 35 (2001) 33–40.
[15] V.K. Gupta, C.K. Jain, I. Ali, S. Chandra, S. Agarwal, Removal of lindane and malathion from wastewater using bagasse fly ash-a sugar industry waste, Water Res. 36 (2002) 2483–2490.

[16] V.K. Gupta, S. Sharma, Removal of zinc from aqueous solutions using bagasse fly ash—a low cost adsorbent, Ind. Eng. Chem. Res. 42 (2003) 6619–6624.

[17] V.K. Gupta, I. Ali, Removal of lead and chromium from wastewater using bagasse fly ash, a sugar industry waste, J. Colloid Interface Sci. 271 (2004) 321–328.

[18] V.K. Gupta, I. Ali, V.K. Saini, Removal of dyes from wastewater using bottom ash, Ind. Eng. Chem. Res. 44 (2005) 3655–3664.

[19] A.K. Jain, V.K. Gupta, A. Bhatnagar, Suhas, Utilization of industrial waste products as adsorbents for the removal of dyes, J. Hazard. Mater. 101 (2003) 31–42.

[20] V.K. Gupta, I. Ali, V.K. Saini, Removal of chlorophenols from wastewater using red mud: an aluminum industry waste, Environ. Sci. Technol. 38 (2004) 4012–4018.

[21] V.K. Gupta, Suhas, I. Ali, V.K. Saini, Removal of rhodamine B, fast green and methylene blue from wastewater using red mud: an aluminum industry waste, Ind. Eng. Chem. Res. 43 (2004) 1740–1747.

[22] L.Y. Song, Y.C. Zhao, G.J. Wang, B. Li, D.J. Niu, X.L. Chai, Biomimetic fat cell (BFC) preparation and for lindane removal from aqueous solution, J. Hazard. Mater. 146 (2007) 289–294.

[23] L.Y. Song, Y.C. Zhao, G.J. Wang, B. Li, D.J. Niu, X.L. Chai, Biomimetic fat cell (BFC) modification and for lindane removal from aqueous solution, J. Hazard. Mater. 151 (2008) 805–810.

[24] J. Ru, H.J. Liu, J.H. Qu, A.M. Wang, R.H. Dai, Removal of dieldrin from aqueous solution by a novel triolein-embedded composite adsorbent, J. Hazard. Mater. 141 (2007) 61–69.

[25] A.M. Alexander, A.M. Elena, N.T. Evgenia, Tracing the source of PCDD/FS and PCBS to Lake Baikal, Environ. Sci. Technol. 34 (2000) 741–747.

[26] A.K. Karena, A.B. Harvey, H.H. Raymond, Biomagnifications of DDT through the benthic and pelagic food webs of Lake Malawi, east Africa: importance of tropic level and carbon source, Environ, Sci. Technol. 35 (2001) 14–20.

[27] I. Costabeber, T. Emanuelli, Influence of alimentary habits, age and occupation on polychlorinated biphenyl levels in adipose tissue, Food Chem. Toxicol. 41 (2003) 73–80.

[28] Z.Q. Chen, Q.X. Wen, J.X. Lian, N.Q. Ren, Preparation and characterization of a lipoid adsorption material and its atrazine removal performance, J. Environ. Sci. 23 (2011) 1293–1298.

[29] T. Goran, R. Vladisavljevic, A. Williams, Recent developments in manufacturing emulsions and particulate products using membranes, Adv. Colloid Interface Sci. 113 (2005) 1–20.

[30] V.C. Srivastava, I.D. Mall, I.M. Mishra, Adsorption of toxic metal ions onto activated carbon. Study of sorption behavior through characterization and kinetics, Chem. Eng. Process. 47 (2008) 1269–1280.

[31] Y.S. Ho, M.G. Kay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[32] W.J. Thoms, B. Crittenden, Adsorption Technology and Design, 1st ed., Butterworth-Heinemann publisher, Burlington, 1998.

[33] D. Ghosh, K. Bhattacharyya, Adsorption of methylene blue on kaolinite, Appl. Clay Sci. 20 (2002) 295–300.

[34] K.L. Lin, J.Y. Pan, Y.M. Chen, R.M. Cheng, X.C. Xu, Study the adsorption of phenol from aqueous solution on hydroxyapatite nanopowders, J. Hazard. Mater. 161 (2009) 231–240.

[35] X.L. Pan, J.L. Wang, D.Y. Zhang, Sorption of cobalt to bone char: kinetics competitive sorption and mechanism, Desalination 249 (2009) 609–614.

[36] L.Y. Song, Y.C. Zhao, W.M. Sun, Z.Y. Lou, Hydrophobic organic chemicals (HOCs) removal from biologically treated landfill leachate by powder-activated carbon (PAC), granular-activated carbon (GAC) and biomimetic fat cell (BFC), J. Hazard. Mater. 163 (2009) 1084–1089.

[37] L. Feng, S.K. Han, L.S. Wang, Z. Zhang, Sorption of phenylthioacetates on natural soil: application of partition-adsorption mechanism and model, Chemosphere 33 (1996) 2113–2120.