# Removal of dieldrin from aqueous solution by a novel triolein-embedded composite adsorbent

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## Abstract

In this study, a novel triolein-embedded activated carbon composite adsorbent (CA-T) was prepared and applied for the adsorption and removal of dieldrin from aqueous systems. Experiments were carried out to investigate the adsorption behavior of dieldrin on CA-T, including adsorption isotherms, adsorption kinetics, the influence of initial concentration, temperature, shaking speed, pH and the addition of humic acid (HA) on adsorption. The adsorption isotherms accorded with Freundlich equation. Three kinetics models, including pseudo-first-order, pseudo-second-order and intraparticle diffusion models, were used to fit the experimental data. By comparing the correlation coefficients, it was found that both pseudo-second-order and intraparticle diffusion models were used to well describe the adsorption of dieldrin on CA-T. The addition of HA had little effect on dieldrin adsorption by CA-T. Results indicated that CA-T appeared to be a promising adsorbent for removing lipophilic dieldrin in trace amount, which was advantageous over pure granular activated carbon (GAC). The adsorption rate increased with increasing shaking speed, initial concentration and temperature, and remained almost unchanged in the pH range of 4–8. Thermodynamic calculations indicated that the adsorption reaction was spontaneous with a high affinity and the adsorption was an endothermic reaction.
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## 1. Introduction

Persistent organic pollutants (POPs), such as organochlorines, have been of great concern due to their characteristics of toxicity, persistency and bioaccumulation, despite bans on production and usage [1–3]. Many of these compounds are considered to act as environmental hormones, which disrupt reproductive cycles of humans and wildlife [4]. Although methods to remove residual POPs from the environment have been taking on increasing attention internationally in recent years [5], most hazardous vestigial POPs with low water solubility are especially difficult to be eliminated from water. Activated carbon, with a high degree of porosity and an extensive surface area, has been widely used as an effective adsorbent for sev-

eral organic compounds of concern in water and wastewater treatment [6–8]. However, with poor selectivity to organic pollutants and saturation-prone property, activated carbon needs to be regenerated frequently during the adsorption process, and it cannot remove hydrophobic POPs in trace or ultratrace amounts near the environmental level from water satisfactorily. Consequently, it is attractive to develop novel adsorbents to remove organic micropollutants from water efficiently.

Based on the bioaccumulative property of POPs in fatty tissue [9], a novel triolein-embedded activated carbon composite adsorbent (CA-T) was developed in this research. The adsorbent is mainly composed of the supporting activated carbon and the surrounding triolein-embedded cellulose acetate membrane. Several researchers have found that triolein has a high accumulating capacity ($10^5$–$10^7$) for trace lipophilic chemicals [10,11]. Moreover, triolein is naturally found in fatty tissue of animals, and so it is inexpensive to purchase and safe to use in adsorption procedures. Cellulose acetate, a particularly useful polymer for preparing hybrid materials, was used to combine triolein with activated carbon. Cellulose acetate can be easily molded

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into different forms, such as membranes, fibers and spheres [12], and its hydrophilicity improves the accessibility of aqueous solutions to the surface of hybrid materials. The molecular size-exclusion limit of cellulose acetate membrane is similar to that of the biomembrane, while triolein constitutes lipid pools that can accumulate hydrophobic organic contaminants. Accordingly, the novel triolein-embedded composite adsorbent was prepared with these pollution-free and environmental-friendly raw materials.

This paper focuses on investigating the adsorption behavior of dieldrin, a model contaminant, on the novel triolein-embedded composite adsorbent, compared to the commercially used granular activated carbon (GAC) and to the composite adsorbent containing no triolein (CA). Batch adsorption experiments were carried out to study the adsorption isotherms and adsorption kinetics. The effects of different factors on the removal rate, such as initial concentration, temperature, shaking speed, pH and the addition of humic acid were also studied in detail.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Adsorbent
Granular activated carbon ZJ-15 (GAC, Xinhua Acitvated Carbon Co. Ltd., Shanxi, China) was selected in this study, which is widely used in the water treatment plants in China and offers a high purity level. Triolein (>99% purity) was purchased from Sigma Chemical Co. (St. Louis, MO, USA), and cellulose acetate (2.5 degree of acetylation) was obtained from Shanghai Chemical Reagent Co. (Shanghai, China). Materials for the preparation of the composite adsorbent also included acetone (A.R.), 1,4-dioxane (A.R.) and magnesium perchlorate (A.R.), which were all purchased from Beijing Chemical Reagent Co. (Beijing, China). Magnesium perchlorate was ground in a mortar to remove coarse particles before use.

Preparation method had been shown in previous published papers and patents [13,14] and was briefly described here. Dissolving cellulose acetate with acetone and 1,4-dioxane resulted in the formation of a mixed membrane solution, which was used to coat the surface of GAC. Magnesium perchlorate was added as an additive, and certain amount of triolein was also added. Then the mixture was stirred at room temperature for 48 h to dissolve triolein in membrane solution homogeneously. After that, activated carbon was dipped in the solution for 5 min and then taken out and put in an aerator for 1 min to make solvent evaporate. The composite adsorbent was immersed in a water coagulation bath (25 °C) for at least 10 min to ensure complete phase separation, and then rinsed out with deionized and distilled water. For comparison, activated carbon modified with cellulose acetate only (CA) was prepared with the same method. All adsorbents were kept in deionized water and stored in a refrigerator at 4 °C until use.

#### 2.1.2. Adsorbate
Dieldrin, which is defined as one of the initial 12 POPs, according to the Stockholm Convention on POPs [15], has been used extensively as an insecticide until 1970s, and can still be found in the different components of environment in many countries and areas at the present time [16,17]. In this study, dieldrin was chosen as a model chemical to represent toxic POPs. The molecular weight of dieldrin is 381, the water solubility is 0.195 mg l$^{-1}$ [18], and the octanol–water coefficient (log $K_{ow}$) is in the range of 4.30–5.48 [19,20], indicating comparatively strong hydrophobicity.

Stock solution was prepared by dissolving appropriate quantities of pesticides-grade standard (99.0% purity, Environmental Protection Center of Agricultural Department, Beijing, China) in $n$-hexane, which was refrigerated until use.

Dieldrin solution was prepared by directly adding the dieldrin stock solution to deionized and distilled water without the assistance of organic solvent. Solution was sealed in conical flasks and agitated mechanically for 24 h to obtain homogeneous aqueous solution.

### 2.2. Methods

#### 2.2.1. Adsorption equilibrium
Preliminary kinetic tests were carried out in order to determine the equilibrium time. And it was assumed that equilibrium was attained when no further changes in dieldrin uptake were observed after 48 h.

Adsorption isotherms were obtained by mixing 1 g adsorbent with 100 ml dieldrin solution of different initial concentrations (1, 3, 5, 10, 20 and 50 μg l$^{-1}$). The suspensions were agitated by a mechanical shaker at 170 revolutions per minute (rpm). The temperature was controlled at 25 °C by air bath. Samples for analysis were taken after 48 h contact time.

#### 2.2.2. Adsorption kinetics
Batch adsorption experiments were used to investigate the effects of some major kinetic parameters, such as initial concentration, temperature, shaking speed and pH, on the uptake kinetics of dieldrin on CA-T. Adsorption kinetic test was carried out in 500 ml sealed conical flasks. A liquid volume of 250 ml and an amount of 5 g CA-T were used for all tests. Samples were withdrawn at regular intervals to analyze.

##### 2.2.2.1. Effects of different operating conditions.
Initial concentration ranged between 10 and 30 μg l$^{-1}$, temperature ranged between 5 and 35 °C, and shaking speed ranged between 0 and 170 rpm. Using an Orion 720 APLUS Benchtop meter (Thermo Orion Co., USA), pH that ranged from 4 to 8 was adjusted with 0.1 M HCl or 0.1 M NaOH.

##### 2.2.2.2. Effects of the addition of humic acid (HA).
Humic acid (HA, C.R.), purchased from Huabei Development Center for Special Chemical Reagents (Tianjin, China), was dissolved in deionized and distilled water to model NOMs. HA solution was filtered through a 0.45 μm membrane before use. TOC, measured by Phoenix 8000 TOC Analyzer (Tekmar-Dohrmann Co., USA), served as the parameter for NOMs quantification.

The initial concentration of dieldrin solution was 20 μg l$^{-1}$. HA solution was added to obtain a TOC value of 3 mg l$^{-1}$. The

suspension was shaken at 170 rpm. The initial pH of the solution was 7.0, and the temperature was kept at 25 °C. For comparison, adsorption tests of dieldrin on CA-T, CA and GAC were performed separately under the same operating condition.

### 2.2.3. Analytical procedures

Dieldrin presents in water samples at a trace level, whose analysis requires first an extraction and a concentration. In our experiment, liquid–liquid extraction (LLE) was used for the determination of residual concentrations of dieldrin in samples.

Each water sample (5 ml) was enriched by LLE with 1 ml $n$-hexane (GC grade, Fisher Scientific Company, USA) for three times in a separating funnel. The extracts were evaporated under a gentle stream of nitrogen and concentrated to a volume of 0.5 ml. Anhydrous sodium sulfate of analytical grade (Beijing Chemical Reagent Co., Beijing, China) was added to remove any moisture, which was dried at 450 °C for 4 h before use.

The analysis of residual concentrations of dieldrin was performed on a Agilent 6890N gas chromatograph (Agilent Technologies, USA), equipped with a split–splitless injector and a $^{63}$Ni μ-electron capture detector. A HP-5 capillary column (30 m × 0.32 mm i.d., film thickness of 0.17 μm) was purchased from J&W Scientific (USA). Column temperature was programmed at 85 °C initially, increased at 10 °C min$^{-1}$ to 180 °C, held for 15 min, then ramped at 20 °C min$^{-1}$ to 280 °C, and held for 30 min. The injector temperature was set at 250 °C and the detector at 300 °C, respectively. Nitrogen gas of extra purity (>99.999%) was used as the carrier gas at a flow rate of 1 ml min$^{-1}$ and a pressure of 16 psi. A sample volume of 1 μl was injected in the splitless mode. Chromatograms were recorded and analyzed by the software of HP Chem-Station.

Glassware used throughout the experiment were cleaned by soaking overnight in a 10% (v/v) nitric acid solution, rinsing with deionized and distilled water, and drying at 120 °C for 2 h. Analysis of three blanks (250 ml deionized and distilled water) was subject to assess the interference from the regents and glassware. The blank runs revealed that no impurity influenced the analytical quality. GC analysis was repeated twice for each replicate sample. The recognition of dieldrin in the extracts was based on chromatographic retention time of standard samples by operating HP Chem-Station. The quantitative determination of dieldrin was achieved using the method of external standards and the calibration curves. Recovery of the targeted dieldrin was 87.5 ± 10.5%, which demonstrated that favorable recoveries and good repeatability were obtained in the process of the experiment.

## 3. Results and discussion

### 3.1. Dieldrin adsorption isotherms

The correlation of equilibrium data using either theoretical or empirical equation is essential for adsorption data interpretation and prediction. An important model widely used in removal of hydrophobic organic pollutants from water is the Freundlich isotherm representing a non-linear equilibrium between

the phases (Eq. (1)):

$$q_{eq} = K_F C_{eq}^{1/n} \tag{1}$$

where $q_{eq}$ is the adsorption capacity of an adsorbent at equilibrium (μg g$^{-1}$), $C_{eq}$ the equilibrium concentration of the adsorbate (μg l$^{-1}$) and $K_F$ is an indication of the adsorption capacity of the adsorbent, while the parameter $n$ indicates the effect of concentration on the adsorption capacity and represents the adsorption intensity.

The adsorption capacity of an adsorbent, $q_{eq}$, is calculated by means of equilibrium studies. Eq. (2) establishes the mass balance of process at equilibrium condition:

$$q_{eq} = \frac{V(C_0 - C_{eq})}{m} \tag{2}$$

where $C_0$ is the initial concentration of the adsorbate (μg l$^{-1}$), $m$ the adsorbent mass (g) and $V$ is the solution volume (l).

The adsorption isotherms of dieldrin on CA-T, CA and GAC at 25 °C were presented in Fig. 2. Results showed that CA-T presented a unique adsorption pattern and could remove dieldrin from aqueous solution effectively. The equilibrium adsorption capacity of the tested adsorbents followed the order: CA-T > CA > GAC. For example, at an initial dieldrin concentration of 10 μg l$^{-1}$, the equilibrium adsorption capacity of CA-T, CA and GAC was 1.94, 1.88 and 1.87 μg g$^{-1}$, respectively. The difference between sorption amounts by three adsorbents seemed to be unconspicuous at the same initial dieldrin concentration, which was attributed to the narrow concentration range of dieldrin determined by its poor water solubility. However, it could be seen obviously in Fig. 2 that the difference of sorption amounts between CA-T and the other two adsorbents increased with the increase of equilibrium concentrations. CA-T appeared to be a promising adsorbent for removing dieldrin in trace amount from aqueous solution. Since CA-T had smaller specific surface area compared with the other two (specific surface areas of GAC, CA and CA-T are 797, 723 and 721 m$^2$ g$^{-1}$, respectively), its highest equilibrium adsorption capacity was attributed to the accumulation effect of triolein contained in CA-T on hydrophobic dieldrin. No maximum adsorption value was observed in the
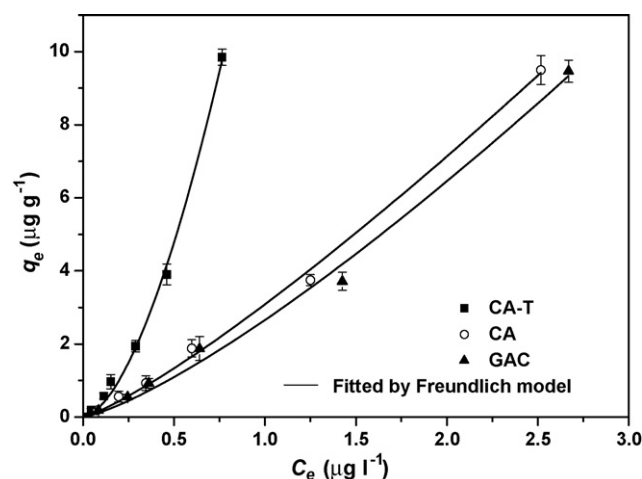


Fig. 1. Dieldrin adsorption isotherms at 25 °C.

Table 1
Freundlich isotherm parameters of dieldrin adsorption

| Adsorbent | $K_F$ | $n$ | $R^2$ |
|---|---|---|---|
| CA-T | 15.32 | 0.595 | 0.997 |
| CA | 3.08 | 0.827 | 0.998 |
| GAC | 2.66 | 0.781 | 0.994 |

isotherm experiments as shown in Fig. 1, which could be due to the low concentration of dieldrin determined by its poor water solubility [18], and the immense adsorption capacity of CA-T.

The adsorption isotherms analysis of experimental data was based on Freundlich isotherms, and the corresponding Freundlich parameters along with correlation coefficients were given in Table 1. The results indicated that the experimental data fitted the Freundlich isotherm well in a range of initial concentrations from 1 to 50 $\mu g\,l^{-1}$, and the correlation coefficients were between 0.994 and 0.998. The magnitude of $K_F$ and $n$ values showed the easiest uptake of dieldrin and the highest equilibrium adsorptive capacity of CA-T.

Two isotherms, Langmuir and Linear isotherms had been additionally regressed with the experimental data to compare their applicability with Freundlich equation. Data analysis indicated that neither linear nor Langmuir isotherms reproduced equilibrium data of CA-T ideally. When experimental data were fitted with linear isotherms, the correlation coefficients of CA-

T, CA and GAC were 0.919, 0.986 and 0.976, respectively. The derivation linearity of the equilibrium data of CA-T showed that dieldrin was not adsorbed onto CA-T by simplex partition mechanism. For Langmuir adsorption isotherm, the regression coefficient values were all lower than 0.5. These results indicated that the adsorption of dieldrin did not follow the Langmuir adsorption isotherm, which might be attributed to the energetic heterogeneity of the adsorbents, since Langmuir isotherm model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface.

### 3.2. Kinetics of dieldrin removal

The kinetics of sorption that describes the solute uptake rate governing the residence time of the sorption reaction is one of the important characteristics that define the efficiency of sorption. Hence, in the present study, the kinetics of dieldrin adsorption on three adsorbents was investigated in detail. The effects of adding HA to the adsorption systems and changing operation conditions were also discussed.

#### 3.2.1. Comparison of adsorbents
Fig. 2(a) shows the adsorption data of dieldrin by three adsorbents at different time intervals. The adsorption of dieldrin onto three adsorbents was found to be time dependent. The adsorption reaction was rapid in the first 3 h, when the residual
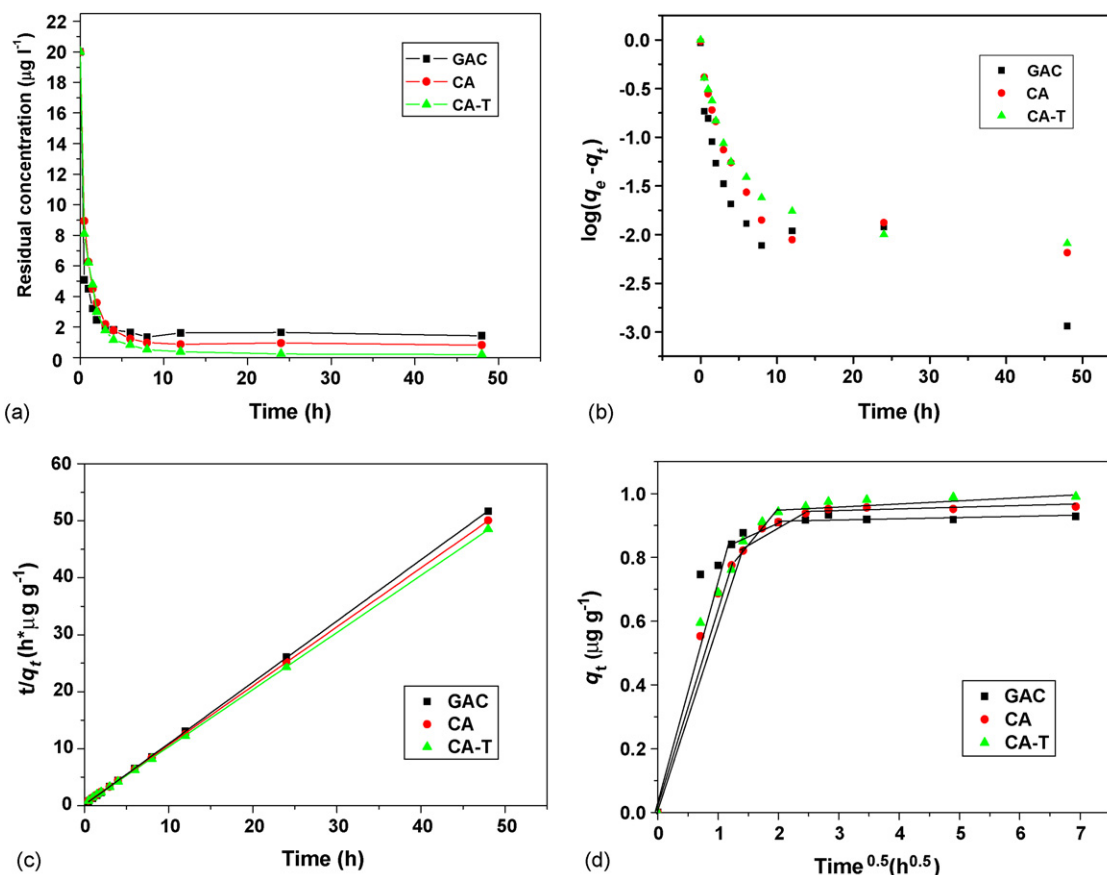


Fig. 2. Dieldrin adsorption kinetics on three adsorbents: (a) experimental data, (b) pseudo-first-order model plot, (c) pseudo-second-order model plot and (d) intra-particle diffusion model plot.

Table 2
Kinetic parameters and correlation coefficients of dieldrin adsorption

| | Pseudo-first-order | | Pseudo-second-order | | | | Intraparticle diffusion | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | $k_1$ (h$^{-1}$) | $R^2$ | $V_0$ ($\mu$g g$^{-1}$ h$^{-1}$) | $q_{eq}$ ($\mu$g g$^{-1}$) | $k_2$ ($\mu$g$^{-1}$ g h$^{-1}$) | $R^2$ | $k_{i,1}$ ($\mu$g g$^{-1}$ h$^{-0.5}$) | $k_{i,2}$ ($\mu$g g$^{-1}$ h$^{-0.5}$) | $k_{i,3}$ ($\mu$g g$^{-1}$ h$^{-0.5}$) | $R^2$ |
| **Adsorbents** | | | | | | | | | | |
| CA-T | 0.0359 | 0.594 | 3.44 | 0.998 | 3.46 | 0.99997 | 0.681 | 0.223 | 0.00815 | 0.951 |
| CA | 0.0371 | 0.514 | 3.47 | 0.965 | 3.73 | 0.99995 | 0.637 | 0.108 | 0.00303 | 0.956 |
| GAC | 0.0434 | 0.600 | 7.35 | 0.930 | 8.50 | 0.99997 | 0.777 | 0.0843 | 0.00218 | 0.891 |
| **Addition of HA (3 mg l$^{-1}$)** | | | | | | | | | | |
| CA-T+HA | 0.0353 | 0.684 | 3.19 | 0.960 | 3.46 | 0.99998 | 0.608 | 0.205 | 0.00778 | 0.930 |
| CA+HA | 0.0351 | 0.559 | 2.70 | 0.951 | 5.19 | 0.99995 | 0.591 | 0.0840 | 0.00278 | 0.901 |
| GAC+HA | 0.0329 | 0.529 | 2.28 | 0.775 | 3.79 | 1 | 0.673 | 0.00658 | 0.000361 | 0.888 |

concentrations reached 1.81, 1.79 and 1.15 $\mu$g l$^{-1}$ for GAC, CA, and CA-T, respectively. GAC had the fastest adsorption rate during that period, which might be due to its larger specific surface area and fresh porous surface that made the adsorption much easier. As time went by, the adsorption rates in all three systems slowed down gradually. CA-T presented higher adsorption capacity and removal efficiency than GAC in the rest of time, which was assumed due to the selective accumulation property of triolein towards hydrophobic dieldrin. At the end of adsorption for 48 h, residual concentrations of dieldrin were 1.42, 0.82 and 0.20 $\mu$g l$^{-1}$ in the reaction systems of GAC, CA and CA-T, respectively. The kinetic result, indicating a higher removal percentage of dieldrin by CA-T than that of GAC, was consistent with the adsorption isotherm test.

Three kinetics models were used, including pseudo-first-order model, pseudo-second-order model and intraparticle diffusion model, in order to investigate the adsorption behavior of three adsorbents and the effects of adding HA to the adsorption systems.

The kinetic rate equation of pseudo-first-order adsorption is expressed as [20]:

$$\frac{dq_t}{dt} = k_1(q_{eq} - q_t) \tag{3}$$

The integrated pseudo-first-order rate equation is written as

$$\log(q_{eq} - q_t) = \log q_{eq} - k_1 t \tag{4}$$

where $q_{eq}$ and $q_t$ are the amounts of adsorbed dieldrin at equilibrium and any time $t$ ($\mu$g g$^{-1}$ adsorbent), respectively, $k_1$ (h$^{-1}$) is the equilibrium rate constant of the first-order sorption, and $t$ is the adsorption time (h). $k_1$ can be calculated according to the linear plot of $\log(q_{eq} - q_t)$ versus $t$. A larger adsorption rate constant $k_1$ usually represents a quicker adsorption rate.

The pseudo-second-order kinetic model can be solved with the following equations [21,22]. The kinetic rate equation is expressed as

$$\frac{dq_t}{dt} = k_2(q_{eq} - q_t)^2 \tag{5}$$

where $k_2$ ($\mu$g$^{-1}$ g h$^{-1}$) represents the pseudo-second-order rate constant for the kinetic model. By integrating Eq. (5) with the

boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the following linear equation can be obtained:

$$\frac{1}{q_{eq} - q_t} = \frac{1}{q_{eq}} + k_2 t \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{V_0} + \frac{1}{q_{eq}} t \tag{7}$$

$$V_0 = k_2 q_{eq}^2 \tag{8}$$

where $V_0$ ($\mu$g g$^{-1}$ h$^{-1}$) is the initial sorption rate. Therefore, the $V_0$ and $q_{eq}$ values of kinetic tests can be determined experimentally by plotting $t/q_t$ versus $t$. $k_2$ can be determined by plotting $t/q_t$ versus $t$ based on Eq. (7).

The most widely applied intraparticle diffusion model for bio-sorption systems is given by Weber and Morris as [23]:

$$q_t = k_i t^{0.5} \tag{9}$$

where $q_t$ is the amount of adsorbate at time $t$ ($\mu$g g$^{-1}$) and $k_i$ is the rate constant ($\mu$g g$^{-1}$ h$^{-0.5}$).

Table 2 and Fig. 2(b)–(d) present the results of fitting experimental data with pseudo-first-order, pseudo-second-order and intraparticle diffusion models, respectively. The adsorption of dieldrin onto three adsorbents did not follow the pseudo-first-order equation, as shown in Fig. 2(b) and Table 2. The correlation coefficients were between 0.514 and 0.600. And Fig. 2(c) and Table 2 indicated that the pseudo-second-order model provided the best correlation of the adsorption kinetics data. The correlation coefficients were above 0.999. Among three adsorbents used in this study, GAC had the fastest initial adsorption rate of 7.35 $\mu$g g$^{-1}$ h$^{-1}$, and CA-T enjoyed the highest equilibrium adsorption capacity of 0.998 $\mu$g g$^{-1}$. Fig. 2(d) was the plot of $q_t$ versus $t^{0.5}$ according to the intraparticle diffusion model, which presented the character of multi-linearity and indicated that two or more steps occurred in the adsorption processes [24]. The first sharper portion was the external surface adsorption or instantaneous adsorption stage. The second portion was the gradual adsorption stage, where the intraparticle diffusion was rate-controlled. The third portion was the final equilibrium stage, where the intraparticle diffusion started to slow down due to the extremely low solute concentration in solution. The intraparticle diffusion constants could be calculated using Eq. (7).

Intraparticle diffusion constants of different stages ($k_{i,1}$, $k_{i,2}$ and $k_{i,3}$) expressed the diffusion rates of each stage in the adsorption process. Results listed in Table 2 indicated that the order of absorption rate was the first stage ($k_{i,1}$) > the second stage ($k_{i,2}$) > the third stage ($k_{i,3}$) for all adsorbents. At the beginning stage, dieldrin was adsorbed by the exterior surface of adsorbents, and the adsorption rates were very fast. The fastest adsorption rate of GAC was assumed due to its large specific surface area. When the adsorption of the exterior surface reached saturation, the molecular dieldrin further entered the particle and was adsorbed by the interior surface of the particle. When the molecular dieldrin diffused in the pore of the particle, the diffusion resistance increased, which caused the diffusion rate to decrease. With decrease of the dieldrin concentration in the solution, the diffusion rate became lower and lower, the diffusion processes reached the final equilibrium stage. Therefore the changes of $k_{i,1}$, $k_{i,2}$ and $k_{i,3}$ could be attributed to the adsorption stages of the exterior surface, interior surface and equilibrium, respectively. However, both $k_{i,2}$ and $k_{i,3}$ of CA-T were much higher than that of GAC, indicating that the adsorption rates of dieldrin on CA-T decreased much slower than GAC. It was estimated due to the special triolein-embedded structure of CA-T. Since triolein had strong accumulating effect to hydrophobic dieldrin, it might increase the equilibrium adsorption capacity and enhance the removal efficiency of CA-T. The correlation coefficients between 0.888 and 0.956 illustrate that experimental data can also be reasonably described by the intraparticle diffusion model.

### 3.2.2. Effects of HA on dieldrin adsorption

Organic contamination is a particular problem in the process of water supply. The adsorption capacity and adsorption rate are lower in natural water than in a single-solute adsorption system in pure water, because activated carbon usually removes not only the target contaminant but also natural organic matters (NOMs) [25]. Using HA to simulate NOMs, experiments were carried out to investigate the effects of NOMs on dieldrin removal by three adsorbents used in our study.

Fig. 3 shows the experimental data of effects of HA on dieldrin adsorption. It could be seen that dieldrin adsorption was significantly affected in GAC system with HA, with a residual concentration of 3.846 $\mu$g l$^{-1}$, while in the other two reaction systems with HA, the addition of HA had little effect on the uptake of dieldrin. The TOC of solution in GAC system reduced from the initial 3 mg l$^{-1}$ to the final 1.296 mg l$^{-1}$, whereas that of solutions in CA-T and CA systems remained almost unchanged. On the whole, CA-T presented a good selectivity to hydrophobic dieldrin, but GAC showed a poor one. The pH of solution was measured in all experiments, and results indicated that it remained almost unchanged at pH 6.8 after adding HA to adsorption systems. Consequently, the effects of pH on the adsorption process could be neglected.

From the pseudo-second-order kinetic model analytical results shown in Table 2, it could be easily found that the initial adsorption rate reduced from 7.35 to 2.28 $\mu$g g$^{-1}$ h$^{-1}$, and the adsorption capacity at equilibrium decreased from 0.930 to 0.775 $\mu$g g$^{-1}$ after adding the HA to GAC system, which indi-
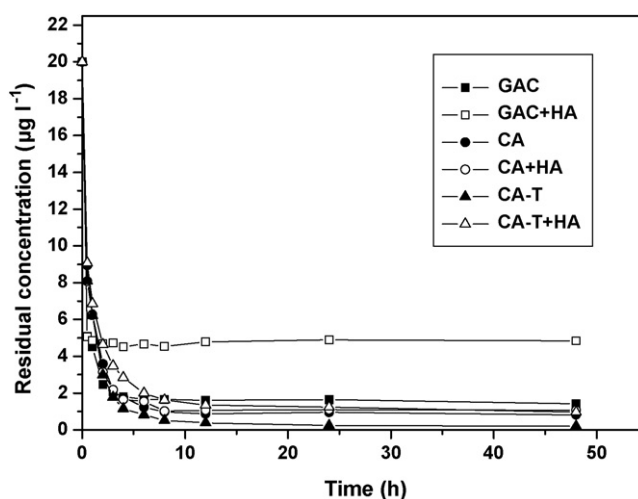


Fig. 3. Effects of HA on dieldrin removal.

cated that the adsorption of dieldrin on GAC was affected by the presence of HA obviously. While the values of the initial adsorption rate and the adsorption capacity at equilibrium of dieldrin adsorbed by CA and CA-T only reduced slightly when HA appeared in the reaction systems. Results of the intraparticle diffusion model also proved that the adsorption rates of dieldrin on GAC were slowed down obviously, especially in the last two stages, and that of CA and CA-T was only decreased in some sort.

### 3.2.3. Effects of some key factors on dieldrin adsorption by CA-T

Fig. 4 shows the effects of the initial concentration, temperature, shaking speed and pH on adsorption behavior of dieldrin on CA-T, which indicated that adsorption reaction was very rapid at the beginning stage, then slowed down gradually. Fig. 4(a) proved that the adsorption rate increased with the increase of the initial concentration, which was probably the result of increase of driving force (DF). The DF of diffusion was very important for adsorption processes and DF changed with solute concentration in bulk solution generally. The increases of dieldrin concentration resulted in the increase of DF, which would increase the diffusion rate of the molecular dieldrin in particles. While at the end of 48 h adsorption, residual concentrations of dieldrin in three solutions with different initial concentrations almost reached the same level. Comparing the experimental results obtained from Fig. 4(b), it could be found that the adsorption of dieldrin onto CA-T speeded up with the increase in temperature, which indicated that this adsorption reaction was endothermic. Fig. 4(c) presented the adsorption of dieldrin onto CA-T under shaking conditions of 0, 80 and 170 rpm. It could be seen that dieldrin adsorption was fast under shaking conditions, and the equilibrium was reached within 12 h at 170 rpm. While under the static condition, the adsorption of dieldrin onto CA-T was a very slow procedure. Within the first 1 h, only about 25% of dieldrin was adsorbed onto CA-T. In the adsorption process, dieldrin was firstly transferred to solid surfaces from bulk solutions and then adsorbed at active sites, which was slow and was a rate
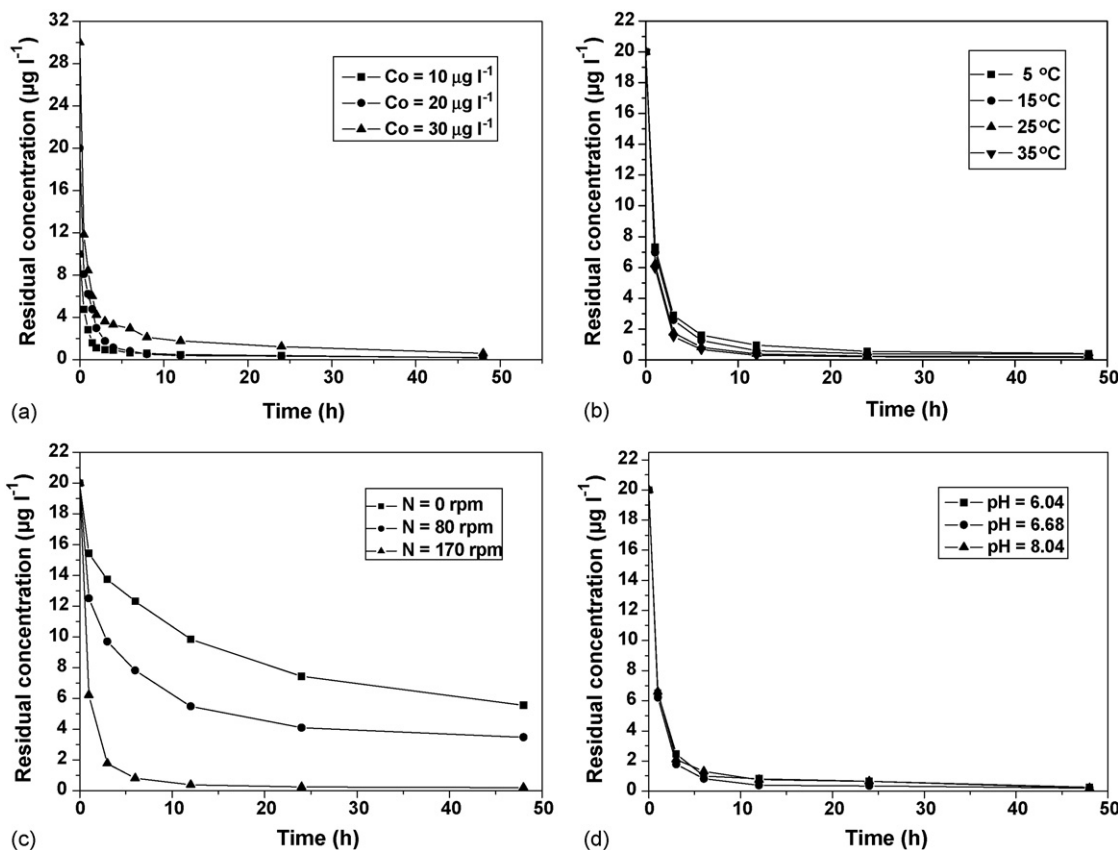
Fig. 4. Effects of experimental conditions on the adsorption of dieldrin on CA-T: (a) initial concentration, (b) temperature, (c) shaking speed and (d) pH.

determining step. When the mixture was shaken with certain rotation speed, the solid particles of adsorbent moved around rapidly in the solutions, and the concentration of dieldrin near adsorbent surface could be very close to the bulk concentration. The external mass transfer of dieldrin was speeded up, and the time consumed to reach equilibrium was shortened. Shaking increased the diffusion in the boundary layer and consequently the adsorption rate. Fig. 4(d) indicated that pH had little effects on the adsorption of dieldrin onto CA-T.

In summary, the adsorption rate of dieldrin on CA-T increased with initial concentration, temperature and shaking speed and there was no significant change in the removal rate of dieldrin in the pH range of 4–8.

### 3.3. Thermodynamic analysis of dieldrin adsorption on CA-T

The thermodynamic analysis of dieldrin adsorption on CA-T with experimental data of different temperatures was conducted. Thermodynamic parameters, such as change in free energy ($\Delta G^{\circ}$), enthalpy ($\Delta H^{\circ}$) and entropy ($\Delta S^{\circ}$), were calculated from the variation of the thermodynamic equilibrium constant $K_0$ with the change in temperature. The calculation methods employed are discussed in detail by Niwas et al. [26]. $K_0$ for the adsorption reaction can be defined as follows:

$$K_0 = \frac{\alpha_s}{\alpha_e} = \frac{\nu_s}{\nu_e}\frac{C_s}{C_e} \tag{10}$$

where $\alpha_s$ is the activity of adsorbed solute, $\alpha_e$ is the activity of the solute in solution at equilibrium, $C_s$ is the surface concentration of dieldrin in millimoles per gram of CA-T, $C_e$ is the concentration of dieldrin at equilibrium (mmol ml$^{-1}$), $\nu_s$ is the activity coefficient of the adsorbed solute and $\nu_e$ is the activity coefficient of the solute in solution. As the concentration of the solute in the solution approaches zero, the activity coefficient approaches unity, reducing Eq. (10) to the following form:

$$K_0 = \frac{\alpha_s}{\alpha_e} = \frac{C_s}{C_e} \tag{11}$$

Values of $K_0$ are obtained by plotting $\ln(C_s/C_e)$ versus $C_s$ and extrapolating $C_s$ to zero. The straight line obtained is fitted to the points based on a least-squares analysis. Its intercept with the vertical axis gives the values of $K_0$. Standard free energy changes ($\Delta G^{\circ}$, kJ mol$^{-1}$) for interactions are calculated from the relationship:

$$\Delta G^{\circ} = -RT \ln K_0 \tag{12}$$

where $R$ is the universal gas constant, 8.314 J mol$^{-1}$ K$^{-1}$, and $T$ is the temperature in Kelvin. The average standard enthalpy change ($\Delta H^{\circ}$, kJ mol$^{-1}$) is then calculated from the Van't Hoff equation:

$$\ln K_0(T_3) - \ln K_0(T_1) = \frac{-\Delta H^{\circ}(T_1-T_3)}{R}\left(\frac{1}{T_3} - \frac{1}{T_1}\right) \tag{13}$$

where $T_3$ and $T_1$ are two different temperatures.

Table 3
Thermodynamic parameters of dieldrin adsorption on CA-T

| $T$ (K) | $K_0$ | $\Delta G^\circ$ (kJ mol$^{-1}$) | $\Delta H^\circ$ (kJ mol$^{-1}$) | $\Delta S^\circ$ (kJ mol$^{-1}$ K$^{-1}$) |
|---|---|---|---|---|
| 288.15 | 2.52 | −18.76 | | 0.082 |
| 298.15 | 4.81 | −21.02 | 33.82 | 0.071 |
| 308.15 | 6.30 | −22.41 | | 0.073 |

Standard entropy changes ($\Delta S^\circ$, kJ mol$^{-1}$ K$^{-1}$) are calculated using the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{14}$$

The values obtained were given in Table 3. A positive value of the standard enthalpy change ($\Delta H^\circ$) indicated that the adsorption of dieldrin on CA-T was endothermic. It was supported by the increasing adsorption of dieldrin with the increase in temperature. Since the free energy changes ($\Delta G^\circ$) were negative and were accompanied by positive entropy changes ($\Delta S^\circ$), the reactions were spontaneous with high affinity for dieldrin [25]. The negative $\Delta G^\circ$ value increased with an increase in temperature, indicating that the spontaneous nature of adsorption is proportional to the temperature.

## 4. Conclusions

A novel composite adsorbent containing triolein was developed, which was found to be effective for the removal of hydrophobic dieldrin from aqueous solutions. The adsorption isotherm data of dieldrin fitted Freundlich equation well, and the adsorption capacity and removal efficiency of CA-T was higher than that of CA and GAC. The adsorption data was well described by both pseudo-second-order kinetics and intraparticle diffusion models. The addition of HA hindered the uptake of dieldrin by GAC obviously, but had little effect on dieldrin adsorption by CA-T, which proved that CA-T had an excellent selectivity to hydrophobic dieldrin. The adsorption rate of dieldrin on CA-T increased with the increase of shaking speed, initial concentration and temperature, and was pH independent in the pH range 4–8. The adsorption reaction was spontaneous with a high affinity and the adsorption of dieldrin on CA-T was an endothermic reaction, indicated by the negative free energy changes accompanied by a positive entropy changes.

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