Removal of ppb-level DDTs from aqueous solution using organo-diatomites
Lingzhi Tan, Shihua Qi, Jiaquan Zhang, Xinli Xing, Wei Chen, Yuan Zhang and Chenxi Wu

ABSTRACT
Three modified organo-diatomites (ODs) were used for removal of \( o,p' \) dichlorodiphenyldichloroethylene (\( o,p' \)-DDE), \( p,p' \) dichlorodiphenyldichloroethylene (\( p,p' \)-DDE) and \( p,p' \) dichlorodiphenyltrichloroethane (\( p,p' \)-DDT) from water. It was found that the adsorption of dichlorodiphenyltrichloroethane (DDT) and its metabolites (DDTs) depended greatly on the type and concentration of modifying agent, the concentration of adsorbent and the initial concentration of DDTs. The hydrophobic characteristics of ODs–DDTs interactions were verified by measuring the amounts of DDTs adsorbed on ODs. The analysis of contact angle and total organic carbon (TOC) measurements revealed that the hydrophilic tails on the ODs surface were replaced with hydrophobic ones by surfactants. The following conditions were strongly suggested to provide the optimum performance for adsorption of DDTs: raw diatomite is modified by cetyltrimethylammonium bromide (CTMAB); dosing quantity of OD is no more than 3.0 g/L. The removal efficiencies of the three pesticides on ODs followed the order: \( p,p' \)-DDT > \( o,p' \)-DDE > \( p,p' \)-DDE. The adsorption efficiencies of ODs for the pesticides followed the order: GZY > GZF > GZYI > GZN. This experiment showed that the fittest models for the experimental data were given by the Redlich–Peterson and homogeneous particle diffusion models.

Key words | adsorption, DDTs, organo-diatomite (OD), surfactants

INTRODUCTION
Organochlorine pesticides (OCPs) are composed of a class of man-made chemicals with pronounced persistence against chemical/biological degradation. They are highly mobile in the environment and have a tendency to bioaccumulate and biomagnify in organisms (Katsoyiannis & Samara 2004). Dichlorodiphenyltrichloroethane (DDT) was the first synthetic OCP to be used on a large scale throughout the world. Due to the toxicity and adverse effects upon humans and biota, its production and use has been banned for decades in many countries (Zhang et al. 2003). However, recent reports have indicated that DDT and its metabolites (DDTs) were still detectable in surface water, soil and sediment both in developed and developing countries (Zhou et al. 2006; Poolpak et al. 2008; Ferrante et al. 2010; Chen et al. 2011; Yang et al. 2012; Zhang et al. 2012). Because of their hydrophobic properties, concentrations commonly vary from several nanograms per liter to hundreds of nanograms per liter in micro-polluted surface waters (Liu et al. 2009), which makes them difficult to treat by conventional water treatment methods.

The adsorption technique is by far the most versatile and widely used method to solve the water pollution. It has already become the favored method for small/medium-scale operations to deal with organic pollution such as phenol, 17\( \beta \)-estradiol, and dexamethasone in the aquatic environment. Various adsorbents, including activated carbon (Fuerhacker et al. 2001; Efremenko & Sheintuch 2006; Lu & Sorial 2009), modified silicates, and porous
glasses (Mishael & Dubin 2005; Zadaka et al. 2007), have been reported to remove organic pollutants from water. Because of the high expense and difficulty in recycling, many adsorbents were limited in their use. The porous minerals, which are cheap and widely available materials, were commonly used as adsorbents for treating organic water pollution, but the hydrophilic layer on their surface decreased their capacity for adsorbing hydrophobic organic compounds. Therefore, organo-clays were mainly designed to promote the adsorption of neutral and hydrophobic pesticides and slowed their releasing speed (Murakami et al. 2004). Recent studies have focused on using surfactant-modified minerals to remove organic contaminants from water (Huttenloch et al. 2001; Lee et al. 2004). Many investigators have studied the adsorption of phenols and chlorinated phenols (Rytwo et al. 2007), naphthalene (Lee & Kim 2002), and polyamine (Blachier et al. 2009) onto organo-clay. The mechanism of the surface modification is based on enlarging the surface area and enhancing the cationic exchange. In addition, some researchers reported that both ion exchange and hydrophobic bonding played important roles in the adsorption of organic compounds (benzene-hexol, mesoxalic acid, and mellitic acid) onto cationic surfactant-modified minerals (Xu & Boyd 1994, 1995a, b). Li et al. (1998) studied the long-term chemical and biological stability of surfactant-modified zeolite. The results showed that the organo-zeolite was completely stable in the investigated pH region (from pH 3 to pH 10), as well as under aerobic and anaerobic conditions. All these results demonstrated that the surfactant-coated minerals were suitable to be designed as effective, safe, and economical environmental materials for long-term in situ remediation of water pollution.

Diatomite is a mineral found in natural sediments, and is formed from the accumulation and compaction of dead diatoms that have sunk to the bottom of water bodies (Goren et al. 2002). It has many excellent properties, such as high porosity, and excellent chemical and thermal resistance. Due to these properties, diatomite can be safely used in the process of wastewater treatment and groundwater pollution control. Similar to the synthetic process of amorphous silica, the reaction of diatomite is closely related to the presence of reactive sites on its surface (Yuan et al. 2004). Many surfactant-modified soils have been studied for the enhanced remediation of hydrophobic organic chemicals (Xu & Boyd 1994; Xu 1995a, b). Therefore, a suitable surface modification technique is essential to improve the organic adsorption ability of the raw diatomite. Meanwhile, diatomite is collected from seas and lakes and has been approved as a food-grade material by the US Food and Drug Administration (FDA). Thus, organic-diatomite can be safely used to remove pesticides in the process of wastewater treatment and drinking water purification.

Other researchers also showed that organic-clay could be used as an effective adsorbent for removing organic pollutants from water (Daifullah & Girgis 1998; Demirbas 2009; Dubey et al. 2009). However, to our knowledge, this is the first study to use organic-diatomites as adsorbents for adsorbing the DDTs in ng-level concentration from contaminated water and to analyze the small-concentration scale adsorption behavior.

The purpose of this paper is to study the adsorption properties of DDTs on natural diatomite and the organo-diatomites (ODs). The adsorption isotherms of the ODs were also studied. Special attention was focused on determining the effects of the surfactant loading, solid content in the suspension, and initial pesticide concentration during the adsorption process.

**MATERIALS AND METHODS**

**Materials and reagents**

All glassware was soaked in a potassium dichromate-sulfuric acid solution and washed in tap water and then deionized water and baked at 450 °C for 4 h before use. All organic solvents (such as acetone, n-hexane, and dichloromethane) are gas chromatography (GC) grade reagents, and the other reagents in this experiment were of analytical grade. All solutions were prepared with deionized water. The standard substances of o,p’-dichlorodiphenyldichloroethylene (o,p’-DDE), p,p’-dichlorodiphenyldichloroethylene (p,p’-DDE), and p,p’-dichlorodiphenyltrichloroethane (p,p’-DDT), as shown in Table 1, were purchased from the Agro-Environment Protection Institute of the Ministry of Agriculture of China. The surfactants (Table 1), which were used as
cationic, anionic, and nonionic surfactants, were cetyltrimethylammonium bromide (CTMAB), sodium dodecyl benzene sulfonate (SDBS), and polyethylene glycol-4000 (PEG-4000) and were purchased from Sinopharm Chemical Reagent Co. Ltd, China. The raw diatomite (88.0% of SiO<sub>2</sub>, 4.5% of Al<sub>2</sub>O<sub>3</sub>, 3.0% of Fe<sub>2</sub>O<sub>3</sub>, and 4.5% other oxides) was purchased from Zhengzhou Donghua Celite Product Co. Ltd, China.

The DDTs aqueous solutions were prepared by directly adding these standard substances to deionized water in sealed conical flasks. The mixtures were then agitated for 8 h using a horizontal shaker at 170 rpm and 25 °C in order to dissolve the organics in water homogeneously.

### Preparation of the ODs

The raw diatomite (GZ) was washed in deionized water to remove fines and other adherent impurities. Then it was dried and baked at 500 °C for 8 h (Murakami et al. 2004) to produce thermally treated diatomite (GZN). After crushing and grinding, the GZN was sieved to particle sizes of 0.063–0.075 mm and stored in tightly stoppered glass bottles for later use. In order to investigate the influence of surfactants on the adsorption of DDTs, the same quantity (500 g) of GZN was added to 0.5 L of the three surfactant solutions with the initial concentrations varying from 1 to 20 mmol/L, respectively. The suspensions were then shaken on a gyratory shaker at 150 rpm for 24 h to reach equilibrium (Lemič et al. 2006). After equilibrium had been established, the solid and aqueous phases were separated by silicon membrane and yielded a solid as ODs. The excess surfactants on the surface of the ODs were removed by repeatedly washing with deionized water. According to the types of surfactants, these ODs were named GZY (modified by CTMAB), GZYI (modified by SDBS), and GZF (modified by PEG-4000).

### Table 1: The related physicochemical properties of DDT and surfactants (25 ± 0.5 °C, pH 6.8)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular formulas</th>
<th>Mol. weight (g/mol)</th>
<th>Water solubility (mg/L)</th>
<th>LogK&lt;sub&gt;ow&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>o,p&lt;sup&gt;-&lt;/sup&gt;-DDE</td>
<td><img src="attachment" alt="image" /></td>
<td>318.03</td>
<td>0.14</td>
<td>6.00&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>p,p&lt;sup&gt;-&lt;/sup&gt;-DDE</td>
<td><img src="attachment" alt="image" /></td>
<td>318.03</td>
<td>0.12</td>
<td>5.70&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>p,p&lt;sup&gt;-&lt;/sup&gt;-DDT</td>
<td><img src="attachment" alt="image" /></td>
<td>354.49</td>
<td>0.025</td>
<td>6.36&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>CTMAB</td>
<td><img src="attachment" alt="image" /></td>
<td>364.45</td>
<td>13,000</td>
<td>−0.48</td>
</tr>
<tr>
<td>SDBS</td>
<td><img src="attachment" alt="image" /></td>
<td>348.48</td>
<td>20,000</td>
<td>−0.45</td>
</tr>
<tr>
<td>PEG-4000</td>
<td><img src="attachment" alt="image" /></td>
<td>3,600–4,400</td>
<td>50</td>
<td>−</td>
</tr>
</tbody>
</table>

<sup>a</sup>Howard & William (1997).
<sup>b</sup>Schwarzenbach et al. (2003).
Physical characterization of diatomite

The total organic carbon (TOC) contents of ODs were obtained with the Leco RC-412 multiphase C determinator (St Joseph, MI, USA) in O2 atmosphere after correcting the total carbon from the inorganic-C content. The BET (Brunauer–Emmett–Teller) surface areas of ODs were determined by N2 physisorption at liquid N2 temperature on a Miraesi KICT-SPA 3000 Instrument (Miraesi, Korea). All pH measurements were measured with the Beckman model 1009 pH Meter (Beckman, CA, USA). The contact angles of the ODs were measured using the sessile drop method on a CAM 101 series contact angle goniometer (KSV Company, Linthicum Heights, MD, USA).

Measuring hydrophobic characteristics of modified diatomite

The hydrophobic characteristics of ODs-DDTs interactions were verified by measuring the amounts of DDTs adsorbed on the ODs. The adsorption efficiencies for DDTs were determined by using a series of different surfactant-loaded OD samples. Blank and control experiments were also considered. All solutions were adjusted at pH 7 with standard buffer with 30 mM MES (pH 6), 30 mM MOPS (pH 7), or 30 mM HEPES (pH 8) (Sinopharm Chemicals, China) and agitated at 25 °C for 24 h.

The adsorption uptakes of the ODs have been investigated at the same initial DDT concentration of 20 ng/L. The ODs, which were modified by the CTMAB solutions with five concentrations (1, 2, 5, 10, 15, and 20 mmol/L), were named as GZY (1), GZY (2), GZY (5), GZY (10), GZY (15) and GZY (20), respectively. Measured quantities from 0.4 to 4.0 g of ODs, which were meshed to 0.15 mm, were added to 500 mL of the pesticide solutions. The suspensions were then vigorously agitated on a reciprocating shaker at 25 °C for 24 h to reach equilibrium (Flores-Céspedes et al. 2006). The mixtures were then centrifuged at 4,000 rpm for 30 min to discard the OD particles and produce 400 mL supernatant for each sample. The concentrations of DDTs in the supernatants were extracted and then measured by gas chromatography–electron capture detector (GC–ECD), according to a modified method based on the USEPA 8080A method (Chen et al. 2009, 2011; Zhang et al. 2013). All the analyses were done in duplicate.

Effect of the concentration of OD in the solution

Measured quantities of the GZY from 0.4 to 4.0 g (six samples in total) were added to 500 mL of solution with the same initial DDT concentration of 13.5 ng/L. The removal efficiencies of the DDTs onto the GZY1 and the GZF were also examined following the same procedure described above.

Isotherm adsorption models and kinetic adsorption models

The equilibrium relationships between the adsorbents and adsorbates were described by adsorption isotherms, which were determined by the residual amount of DDTs in the solution. Further, a standard agitated reactor experimental setup was used to determine the kinetic data. Dynamic contact between the ODs and the pesticide solutions were carried out on a mechanical shaker at its minimum speed. A fixed amount of 0.5 g GZY adsorbents, which were meshed to 0.15–0.2 mm, were shaken with 500 mL of DDTs with the concentrations varying from 4 to 200 ng/L at 25 °C for 5–200 min. In addition, the deionized water without the DDTs served as blank and batches without the ODs served as control. The amounts of DDTs adsorbed on the ODs were determined according to the differences between the initial and the equilibrium pesticide concentrations in the solution. The reproducibility of the results was greater than 95% after three replicates for each experiment.

Small-scale column tests

A pilot test of the ODs as a sub-surface permeable reactive barrier for remediation of contaminated groundwater was conducted at small-scale columns. Each column (2.5 cm internal radius and 30 cm length) was carefully packed with 3.0 g of the GZY or GZN. Both of the adsorbents were meshed to 100 BBS (average 0.15 mm), ensuring that the mixture was homogeneously distributed. The groundwater influent pH and initial concentrations of the DDTs in this experiment were 6.5 and 23.7 ng/L. The influent
water sample was collected at 0.5 m below the water surface from a river in Nan’an, Chongqing in July 2008. The geographic information for the sampling site is E:106°35′1.3″, N:29°25′23.7″. These samples were obtained using clean 1.5 L amber glass bottles. The bottles were rinsed three times with samples, and carefully filled without passing air bubbles through the samples. In this test, the empty bed contact time (EBCT) was set at 5 min. By attaching 10-mL glass gas-tight syringes to the three-way valves, effluent samples (1 L) were collected periodically from effluent out of the column. Meanwhile, the influent with the same concentration was continuously injected into the column. The columns were initially flushed with several pore volumes of distilled water before the DDTs solution was introduced.

RESULTS AND DISCUSSION

BET surface area and TOC of the OD particles

As illustrated in Figure 1, all the TOC contents of the ODs increased with the GZ, whereas the TOC of the GZN declined from 0.03 to 0%. Furthermore, the TOC contents of ODs increased with added amounts of surfactants. It is clear that the surfactants could be attracted onto the diatomite surface and the thermal treatment could effectively remove the organic compound in the raw diatomite. However, different increasing tendencies of TOC contents were shown among the various ODs, in particular for GZY. The TOC of the GZY was highest with 8.24%, which was roughly 274 times greater than that of the GZ. Compared to CTMAB, SDBS and PEG-4000 have a lower affinity to the diatomite surface, although the TOC content of the GZY1 and GZF were increased up to 0.08 and 0.31%, respectively. This phenomenon was caused by the negative charge on the diatomite surface, which produced an attractive force to cationic surfactant and a repulsive force to anionic surfactant (Cheng & Wong 2006). With increasing added surfactants, the electrical properties and available adsorption area of the ODs diminished. Hence, when the amounts of surfactants were over 15 mmol/L, the TOC decreased.

On the other hand, the similar tendency of the ODs surface area and TOC can be seen in Figure 1. The GZY had the highest BET surface area of 7.13 m²/g when it was modified by 15 mmol/L of CTMAB. GZY1 and GZF, which were modified by the surfactants at 15 mmol/L, also resulted in higher BET surface areas. This observation was related to the improvement of the dispersal state of diatomites when the surfactants were added to the diatomites (Nunes et al. 2008). When the amounts of surfactant were over 15 mmol/L the surfactants could be adsorbed on both the inner surface of particles and micropores, which led to the decrease of BET surface areas (Miao et al. 2009; Reddy et al. 2009).

Contact angles

The contact angles of all three ODs, shown in Figure 2, increased after the GZN was modified by the three
surfactants. These results indicated that the modification technique could replace hydrophilic tails with hydrophobic ones on the ODs surfaces. The possible types of interactions between the headgroups of surfactants and organic contaminants can be of hydrophobic nature (van der Waals forces) or can be enhanced further by a stable covalent attachment of the organosilanes to the diatomite surface.

**Removal efficiency of the DDTs by the three adsorbents**

The data obtained from the adsorption tests were used to calculate the adsorption indexes (AIs) (%):

\[ AI = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \]

where \( C_0 \) and \( C_e \) are the concentrations of the DDTs in solution (ng/L) at time \( t = 0 \) and \( t = t_{eq} \), respectively. The AIs of the DDTs adsorbed by different ODs with different loading amounts and surfactant types are presented in Figures 3 and 4. The appearances of the three parts of Figure 3 follow a similar trend, showing that the AIs of the DDTs rose with the increase in loading amounts of surfactants in all investigated solutions. At a certain amount of diatomite, the more surfactants were added the more surfactants were adsorbed onto the diatomite before the surfactant saturation adsorption was reached. When the loading amounts of the surfactants reached 15 mmol/L, the AIs of the DDTs reached their maximums. The maximum AIs of \( o,p'\)-DDE (Figure 3(a)) adsorbed by GZY, GZYI, and GZF were 77.38, 54.66, and 69.51%, respectively. In the case of \( p,p'\)-DDE (Figure 3(b)), the maximum AIs were 68.90% (GZY), 37.11% (GZYI), and 43.91% (GZF). The maximum AIs of \( p,p'\)-DDT (Figure 3(c)) were 81.66% (GZY), 68.26% (GZYI), and 75.98% (GZF). These results were consistent with the TOC contents, which were thought to be sensitive to the adsorption capability of these OCPs.

The results also revealed that GZN had little effect on the removal of DDTs (Figure 4). The AIs of the DDTs adsorbed by the GZN were 4.85% of \( o,p'\)-DDE, 0.57% of \( p,p'\)-DDE, and 2.37% of \( p,p'\)-DDT. Compared with the GZN, the three ODs showed much better removal efficiencies. The capacities and efficiencies of the ODs on pesticide adsorption enhanced significantly. The removal...
efficiencies of the GZY were 69.38% (o,p'-DDE), 64.90% (p,p'-DDE), and 75.66% (p,p'-DDT), respectively. When using GZYI as the adsorbent, the AIs were 51.66% (o,p'-DDE), 37.11% (p,p'-DDE), and 58.98% (p,p'-DDT). In the case of GZF, the AIs were 67.51% (o,p'-DDE), 38.91% (p,p'-DDE), and 72.37% (p,p'-DDT).

The results presented in Figures 3 and 4 show that the adsorption efficiencies of all three pesticides on the ODs followed the order: GZY > GZF > GZYI > GZN. Hence, the GZY was the most efficient material for adsorbing all three pesticides. As well, the TOC of the three ODs followed the same order. It could be concluded that the higher TOC values of the ODs produced the better adsorption capacity of organic compounds.

It also should be emphasized that the differences in removal efficiencies of DDTs were caused by the types of surfactants and solutes. The increase in AIs of the three pesticides, at the given concentrations, could be ascribed to the intensification of the hydrophobic properties on the surface of the ODs. Other studies also showed that the removal efficiency of surfactant-modified materials significantly increased compared with the raw minerals (Ko et al. 1998; Richards & Bouazza 2007). They indicated that the increase of the adsorption capacity may be ascribed to the ligand exchange on the mineral surface. The fact that the DDTs removal efficiency of GZY and GZF were higher than that of GZYI was amazing. The lesser amount of DDTs adsorbed on the GZYI may be caused by the negative charge on the diatomite surface which repelled the anionic surfactant. The results of TOC also provided evidence for this conclusion.

Meanwhile, it was also observed that the AIs of o,p'-DDE and p,p'-DDT were higher than that of p,p'-DDE. This was because these two chemicals (o,p'-DDE and p,p'-DDT) had more hydrophobic properties and higher octanol-water partition coefficients (K_{ow}, as shown in Table 1) than p,p'-DDE. The K_{ow} was also closely related to the accumulation abilities of organic compounds on the OD surface. The increasing rate of AI of p,p'-DDT adsorbed by the GZY was 1.18 times that of p,p'-DDT and 1.05 times that of o,p'-DDE. In the case of the GZYI, at the same concentrations, the increasing rate of AI of p,p'-DDT was 1.84 times that of p,p'-DDT and 1.25 times that of o,p'-DDE. The increasing rate of AI of p,p'-DDT adsorbed by GZF was 1.18 times that of p,p'-DDT and 1.73 times that of o,p'-DDE. The smaller amounts of p,p'-DDE adsorbed on the ODs were also probably the result of the repulsive forces between the adsorbate molecules and the weakly bound counterions.

Removal efficiency of the concentration of the ODs in solution

Previous studies of the adsorption behavior by organo-minerals reported that the relationship between the adsorption efficiency and the concentration of the adsorbent was not linear (Bouffard & Duff 2000; Daković et al. 2003). A similar result was also obtained from the adsorption of DDTs onto the GZY in this experiment.

The three curves (Figure 5) of the AIs showed that there was a small decrease at the suspension concentrations of 1 g/L in each curve. The AIs of the DDTs reached maximums when the concentrations of the ODs increased to 3 g/L. When the concentrations reached 4 g/L, another small declining tendency appeared in every curve. However, the AIs of the DDTs were still higher than those at the initial suspensions (0.2 g/L) for each pesticide at this time. This appearance might indicate that the OD particles agglomerated with the large particles. The rate of adsorption was due to the availability of the specific surface area on the adsorbent when the adsorption process was dependent on the surface morphology. Because the tiny cracks and
channels on the surface of the particles provided added surface area for small particles, the DDTs were more easily adsorbed onto small particles compared with large particles. These results indicated that using OD small particles could give more interfacial areas and better removal effects, which provided a potential method for the scientific application and the practical arrangements necessary for avoiding organic water pollution.

In contrast to the AIs of the DDTs, the actual amount of the DDTs adsorbed per unit mass of adsorbent decreased with the increase in suspension concentration (Figure 5). At lower concentrations, the ratio of available surface areas of the unit mass for adsorbing the DDTs was larger. The amounts of DDTs adsorbed were 107 and 5 ng/g of o,p'-DDE, 63 and 4 ng/g of p,p'-DDE, 112 and 7 ng/g of p,p'-DDT, for suspension concentrations of 0.2 and 4 g/L, respectively. The results showed that the adsorption efficiencies of the pesticides were also related to the $K_{ow}$ of each pesticide. According to Table 1, the log$K_{ow}$ of the three DDTs followed the order: log$K_{ow}$ p,p'-DDT was more than 6.3, while the log$K_{ow}$ of o,p'-DDE and p,p'-DDE were 6.00 and 5.70. The adsorption efficiencies of the DDTs using the three adsorbents followed the same order: p,p'-DDT > o,p'-DDE > p,p'-DDE.

**Adsorption isotherms**

To describe the adsorption behavior of the OD adsorption, the isotherms were prepared for the DDTs. The four equilibrium uptake isotherms (Equations (1)–(4)) were used to correlate the equilibrium data (Redlich & Peterson 1959; Chu & Chan 2003; Wang & Keller 2008).

- Linear: $C_s = M + KC_w$ (1)
- Freundlich: $C_s = KC_w^\beta$ (2)
- Langmuir: $C_s = KC_wM/(1 + KC_w)$ (3)
- Redlich – Peterson: $C_s = KMC_w^\beta/(1 + KC_w)$ (4)

where $C_s$ is the amount of the DDTs adsorbed per unit mass of adsorbent, $C_w$ is the equilibrium concentration of the DDTs, $K$ and $\beta$ are the surface adsorption equilibrium constant in each equation, $M$ is the constant that is determined by heat content during this adsorption according to the Redlich–Peterson model or the maximum amounts adsorbed per gram of the ODs according to Langmuir.

According to the $K$ of the Langmuir model, the adsorption capacities may be 8.958, 9.367, and 10.05 L/ng for o,p'-DDE, p,p'-DDE, and p,p'-DDT (Table 2), respectively. However, the limiting factor in the adsorption experiments was the low water solubility of the DDTs in this research (Table 1). The Langmuir model might not exactly interpret the adsorption behavior of DDTs with the ODs. Examining correlation coefficients ($R^2$), we found that the fittest model for the experimental data was the Redlich–Peterson model (Table 2). According to the assumption of the Redlich–Peterson isotherm theory, there is a homogeneous monolayer and bilayer coverage on the surface of the adsorbate. The results indicated that the interaction happened both in the monolayer and bilayer between adsorbate and the ODs surface. The adsorption more likely depended on the Redlich–Peterson model for the equilibrium concentration of the pesticide in solution (Figure 6).

**Batch kinetic model**

The adsorption of non-polar organic compounds has been reported to be a complex process (Murakami et al. 2004), in which the properties of the adsorbent and solute play a...
The adsorption process occurs within the surfactant organic layer in the surface and liquid-filled pores inside the diatomite. The kinetic model selected to describe this adsorption is the homogeneous particle diffusion model. The rate of the reaction was assumed through the following processes: (1) the diffusion of pesticide through the surfactant phase surrounding the diatomite; (2) the diffusion of the pesticides through the matrix of the diatomite; (3) the chemical reaction with the functional groups attached to the matrix (Warshawsky 1984). Previous studies have reported that the adsorbent phase could effectively control the diffusion of organic contamination from solution onto adsorbent particles (Boyd et al. 1971). In this case, the differential and algebraic equation (Valderrama et al. 2008) is given below:

\[
X(t) = 1 - 6 \sum_{z=1}^{\infty} \frac{1}{z^2} \exp \left[ -\frac{z^2 \pi^2 D_e t}{r^2} \right]
\]

where \( X(t) \) is the fractional attainment of equilibrium at time \( t \), \( D_e \) the effective diffusion coefficient of pesticides in the diatomite phase (m²/s), \( r \) the radius of the diatomite particle assumed to be spherical (m), and \( z \) is an integer.

\( X(t) \) can be calculated by the equation:

\[
X(t) = \frac{c_t}{c_e}
\]

where \( c_t \) (ng/g) and \( c_e \) (ng/g) are the concentrations of the solutes loading on the diatomite phase at time \( t \) and when equilibrium is attained (ng/g), respectively.
When Equation (1) fits the whole range \( 0 < X(t) < 1 \), it can be simplified as the following expression:

\[- \ln(1 - X^2(t)) = 2Kt, \quad \text{where} \quad K = \frac{\pi^2D_e}{r^2} \quad (7)\]

If the surfactant film diffusion controls the rate of this adsorption, Equation (1) can be expressed as:

\[- \ln(1 - X(t)) = 2K_{li}t, \quad \text{where} \quad K_{li} = \frac{3D_eC_r}{rC_r} \quad (8)\]

Figure 7 shows the results of the DDTs adsorption kinetics in the form of Equations (7) and (8) for the model mentioned above. It can be observed that the model fits the data satisfactorily in almost all the range for the adsorbent-phase diffusion, with some fluctuation in the initial time for the three pesticides. The evidence that the trends of Equation (8) did not give a linear dependence indicated that the film diffusion did not happen as the controlling step. The results of the linear regression analysis for Equation (7) are shown in Table 3. The results indicated that the reaction layer was very thin and the surfactant film can be adjacent to the particles. The linear correlation coefficients \( (R^2) \) indicated a good fit for this model.

**Small-scale column tests**

Column tests were conducted to determine \( p,p' \)-DDE or \( p,p' \)-DDT removal efficiencies for both GZY and GZN. The bulk densities of the two materials were measured to be 0.23 and 0.20 g/mL for GZY and GZN, respectively. The measuring bulk density method is described in the Soil Quality Test Kit Guide, Section I, Chapter 4, pp. 9–13 (United States Department of Agriculture 2001).

Different flow rates were applied to have the same EBCT (5 min) for each material: 4.3 (GZY) and 5.0 mL/min (GZN). Thus, effluent samples of GZY and GZN were collected every 5.8 and 3.3 h. The time-series plots of \( p,p' \)-DDE and \( p,p' \)-DDT concentrations in the effluents are shown in Figure 8. It showed that the GZY could effectively remove both \( p,p' \)-DDE or \( p,p' \)-DDT, whose concentrations were reduced to around 5 ng/L (\( p,p' \)-DDT) and 6.5 ng/L (\( p,p' \)-DDE), respectively. In contrast, neither of the two

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**Figure 7** Test of the kinetic model equations \( f(x) \) vs time \( t \) defined by the homogeneous particle diffusion model for pesticides adsorption on GZY.
face of the ODs. The removal efficiency increased with the increase in adsorbent concentrations. When the concentration of adsorbent increased to 3.0 g/L, the AIs of the ODs reached the maximum values in the experiment. Comparing the $R^2$ values of the isotherms and kinetic models of the DDTs, the fittest models for the experimental adsorption data were given by the Redlich–Peterson and homogeneous particle diffusion models.

### CONCLUSION

In this study, the surfactant-modified diatomites were developed and applied for removal of the DDTs from contaminated water. The results of BET surface area, contact angle, and TOC measurements revealed that surfactants increased the surface area of the ODs and replaced hydrophilic tails with hydrophobic ones on the surface of the ODs. The removal efficiencies of the three pesticides followed the order: $p,p'$-DDT > $o,p'$-DDE > $p,p'$-DDE. The adsorption efficiencies of the diatomites for the pesticides followed the order: GZY > GZF > GZI > GZN. The AIs of pesticides increased with the increase in adsorbent concentrations. When the concentration of pesticides was effectively removed by the GZN. These results indicated that the GZY produced a much better performance than the GZN.

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### REFERENCES


Daković, A., Tomašević-Čanović, M., Rottinghaus, G., Dondur, V. & Mašić, Z. 2003 Adsorption of ochratoxin A on octadecyldimethyl benzyl ammonium


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