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Effect of an eco-friendly o/w emulsion stabilized with amphiphilic sodium alginate derivatives on lambda-cyhalothrin adsorption–desorption on natural soil minerals

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ABSTRACT

The effects of amphiphilic O/W emulsions, stabilized by the alkyl polyglycoside (APG) or cholesterol-grafted sodium alginate (CSAD)/APG systems, on lambda-cyhalothrin adsorption/desorption mechanisms on natural soil minerals (i.e., illite and kaolinite) were investigated. Sorption and desorption of lambda-cyhalothrin onto soil minerals was studied via batch equilibration to give insight into the adsorption equilibrium, kinetics, and thermodynamics of lambda-cyhalothrin adsorption onto minerals. The results indicate the following: (i) The adsorption processes for the APG system and CSAD/APG system include: rapid adsorption, slow adsorption, and adsorption equilibrium. The adsorption kinetics of pesticide on illite and kaolinite are in accordance with the Ho and McKay model, and the adsorption isotherm conforms to the Freundlich model. In addition, the adsorption processes of pesticide for the two systems on minerals were spontaneous and feasible ($\Delta G^{\circ} < 0$), endothermic ($\Delta H^{\circ} > 0$), and mainly involved chemical bonding ($\Delta H^{\circ} > 60$). (ii) The equilibrium adsorption percentages of the pesticide on illite for the APG system and CSAD/APG system were 42.4% and 64.8%, and the corresponding equilibrium adsorption percentages on kaolinite were 40.8% and 61.8%, respectively. Moreover, the pesticide adsorption rate $K_{2-CSAD/APG}$ was faster than K_{2-APG} , and its adsorption capacity $K_{f-CSAD/APG}$ was greater than K_{f-APG} . Meanwhile, the pesticide desorption K_{fd} in the CSAD/APG system was smaller than that in the APG system. As a result, this eco-friendly O/W emulsion based on amphiphilic sodium alginate derivatives might provide a green pesticide formulation, since it could reduce the amount of lambda-cyhalothrin entering aquatic systems to threaten non-target fish and invertebrate species.

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Introduction

A pesticide product developed by Zeneca Group PLC, lambda-cyhalothrin [cyano(3-phenoxyphenyl) methyl (1S,3S)-3-[(1Z)-2-chloro-3,3,3-trifluoroprop-1-en-1-yl]-2,2-dimethylcyclopropanecarboxylate] is a third-generation pyrethroid insecticide, a class that includes deltamethrin, cypermethrin, cyfluthrin, and beta-cypermethrin (esfenvalerate, meothrin) (Pauluhn, 1999). This insecticide possesses a unique chemical configuration consisting of a dimethyl cyclopropane carboxylate moiety (Seenivasan and Muraleedharan, 2009) and has been extensively used for the control of a wide variety of insect pests in agriculture (Davey et al., 1992; Mathirajan et al., 2000; Oudou and Hansen, 2002; Liu et al., 2013). The widespread use of lambda-cyhalothrin has resulted in residues detected in irrigation and storm runoff water, and especially in their associated sediments, which have been found to be toxic to aquatic organisms including fish and amphipods (He et al., 2008; Xu et al., 2016; Tu et al., 2016).

The rapid development of modern agriculture has resulted in environmental pollution problems from pesticides, such as surface water and soil pollution. A very small fraction of pesticides applied to crops reaches the target, whereas a large fraction enters the environment by direct losses, spray drift, runoff, or incorporation into contaminated crop residues (Singh and Cameotra, 2013). Therefore, the persistence and adsorption capacity of pesticides determine their residence time and allocation proportion in soil-water systems (Qin et al., 2004; El et al., 2007; Tan et al., 2015; Yue et al., 2017). The factors that can affect the adsorption of pesticides on soil are numerous and complex. The main influencing factors are the composition of the soil (Cavanna et al., 1998) and the physical and chemical properties (Chiou et al., 1979), as well as the molecular structure and physicochemical properties of the pesticide itself. In addition, external factors, such as temperature (Fusi et al., 1993), pH (Boivin et al., 2005), cation exchange capacity (Pusino et al., 1993), surfactants (Kile et al., 1990), and polymers (Rubio-Bellido et al., 2016), have some effect on the adsorption of pesticides on the soil. The use of lambda-cyhalothrin pesticides represents a water quality risk because of their migration from soil to water, and prevention of pollution of water resources is considerably cheaper than restoration (Rojas et al., 2015). The half-lives of lambda-cyhalothrin were found to be in the range of 1.56 to 5.30 days in soils (Gong et al., 2013), and if the pesticide can be adsorbed on the soil during this time, it can prevent lambda-cyhalothrin entering aquatic systems via runoff to threaten non-target fish and invertebrate species. The important constituents of soil particles include humic and fulvic acids, silica, metal oxides and clay minerals (Ishiguro and Koopal, 2016). The main soil components are composed of clay and organic matter, which cause the sorption of pesticides in soil (Spark and Swift, 2002), and the major types of clay minerals include kaolinite and illite. These serve as natural adsorbents for a number of pollutants from contaminated waters (Lee and Tiwari, 2012). Moreover, the large-scale application of clay minerals has played an important role in soil and environmental protection for decades (Kühnel, 1990). Therefore, this study focused on the

objective of decreasing water pollution by increasing the adsorption of pesticides on clay.

Compared with traditional pesticide formulations, the use of pesticides in water emulsions is a water-based, low-toxicity, and environmentally friendly green technology (Zhang et al., 2013), which markedly reduces the use of organic solvents, and presents good prospects for application. In recent years, as environmental awareness has increased, more and more researchers have tended to use sustainable surfactants, such as alkyl polyglucosides (APGs) (Iglauer et al., 2004; Yin and Zhang, 2013; Hu et al., 2017). APG is a nonionic surfactant made from fatty alcohols and glucose derived from starch, which can be widely used in many areas due to its non-toxicity and easily degradability in the environment (Zhang et al., 2011). Studies have shown that the presence of surfactants plays an important role in soil washing applications and bioremediation (Liu et al., 1991; Bramwell and Laha, 2000). However, many years of research have found that most of the water emulsions use small-molecule surfactants as stabilizers, which makes it difficult to maintain the system for a long time. In practical applications, the stability of the emulsion can be promoted by adding a certain amount of polymer (Benichou et al., 2007). Sodium alginate is a natural polysaccharide extracted from brown algae and some bacteria; sodium alginate consists of polymer blocks made of two kinds of acid, β -D-mannuronic acid and α -L-guluronic acid (Gorin and Spencer, 1966; Govan et al., 1981). With numerous free hydroxyl and carboxyl groups distributed along its skeleton, sodium alginate is an ideal candidate for chemical functionalization. The formation of alginate derivatives by functionalizing the available hydroxyl and carboxyl groups can alter its properties, such as solubility, hydrophobicity, physicochemical properties, and biological properties. Derivatives of amphiphilic sodium alginate obtained by hydrophobic modification have been applied in drug delivery and tissue engineering (Pawar and Edgar, 2012; Yang et al., 2007). Cholesterol-grafted sodium alginate (CSAD) is a novel water-soluble amphiphilic polymer synthesized by grafting cholesterol onto sodium alginate with *N,N'*-dicyclohexylcarbodiimide as a coupling agent and 4-(*N,N'*-dimethylamino) pyridine as a catalyst at room temperature (Yang et al., 2007). In aqueous solutions, the hydrophobic groups of CSAD accumulate as hydrophobically associated polymers owing to hydrophobic interactions, thereby causing the macromolecular chains to form intra- and intermolecular associations (Piculell et al., 2015). Moreover, with the study of different types of surfactants and polymers, researchers have proposed different models of the interaction between the two compounds, such as the “pearl necklace” model, “sphere” model, “inflated cage” model, and others (Shirahama et al., 1982; Nagarajan, 1985; Chari, 1992). Previously, our group has reported the formation of polymer-surfactant complexes, where *n*-octyl- β -D-glucopyranoside is adsorbed on the CSAD molecules through hydrophobic interaction to cooperatively form large polymer-surfactant complexes (Huang et al., 2015). Highly comprehensive and in-depth studies of aqueous emulsions stabilized by hydrophobic associative polymers and surfactant have been conducted (Pons et al., 1997; Nestor et al., 2008). This experiment used two water emulsion systems simultaneously to study the adsorption of pesticides

on soil minerals, which can simulate pesticide adsorption in the actual process effectively.

This work aimed to gain insight into the adsorption behavior of lambda-cyhalothrin in two water emulsions in a soil mineral–water system, mainly regarding its adsorption–desorption behavior in the presence of CSAD, to reduce pesticide pollution of the water environment.

1. Materials and methods

1.1. Chemicals and soil minerals

Technical grade (96.4%) lambda-cyhalothrin was provided by Hainan Brocade Technology Co., Ltd. Alkyl polyglycoside (APG1214) was purchased from Shanghai Fine Chemical Co., Ltd. CSAD was provided from our laboratory (Huang et al., 2015). Illite and kaolinite, which are common and abundant minerals in soils, were obtained from mineral processing plants, Lingshou County in China. The main properties of illite and kaolinite are shown in Table 1.

1.2. Preparation of aqueous emulsion

First, lambda-cyhalothrin was dissolved in an appropriate amount of xylene and added to a certain amount of APG as the oil phase; next, 4 mL of 5 g/L CSAD solution was added to ultra-pure water as the water phase (for water emulsion without CSAD, ultra-pure water was used directly as the water phase); finally, the aqueous phase was mixed with the oil phase and sheared at 25,000 r/min for 30 min. The resulting mass fractions of lambda-cyhalothrin, APG, and xylene in stable aqueous emulsion were 2%, 4%, and 6%, respectively.

1.3. Lambda-cyhalothrin adsorption kinetics

The lambda-cyhalothrin adsorption kinetics on soil minerals in different water emulsion systems were investigated using a batch equilibration procedure. First, the water emulsion of the two different systems was diluted to prepare solutions with $C_{APG} = 0.1$ g/L (surfactant micelle concentration), and 1.0 g of illite or kaolinite was transferred to 20 mL centrifuge tubes, to which 10 mL of the above-mentioned diluent of the APG or CSAD/APG system was added. Second, all tubes were immediately sealed and mechanically shaken for 10, 30, 60, 120, 180, 300, 480, 720, 1080, or 1440 min in a constant temperature oscillation tank at 25 °C. Then, the suspensions

were centrifuged at 5000 r/min for 6 min, 1 mL of the supernatant was added to a 10 mL small glass bottle, and 5 mL chromatographically pure *n*-hexane for extraction after oscillation. Finally, the pesticide content of 1 mL upper layer extract was determined by a 6980 N Gas Chromatograph (Agilent, USA) equipped with an ECD detector. The conditions used were as follows: DB-1 (30 m × 0.25 mm × 0.25 μm) quartz capillary column; inlet temperature, 230 °C; column temperature, 250 °C; detector temperature, 320 °C; carrier gas flow rate, 1.0 mL/min; split ratio, 50:1 and injection volume, 1.0 μL.

1.4. Lambda-cyhalothrin adsorption isotherm

The lambda-cyhalothrin adsorption isotherms on soil minerals in different water emulsion systems were obtained by batch equilibration as described above. Different dilutions used for the study were 0.008, 0.02, 0.04, 0.08, 0.1, 0.2, 0.4, and 0.8 g/L of APG mass concentration, and all oscillation experiments were conducted for 720 min.

1.5. Lambda-cyhalothrin adsorption enthalpy

The lambda-cyhalothrin adsorption enthalpy on soil minerals in different water emulsion systems was determined using batch equilibration as described above. The entire experiment was the same as the adsorption isotherm experiment, with temperature levels adjusted from 35 to 45 °C.

1.6. Lambda-cyhalothrin desorption

Desorption experiments were performed immediately after the adsorption experiments. The entire reaction mixture was centrifuged, and the supernatant was decanted carefully. The same amount of decanted supernatant was replaced with distilled water, and then the subsequent procedure followed that of the adsorption experiment.

1.7. Data analysis

The pseudo-first-order kinetic model (Eq. (1)), pseudo-second-order kinetic model (Eq. (2)), and intra-particle diffusion model (Eq. (3)) were used to fit the adsorption kinetics:

$$\log_{10}(Q_e - Q_t) = \log_{10}Q_e - 0.4342K_1t \quad (1)$$

where Q_t (μg/g) and Q_e (μg/g) are the amounts of lambda-cyhalothrin adsorbed at time t and under equilibrium conditions, respectively; K_1 (min⁻¹) is the model rate constant for the adsorption.

$$\frac{t}{Q_t} = \frac{1}{K_2Q_e^2} + \frac{t}{Q_e} \quad (2)$$

where K_2 (g/μg/min) is the model rate constant for the adsorption.

$$Q_t = x_i + k_i t^{1/2} \quad (3)$$

where x_i (μg/g) is a constant proportional to the boundary layer thickness and k_i (μg/g/min^{1/2}) is the intra-particle diffusion rate constant.

Table 1 – Properties of soil minerals.

Soil mineral	pH	Conductivity	Specific surface area	Cation exchange capacity
		(μS/cm) (25 °C)	SAA (m ² /g)	CEC (cmol/kg)
Illite	9.59	86.4	6.64	0.71
Kaolinite	6.12	14.12	4.83	0.06

The Langmuir (Eq. (4)) and Freundlich (Eq. (5)) models were used to fit the adsorption and desorption isotherms.

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (4)$$

where C_e ($\mu\text{g/L}$) is the equilibrium concentration in solution, q_e ($\mu\text{g/g}$) is the amount of lambda-cyhalothrin adsorbed by a mass of soil mineral, q_m ($\mu\text{g/g}$) is the maximum adsorption capacity, and K_L is a constant related to the affinity between the adsorbent and the adsorbate.

$$\log Q_e = \log K_F + n_F \cdot \log C_e \quad (5)$$

where K_F is the adsorption equilibrium constant representing the adsorption capacity and n_F is a constant indicative of adsorption intensity.

The thermodynamic parameters for the adsorption processes were obtained by the following equations:

$$\Delta G^0 = -RT \ln K_F \quad (6)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (7)$$

where T (K) is the absolute temperature, R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is the gas constant, ΔG^0 (kJ/mol^3) is the standard Gibbs free energy, ΔH^0 (kJ/mol) is the standard enthalpy change, and ΔS^0 (kJ/mol) is the standard entropy change.

2. Results and discussion

2.1. Critical micelle concentration of APG in water emulsion

The surface tension of the CSAD/APG and APG system water emulsions under different APG contents is shown in Fig. 1. With the increase in CAPG, that is, the decrease in the dilution multiple of the water emulsion, the surface tension of both systems decreased first and then reached equilibrium. The equilibrium concentration of APG in both systems was 0.1 g/L, and the corresponding surface tension was close to 29 mN/m, indicating that APG played a leading role in determining the

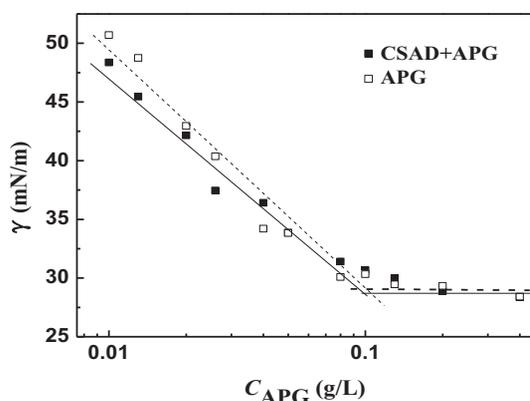


Fig. 1 – Surface tension of the two solution systems under different APG contents.

surface tension of the solution. Moreover, the surface activity of CSAD was small, and was minimally affected by the surface tension of the solution. Therefore, the critical micelle concentration of APG in the two system solutions was determined as 0.1 g/L.

2.2. Adsorption kinetics

Fig. 2a and b show the adsorption kinetics of the pesticide in the two different systems on illite and kaolin, respectively. The adsorption capacity of the pesticide on the soil minerals increased rapidly in the first 30 min. At this point, the adsorption capacities of pesticide in the APG and CSAD/APG systems on illite were 21.5% and 52.0%, respectively; the adsorption capacities on kaolinite were 22.0% and 49.1%, respectively. With the prolongation of time, the adsorption capacity increased gradually, and the adsorption process basically reached equilibrium at 720 min. At the same time, the pesticide adsorption capacities for the APG and CSAD/APG systems on illite were 42.4% and 64.8%, respectively; the adsorption capacities on kaolinite were 40.8% and 61.8%, respectively. Therefore, 720 min was used as the equilibrium time for the adsorption isotherm experiments.

The fitting parameters of pseudo-first-order, pseudo-second-order and intra-particle diffusion models for two different pesticide systems adsorbed on illite and kaolinite are shown in Table 2.

The correlation coefficients showed the superior fit of pseudo-second-order model, suggesting that the adsorption rate was mainly dependent on the available adsorption sites rather than the concentration of the pesticide in solution. This finding indicated that the adsorption process was mainly controlled by chemical adsorption. The entire adsorption process under this kinetic model included external liquid film diffusion, surface adsorption, and particle diffusion. For pesticide adsorption on illite, the adsorption constant K_2 of the CSAD/APG system was larger than that of the APG system, indicating that the adsorption rate of the pesticide in the CSAD/APG system was fast on the illite surface. This finding was possibly attributed to APG reaching its critical micelle concentration and forming a micelle (at this time, the oil phase that dissolved the pesticide was wrapped by the micelle); a mixed micelle with CSAD was formed, and the chemical bond energy of the mixed micelle combined with surface adsorption sites on illite was stronger than that of the APG micelle combined with surface adsorption sites on illite. Therefore, the pesticide in the CSAD/APG system was easily adsorbed on the soil mineral, thereby reducing the pesticide pollution in water. When the surface adsorption on illite reached saturation, the small pesticide molecules might also be adsorbed on the inner surface of soil mineral particles by intra-particle diffusion until the adsorption process reached saturation, which primarily explained the trend in Fig. 2. For the adsorption on kaolinite, given that the specific surface area of kaolinite was lower than that of illite, the adsorption surface on kaolinite was small and the pesticide adsorption capacities of the two systems were low.

Fig. 3a and b show the fitting lines of the adsorption of pesticide on illite and kaolinite, respectively, based on the

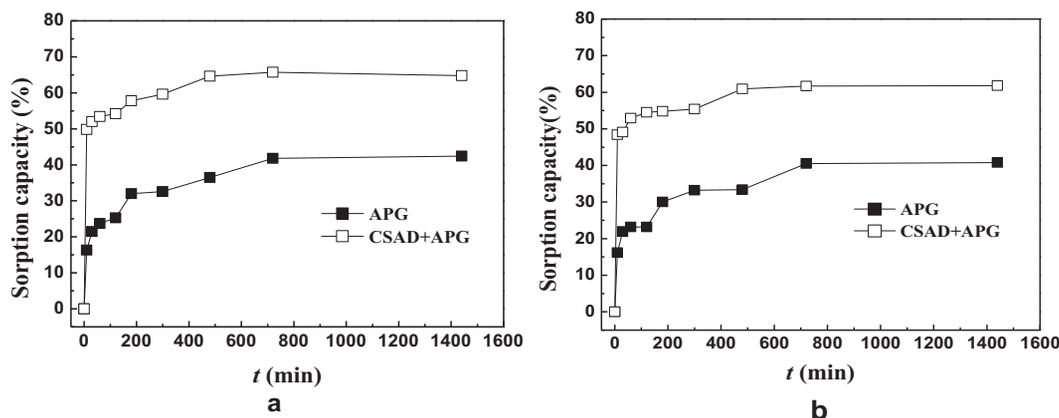


Fig. 2 – Adsorption equilibration curves of pesticide on illite (a) and kaolinite (b) in two emulsion systems.

pseudo-second-order model. The slope of the CSAD/APG system was smaller than that of the APG system, that is, the equilibrium adsorption capacity of the pesticide on illite and kaolinite in the CSAD/APG system was larger than that of the APG system, as shown in Fig. 2a and b, respectively.

2.3. Adsorption isotherms

The isotherm parameters of the Langmuir and Freundlich models for pesticide adsorbed on illite and kaolinite are listed in Table 3.

The correlation coefficients showed that the Freundlich model was highly suitable for explaining the isothermal adsorption process, in accordance with adsorption on soil particles with a non-uniform surface. For the pesticide adsorption on illite, the adsorption constant K_F of the CSAD/APG system was larger than that of the APG system, indicating that a large fraction of pesticide was adsorbed on illite in the CSAD/APG system. Simultaneously, the maximum adsorption capacity Q_m values based on the Langmuir model fit of the CSAD/APG system and APG system were 3399.05 and 2104.73 $\mu\text{g/g}$, respectively. These values indicated that the adsorption capacity of the CSAD/APG system for pesticides was greater than that of the APG system. For adsorption on kaolinite, the explanation for the observed small adsorption capacity was as discussed in the section on adsorption kinetics.

Fig. 4a and b show the fitting lines of the Freundlich isotherm model for the adsorption of pesticide on illite and

kaolinite, respectively. As shown in the figure, the larger the intercept of the line, the greater the pesticide adsorption capacity. Therefore, the pesticide adsorption capacity of illite or kaolinite in the CSAD/APG system was larger than that of the APG system.

2.4. Adsorption thermodynamics

The thermodynamic parameters for the adsorption of pesticides for the two systems on illite and kaolinite are shown in Table 4. The negative values of ΔG^0 in the temperature range of 298–318 K indicated that the adsorption processes of pesticides on illite or kaolinite were spontaneous and feasible. The positive values of ΔH^0 showed that the adsorption was an endothermic reaction. At the same time, the magnitude of ΔH^0 could reflect the adsorption force between the adsorbate and the adsorbent, and Tan et al. (2015) reported on the relationship of ΔH^0 with the adsorption mechanism. When $4 < \Delta H^0 < 10$, the adsorption process may be dominated by van der Waals forces; when $\Delta H^0 \approx 5$, the adsorption process may be dominated by hydrophobic bonding; when $2 < \Delta H^0 < 40$, the adsorption process may be dominated by hydrogen bonding; when $\Delta H^0 \approx 40$, the adsorption process may be dominated by ion exchange; when $2 < \Delta H^0 < 29$, the adsorption process may be dominated by dipole bonding; and when $\Delta H^0 > 60$, the adsorption process may be dominated by chemical bonding. The table shows that the values of ΔH^0 exceeded 60, indicating that chemical bond was most probably involved, as was consistent with the results discussed above in the section on

Table 2 – Fitting parameters of pseudo-first-order, pseudo-second-order and intra-particle diffusion models for pesticide sorbed on illite and kaolinite.

		Pseudo-first-order		Pseudo-second-order		Intra-particle diffusion		
		K_1	r^2	K_2	r^2	k_i	x_i	r^2
Illite	APG	0.0038	0.97	1.38×10^{-5}	0.99	24.87	591.30	0.90
	CSAD+APG	0.0026	0.43	3.05×10^{-5}	1.00	19.85	2183	0.82
Kaolinite	APG	0.0033	0.88	1.63×10^{-5}	0.99	20.99	513.31	0.87
	CSAD+APG	0.0026	0.68	3.10×10^{-5}	1.00	17.25	2011.10	0.83

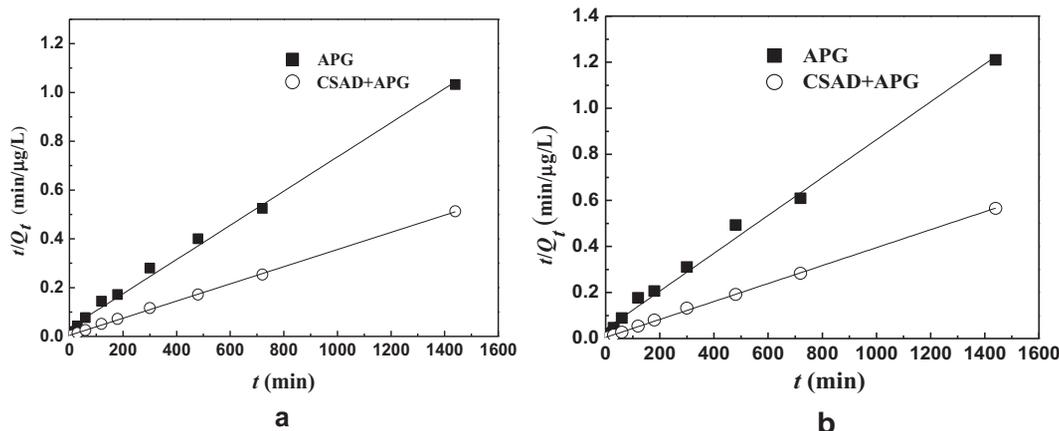


Fig. 3 – Pseudo-second-order model of pesticide sorbed on illite (a) and kaolinite (b).

adsorption kinetics. However, the adsorption ΔH^0 of pesticide in the CSAD/APG system was larger than in the CSAD/APG system, suggesting that the chemical bond energy of pesticide adsorbed on the soil minerals for the CSAD/APG system was stronger than that the soil minerals for the CSAD system (See Table 5).

2.5. Desorption behavior of lambda-cyhalothrin on soil mineral

Given that the isotherm model of the adsorption process was in accordance with the Freundlich model, the desorption process was also fitted by the Freundlich model as the inverse of the adsorption process. Table 4 shows the desorption isotherm parameters of the Freundlich model for the pesticide system. A comparison of Table 3 shows that the K_{Fd} value of the desorption process was markedly lower than that of the adsorption process, indicating that the degree of desorption was extremely small. Moreover, the K_{Fd} value for the CSAD/ APG system was smaller than that for the APG system in the desorption process, suggesting that the desorption of pesticide from the CSAD/ APG system was weak. That is, the migration resistance of the pesticide from the soil mineral to water was large, supporting the above-mentioned fact that the pesticide adsorption capacity in the CSAD/ APG system was greater than that in the APG system. In other words, the greater the adsorption capacity of soil minerals for pesticide, the weaker the migration capability of pesticide in the desorption process.

2.6. Adsorption mechanism

On the basis of the aforementioned adsorption kinetics, adsorption isotherms, adsorption thermodynamics and desorption, the adsorption mechanism was summarized as follows. Several models can be used to express the mechanism of solute sorption onto a sorbent: the pseudo-first-order kinetic model, the pseudo -second-order kinetic model, and the intra-particle diffusion model. A good fit to pseudo-second-order kinetic model indicated that the adsorption force of pesticide on soil mineral was mainly controlled by chemical bonding ($\Delta H^0 > 60$). The isotherm adsorption could be better fitted by the Freundlich model, suggesting that the adsorption process occurred on a heterogeneous surface. Hence, the sorption of pesticide on illite and kaolinite in CSAD/ APG and APG systems consists of three stages: (1) Fast sorption: external liquid film diffusion. The adsorption of pesticide on soil minerals increased rapidly within the first 30 min of the adsorption experiment, and the adsorption capacities for pesticide in the APG and CSAD/ APG systems on illite were 21.5% and 52.0%, respectively; the adsorption capacities on kaolinite were 22.0% and 49.1%, respectively. The surfactant APG in the solutions of the two systems reached its critical micelle concentration, and the critical micelles encapsulated the pesticide molecules dissolved in the oil phase at this point. (2) Slow sorption: surface adsorption. When the time of adsorption on the mineral soils was 30 to 720 min, the adsorption capacity increased gradually, the adsorption process basically reached equilibrium at 720 min, and the adsorption capacities of pesticide for the APG and CSAD/ APG systems on illite were 42.4% and 64.8%, respectively; the adsorption capacities on kaolinite were 40.8% and 61.8%, respectively. Clearly, the adsorption rate of the mixed micelles was faster than that of APG micelles ($K_{2-CSAD/APG} > K_{2-APG}$), and the adsorption capacity of the mixed micelles was greater than that of APG micelles ($K_{F-CSAD/APG} > K_{F-APG}$). Compared with the APG system, the CSAD hydrophobic micro-area formed by hydrophobic association would form mixed micelles with the APG micelles, which can adsorb more micelles on the surface of particles and be rapidly adsorbed on the surface active sites of the soil mineral

Table 3 – Fitting parameters for the adsorption isotherms of pesticide on illite and kaolinite.

		Langmuir		Freundlich			
		Q_m	K_L	r^2	n_f	K_F	r^2
Illite	APG	2104.73	0.00038	0.73	0.79	1.94	0.84
	CSAD+APG	3399.05	0.00029	0.96	0.64	8.54	0.97
Kaolinite	APG	3112.25	0.00017	0.87	0.86	1.09	0.94
	CSAD+APG	3229.06	0.00022	0.93	0.75	2.99	0.99

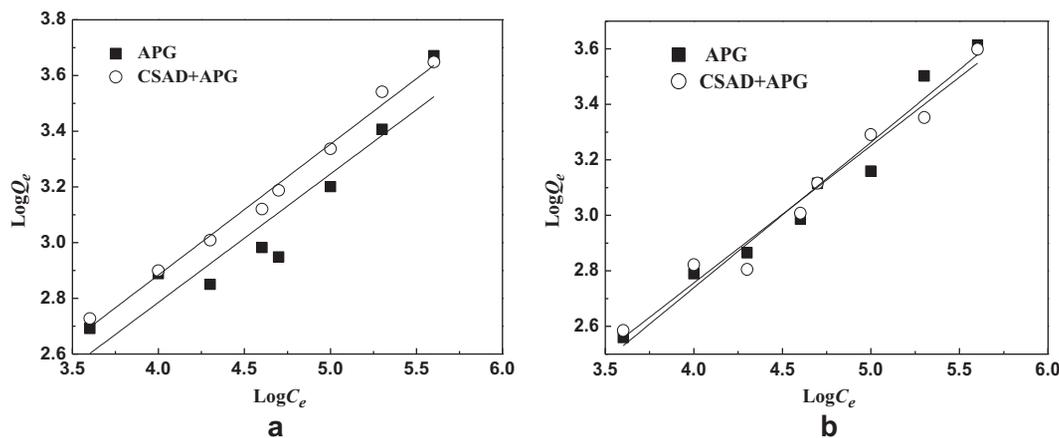


Fig. 4 – Freundlich sorption isotherms of pesticide on illite (a) and kaolinite (b).

Table 4 – Thermodynamic parameters for pesticide adsorbed on illite and kaolinite.

		Temperature (K)	K_F	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol/K)		
Illite	APG	298	1.94	-1.64	63.04	0.22		
		308	6.14	-4.65				
		318	9.67	-6.00				
	CSAD+APG	298	8.54	-5.31			65.51	0.23
		308	32.56	-8.92				
		318	45.38	-10.09				
Kaolinite	APG	298	1.09	-0.21	74.16	0.25		
		308	4.76	-4.00				
		318	7.23	-5.23				
	CSAD+APG	298	2.99	-2.71			87.98	0.35
		308	11.98	-4.73				
		318	28.05	-8.81				

by chemical bonding. (3) Sorption equilibrium: particle diffusion. When the adsorption of active sites reached saturation, the small pesticide molecules dissolved in the oil phase were slowly adsorbed onto the inner surfaces by intra-particle diffusion, and the entire adsorption process reached equilibrium when the intra-particle diffusion reached saturation.

3. Conclusions

The effect of amphiphilic emulsions stabilized by APG or CSAD/APG on lambda-cyhalothrin adsorption/desorption mechanisms on illite and kaolinite was investigated. The results indicate that pesticide adsorption for the APG system and CSAD/APG system on illite and kaolinite is a chemical

adsorption process. The pesticide adsorption rate K_{2-APG} is faster than $K_{2-CSAD/APG}$, and its adsorption capacity $K_{F-CSAD/APG}$ is greater than K_{F-APG} . Meanwhile, the pesticide desorption K_{Fd} in the CSAD/APG system was smaller than that in the APG system. The primary reason for this phenomenon is that the CSAD/APG system has a synergetic effect when CSAD and APG are combined. Another internal reason might be that the extra addition of CSAD can lead to a stronger form of chemical bonding between the CSAD and surface active sites of soil minerals. As a result, the eco-friendly O/W emulsion based on the amphiphilic sodium alginate derivatives might provide an efficient and sustainable pesticide formulation for remediation of lambda-cyhalothrin polluted water environments.

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Table 5 – Freundlich parameters for the desorption of pesticide from illite and kaolinite.

	Illite			Kaolinite		
	n_F	K_{Fd}	r^2	n_F	K_{Fd}	r^2
APG	1.73	0.0015	0.81	1.73	0.021	0.94
CSAD+APG	2.52	0.0000025	0.95	2.32	0.000020	0.90

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