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Research Article

Properties of Avermectin Delivery System Using Surfactant-Modified Mesoporous Activated Carbon as a Carrier

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The sensitivity of avermectin to several environmental factors, especially light, causes low pesticidal activity and environmental pollution. In this study, surfactant-modified mesoporous activated carbon (MAC) was employed to absorb avermectin (Av) in order to improve its photostability and allow for sustained release of avermectin. The results suggest that sodium dodecyl sulfate (SDS) modified MAC has excellent absorption of avermectin, and the absorption can be represented by the Langmuir isotherm model. The Av-MAC-SDS delivery system significantly improves sustained release of avermectin and also effectively inhibits the photodegradation of avermectin. These results indicate that SDS-modified MAC can be used as a carrier for avermectin to improve its pesticidal activity and reduce pesticide residues.

1. Introduction

Pesticides are indispensable in agricultural production. Environmental pollution caused by the misuse of chemical pesticides, however, is becoming more and more serious [1, 2]. Because of this, biopesticides have attracted increasing attention for their high bioefficiency, safety, and other environmentally friendly traits that are consistent with the requirements of sustainable agriculture [3]. Avermectin is a class of macrocyclic lactones isolated from the soil organism *Streptomyces avermitilis*. It has excellent pesticidal activity in agricultural systems due to high efficiency, low toxicity, and high selectivity. However, its conventional formulations still have some shortcomings, such as environmental sensitivity and short duration of effect. In order to improve the pesticidal activity of avermectin, it is preferable to adsorb avermectin onto some forms of adsorbent that can prevent degradation and consequently avoid the loss of pesticidal activity.

Activated carbon is an adsorbent material with a large surface area. Because of its well-developed pore structure and chemical stability, it has been widely used for purification, especially for purifying air and water [4, 5]. In the last decade, it has been extensively used for the prevention of environmental pollution [6–8], and in pharmaceutical applications [9] and the catalytic industry [10] as well. As a carrier of chemical pesticides, activated carbon protects the active ingredients and allows for sustained release of the active ingredients [11]. However, research about mesoporous activated carbon (MAC) loaded with biopesticides has been limited. Our previous work shows that MAC allowed for sustained release and UV-shielding of avermectin [12], and the surface acidic groups of MAC, especially carboxyl groups, showed a significant negative correlation with adsorption of avermectin [13].

In this study, MAC with a Brunauer-Emmett-Teller (BET) surface area greater than 1200 m^2/g was modified with surfactants. The BET surface area of MAC before and after modification was tested using a surface area analyzer. The avermectin loading capacity of modified MAC was compared with other conventional pesticide carriers by analyzing

the absorption of avermectin from a methanol solution. Avermectin adsorption data were also modeled using both Langmuir and Freundlich classical adsorption isotherms. Finally, the sustained release properties and resistance to photodegradation of the delivery system were analyzed and evaluated.

2. Materials and Methods

2.1. Materials. Avermectin was purchased from Qilu Pharmaceutical Co., Ltd. (Inner Mongolia, China). Mesoporous activated carbon and bentonite were obtained from Sigma-Aldrich Shanghai Trading Co., Ltd. (Shanghai, China). Sodium dodecyl sulfate (SDS) and tetrabutylammonium bromide (TBAB) were purchased from J&K Scientific Ltd. (Beijing, China). Kaolin and diatomite were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). HPLC grade methanol was purchased from Thermo Fisher Scientific (Beijing, China). Other chemicals were purchased from the Beijing Chemical Factory, China. All chemicals were of analytical grade and were used as received. The water used in all analytical experiments was Milli-Q water (18.2 MΩ·cm, TOC ≤ 4 ppb) prepared using a Milli-Q Advantage A10 system (Millipore, Milford, MA, USA).

2.2. Preparation of the Modified MAC with Different Surfactants. MAC was first purified several times with ultrapure water to remove adsorbed impurities and metal ions. Then it was filtered and oven dried at 100°C for 10 h. Five g of purified MAC was suspended in 500 mL of 10 mmol/L SDS and TBAB solution with stirring at 25°C for 10 h. The mixture was filtered, thoroughly rinsed with ultrapure water to remove excess surfactant, and oven dried at 60°C for 8 h.

2.3. Characterization of MAC. The Brunauer-Emmett-Teller (BET) measurements of MAC and pore structure analysis were conducted at −196.15°C using a surface area analyzer (Tristar II 3020, Micromeritics Instrument Co., Norcross, GA, USA). The pore size distribution was calculated with the Barrett-Joyner-Halenda (BJH) method. An elemental analyzer (EA2400, PerkinElmer Inc., Shelton, CT, USA) was used to examine changes in C, H, and N contents using the Pregl-Dumas Method before and after the modification.

2.4. Determination of Avermectin Content. The avermectin concentration of the suspension was determined by high performance liquid chromatography (HPLC) (Agilent 1260, Agilent Technologies, Ltd., Santa Clara, CA, USA) using a C18 column (5 um, 4.6 mm × 150 mm, Agilent Technologies, Ltd., Santa Clara, CA, USA) at room temperature. The mobile phase was composed of methanol and water (90 : 10). The flow rate was 1.0 mL/min, and a UV detector wavelength of 245 nm was used. The initial concentration of avermectin standard solutions was C_0 (mg/mL). Pesticide-loading capacity (Q_t) was calculated according to the following formula:

$$Q_t = \frac{(C_0 - C_t)\,V}{m}, \tag{1}$$

where V is the solution volume and m is the mass of adsorbent.

2.5. Modeling of Adsorption Isotherms. Batch equilibrium studies were carried out by adding 200 mg MAC-SDS into a series of 150 mL Erlenmeyer flasks with 40 mL of an avermectin methanol solution at different concentrations. The flasks were maintained at 25°C for 24 h. After centrifuging at 10,000 rpm for 10 min, the equilibrium concentration of avermectin in the supernatant was determined by HPLC. The amount of adsorbed Av at equilibrium, Q_e, was calculated by

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

where C_0 and C_e are the concentrations of avermectin at initial and equilibrium stages, respectively; V is the volume of the suspension; and m is the mass of MAC-SDS.

2.6. Investigation of Sustained Release Behaviors of Av-MAC-SDS. The release profiles of avermectin from Av-MAC-SDS samples were investigated as follows: 100 mg Av-MAC-SDS samples were suspended in 20 mL methanol. The suspension was transferred to a dialysis bag. After tightly sealing the dialysis bag it was put into 100 mL methanol as the release medium. The release rate of avermectin from the Av-MAC-SDS sample was calculated by measuring the concentrations of avermectin dissolved in the release medium at different times to evaluate the sustained release property. The concentrations of avermectin were measured using HPLC by collecting 1.0 mL of the release media outside of the dialysis bag at different intervals of 24, 48, 72, 100, 150, 210, and 260 h. Free avermectin was used as a control.

2.7. Photolysis Experiments of Avermectin in Av-MAC-SDS. The photolytic behavior of avermectin in Av-MAC-SDS was evaluated by the thin-film method described in reference [14], with free avermectin as a control. Ten mL of the methanol suspension of Av-MAC-SDS was placed in several uncovered glass Petri dishes and dried in air at room temperature to form thin films. The glass Petri dishes with thin films were then placed in a Xenon-arc photostability test chamber (XT5409-XPC80, Xutemp Temptech Co. Ltd., Hangzhou, China), at a constant temperature of 25°C. The Petri dishes were removed from the chamber after 24, 48, and 72 h. Av-MAC-SDS was then recovered by rinsing the thin films with 5 mL methanol, followed by ultrasonic treatment for 10 min. The suspension was centrifuged and the supernatant was collected and analyzed by HPLC to determine the remaining concentrations of avermectin. The degradation of free avermectin was performed under the same conditions.

3. Results and Discussion

3.1. Characterization of Modified MAC. Table 1 shows the BET surface area, total pore volume, and pore size of MAC before and after modification with the cationic surfactant TBAB and the anionic surfactant SDS. The modification did

Table 1: BET surface area, total pore volume, and pore size of MAC and surfactant-modified MAC.

Carrier	BET surface area m^2/g	Total pore volume m^3/g	Pore size nm
MAC	1232.89	1.08	6.22
MAC-SDS	707.39	0.63	6.19
MAC-TBAB	831.40	0.65	6.10

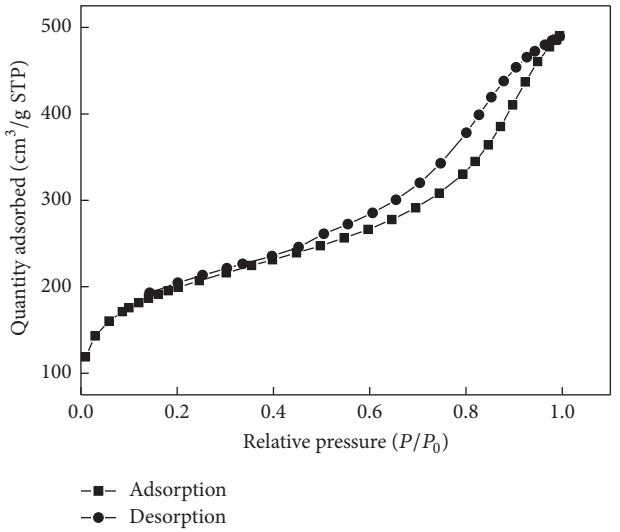

Figure 1: The nitrogen adsorption-desorption curves of MAC-SDS.

Table 2: Element contents of MAC and surfactant-modified MAC.

Carrier	C contents %	H contents %	N contents %
MAC	69.76	3.02	0.96
MAC-SDS	76.49	3.24	0.91
MAC-TBAB	78.07	3.33	1.14

not cause significant changes in average pore size. According to the classification of the International Union of Pure and Applied Chemistry (IUPAC), the pores of adsorbents are grouped into micropore ($d < 2$ nm), mesopore ($d = 2$–50 nm), and macropore ($d > 50$ nm) [15]. The average pore sizes of MAC before and after the modification were within the mesopore range of the IUPAC classification. The mesoporous structure of MAC-SDS can also be observed from the nitrogen adsorption and desorption isotherms [16] in Figure 1. Table 2 shows the C, H, and N contents of MAC before and after modification with surfactants. Compared with nonmodified MAC, the C content of modified MAC with surfactants dramatically increased, which indicated that the surfactants had been grafted onto the MAC.

3.2. Adsorption Capacity. The adsorption of MAC for avermectin in solution before and after modification was compared with other commonly used pesticide carriers (talc, bentonite, kaolin, and diatomite). Batch studies were carried out by adding 200 mg absorbents into a series of 150 mL Erlenmeyer flasks with 20 mL of 8 mg/mL avermectin methanol solution. As shown in Table 3 and Figure 2, because of the large special surface area and well-developed pore structure of MAC, the adsorption performance of MAC for avermectin was significantly better than talc, bentonite, kaolin, and diatomite. The adsorption capacity of MAC is mainly related to pore structures and surface chemical properties [17] and was improved after modification with surfactants. The nonpolar alkyl aliphatic chains of surfactants may enhance the adsorption of MAC for avermectin.

Table 3: The adsorption capacity for avermectin with different carriers.

Carriers	Amount of adsorbed avermectin mg/g
MAC-SDS	275.4
MAC-TBAB	204.4
MAC	156.7
Talc	36.6
Bentonite	35.4
Kaolin	30.7
Diatomite	4.7

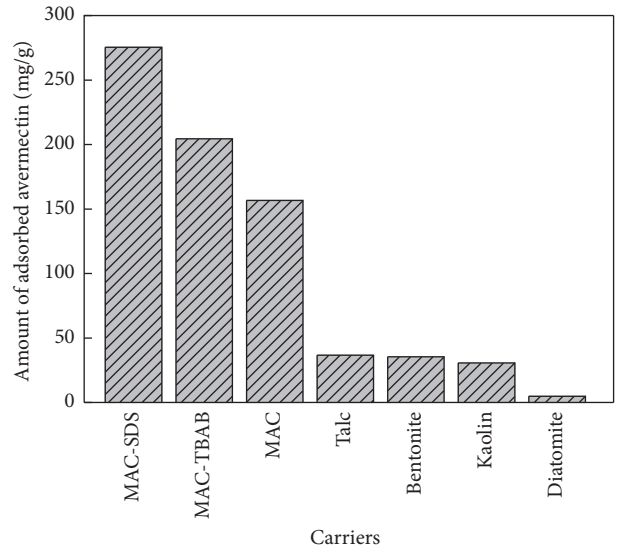

Figure 2: The adsorption capacity for avermectin with different carriers.

3.3. Adsorption Isotherms. The results obtained for the adsorption of avermectin were examined using Langmuir and Freundlich isotherm models [18–20]. The correlation coefficient (R^2) was used to evaluate the adequateness of the different models to fit the adsorption process.

The Langmuir isotherm model, which is based on the assumption that the maximum adsorption corresponds to

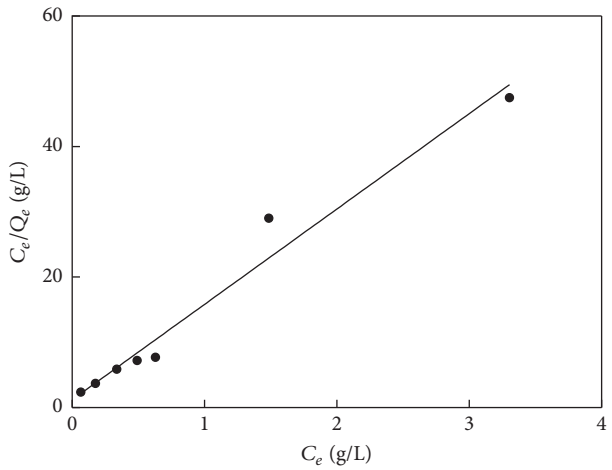

Figure 3: The Langmuir isotherm model of avermectin adsorbed by MAC-SDS.

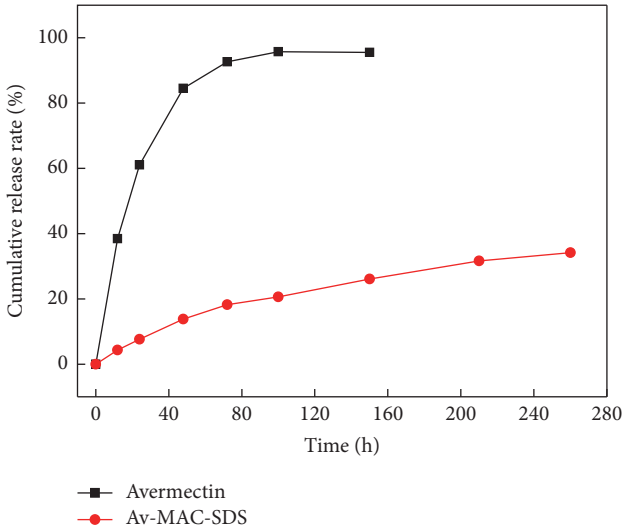

Figure 4: Release profile of avermectin loaded by Av-MAC-SDS.

a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between adsorbed molecules, is given by the following equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e, \tag{3}$$

where Q_e (mg/g) and C_e (mg/mL) represent the amount of adsorbed avermectin per unit mass of MAC-SDS and avermectin concentration at equilibrium, respectively; and Q_0 and b refer to the Langmuir constants for MAC-SDS, which are related to the maximum avermectin adsorption capacity to form a complete monolayer on the surface of MAC-SDS and an affinity parameter, respectively.

The Freundlich model is an empirical equation based on adsorption on a heterogeneous surface. It is assumed that the most active sites are bound first and then the binding strength decreases with an increase in the number of sites bound. The Freundlich isotherm is depicted in the following equation:

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

where K_F and n are the characteristic Freundlich constants that are related to adsorption capacity and intensity, respectively. These parameters can be obtained from the linear plot of $\ln Q_e$ versus $\ln C_e$, which has a slope of $1/n$ and an intercept of $\ln K_F$.

The correlation coefficient obtained from the Langmuir model was found to be $R^2 = 0.9657$ for the adsorption of avermectin on MAC-SDS (Figure 3). For the Freundlich model, the R^2 was 0.5042. These results indicate that the adsorption of avermectin on MAC-SDS can be represented by the Langmuir model.

3.4. Sustained Release Behaviors of Av-MAC-SDS. Figure 4 shows the release behaviors of free avermectin and avermectin from Av-MAC-SDS. Almost the entire amount of free avermectin had been released after 72 h. Compared with free avermectin, the initial burst release of Av-MAC-SDS was not obvious. As expected, Av-MAC-SDS exhibited slower release rates due to the rich pore structure, which slowed the release of avermectin. The release rate of Av-MAC-SDS was relatively fast at the initial stage and then gradually slowed down with increased time, as the avermectin adsorbed on the surface of Av-MAC-SDS was easier to release than the avermectin loaded within the carriers.

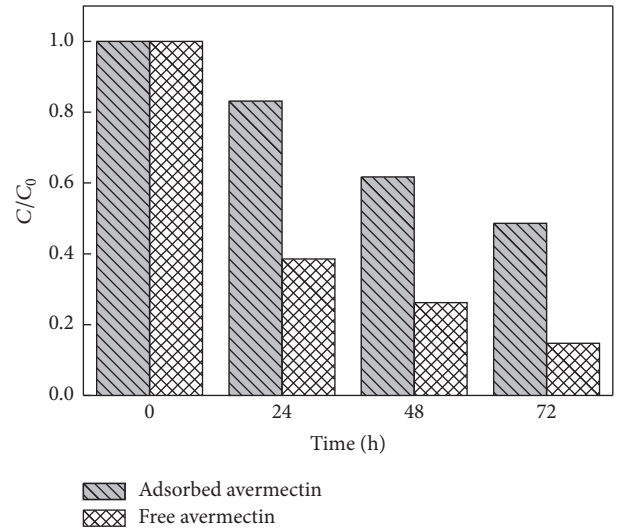

Figure 5: Change in normalized concentration of free and adsorbed avermectin by Av-MAC-SDS to UV irradiation time.

3.5. Effects of Av-MAC-SDS on Photodegradation of Avermectin. Figure 5 shows the changes of normalized concentrations of avermectin, which are the ratio of remaining concentrations to the initial concentrations of avermectin, under UV irradiation for 0, 24, 48, and 72 h for Av-MAC-SDS and free avermectin, respectively. The photolytic rates of avermectin were 16.9% and 61.4%, respectively, for Av-MAC-SDS

and free avermectin after 24 h, indicating that Av-MAC-SDS could protect avermectin from photodegradation. The photolytic rates reached 51.4% and 85.3%, for Av-MAC-SDS and free avermectin, respectively, after 72 h of UV irradiation. The results further confirmed the capability of Av-MAC-SDS for protecting avermectin from photodegradation.

4. Conclusion

In summary, surfactant-modified MAC was employed as the carriers for avermectin. The average pore sizes of modified MAC were still within the mesopore range. The surfactant-modified MAC, especially the SDS-modified MAC, showed an excellent adsorption for avermectin. The adsorption equilibrium of avermectin by SDS-modified MAC could be fitted by the Langmuir isotherm model. In addition, the MAC-SDS delivery system could significantly improve sustained release of avermectin and also effectively inhibits the photodegradation of avermectin, which is favorable to overcome the environmental sensitivity of biopesticides and improve efficacy in crops protection.

Abbreviations

Av-MAC-SDS:	Avermectin with sodium dodecyl sulfate modified mesoporous activated carbon
BET:	Brunauer-Emmett-Teller
BJH:	Barrett-Joyner-Halenda
HPLC:	High performance liquid chromatography
IUPAC:	International Union of Pure and Applied Chemistry
MAC:	Mesoporous activated carbon
MAC-SDS:	Sodium dodecyl sulfate modified mesoporous activated carbon
SDS:	Sodium dodecyl sulfate
TBAB:	Tetrabutylammonium bromide.

Conflicts of Interest

The authors declare no competing financial interest.

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