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THE SORPTION BEHAVIOR OF COMPLEX POLLUTION SYSTEM COMPOSED OF ALDICARB AND SURFACTANT—SDBS☆

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Abstract—The behavior of complex pollution system in soil composed of aldicarb, a carbamate pesticide, and sodium dodecylbenzenesulfonate (SDBS), an anionic surfactant, was studied by the experiment of shaking sorption balance. The range of concentration of aldicarb and SDBS was 0.4–5.0 and 1–1000 mg/kg of dried soil, respectively. Linear sorption isotherm was well fitted for these two chemicals. SDBS can decrease the sorption of aldicarb in soil remarkably. While the concentration of SDBS increased from 0 to 1000 mg/kg, the linear sorption coefficient can be decreased by 50%. But aldicarb showed no effect on the sorption of SDBS in experiment. In addition the mechanism of the effect of SDBS on sorption of aldicarb was discussed. © 2001 Elsevier Science Ltd. All rights reserved

Key words—aldicarb, sodium dodecylbenzenesulfonate, complex pollution system, sorption, soil

INTRODUCTION

After a pesticide is applied into soil, it has several behaviors as follows: sorption onto the soil particles, transfer in vertical and horizontal directions, degradation including chemical and biological transformations, uptake by plants, and volatilization into atmosphere, and so on. Among these cases, sorption/desorption is the dominant factor affecting the environmental chemical behavior of pesticide.

In general, pesticide is mainly combined onto clay mineral matter and soil organic matter (SOM) after entering into soil particles. Clay has high sorption capacity because of its complex porous surface. Soil organic matter is often regarded as a partition medium in studies of sorption of pollutants, but in the meanwhile much attention should be paid to the various functional groups and particular sites in humic substances which are the primary components of SOM. Pesticide molecules can be adsorbed onto these groups and sites by adsorption or specific interaction, which results in the occurrence of a strong non-partition effect. In fact, it is difficult to explain clearly the difference between sorption and partition. Usually partitioning into soil is thought as a major reason for sorption of chemicals. Sorption/desorption of pollutants has a strong effect on their fate and distribution. Therefore, sorption plays an important role in the establishment of actual environmental quality standard of soil and improvement of efficiency of remediation technologies. There is large body of literature concerned with thermodynamics and kinetics of sorption process (Graber and Borisover, 1998; Pignatello *et al.*, 1993; Weber and Miller, 1983, 1988; Voice and Weber, 1983).

As a systemic carbamate pesticide, aldicarb [2-methyl-2-(methylthio) propionaldehyde *O*-(methyl carbamoyl) oxime] has given excellent control of a wide range of phytophagous insects, nematodes and mites. Since 1962 this pesticide had been developed in Union Carbide Corporation, it has been registered for use on numerous crops in over 70 countries throughout the world at present. In China, it has been registered for use on peanuts, cotton and tobacco since 1986.

Surfactants, used in detergents for home laundry and institutional and industrial cleaning, have entered into the environment largely. Especially in rural area, incalculable amount of surfactants have been released into soil environment with the discharge of domestic sewage. Although surfactants are not very toxic to plants or animals, they can change the physical, chemical and biological properties of soil. In the meanwhile surfactants have complex effects on the behavior of other contaminants by solubilization and catalysis (Haigh, 1996).

A great variety of pollutants constitute a complex pollution system jointly in natural environment. For

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these pollutants in this complex system, there are mutual interactions among each other, which makes the behavior of each pollutant different from that of the one existing singly. Unfortunately this complex effect between various pollutants has not attracted enough attention of environmentalists. In this paper aldicarb, a carbamate pesticide, and sodium dodecylbenzenesulfonate, a typical anionic surfactant, were chosen to make up a complex pollution system. The sorption behavior of this complex system in soil was studied and the emphasis was on the influence of SDBS on the sorption of aldicarb.

MATERIALS AND METHODS

Apparatus and reagents

Apparatus. Gas chromatograph—M600D (made by Yong Lin Company, South Korea) with Hewlett-Packard flame photometric detector equipped with 394 nm sulfur interference filter and stainless-steel column (2 m long and 2 mm id) packed with 5% Carbowax 20 M on 100–120 mesh Chromosorb W-Hp. GC conditions: column temperature 150°C; detector temperature 220°C; detector gases—hydrogen 80 ml/min, air 100 ml/min; injection port temperature 240°C; flow of nitrogen carrier gas 20 ml/min, range 5.

Pesticides. Analytical-grade aldicarb was purchased from Tianjin Institute of Pesticide Industry. The purity of analytical-grade chemical is better that 99%.

Chemicals. Dichloromethane, trichloromethane, and ethanol were of analytical grade and redistilled to purify. Acetic acid (10%), sodium hydroxide (4%) and vitriol aqueous solution (3%) were prepared freshly. Sodium dodecylbenzenesulfonate was of chemical purity grade and needed purifying. Methylene blue solution and 1% phenolphthalein indicator were prepared as per the literature (National Environmental Protection Bureau of China, 1989).

Soils. Surface soils (0–30 cm) used in this study were collected from suburban farmland of Tianjin. The soil was loam sand. This site had no history of aldicarb application prior to the collection of soil samples. After being taken to laboratory, these soil were laid open and air-dried. Dry soils were then ground in a mill and sifted through a sieve of 20 mesh.

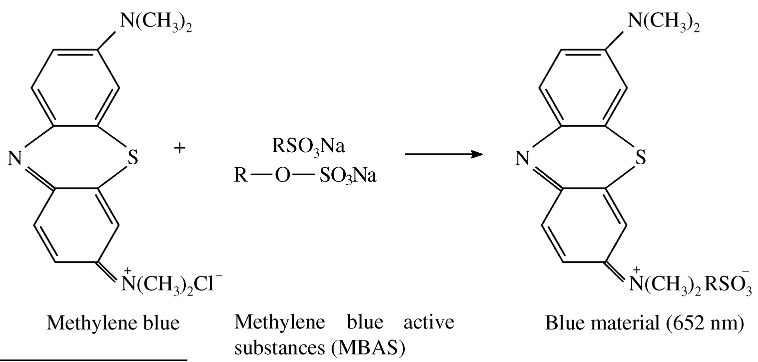
Selected properties of the soils used in this study are shown in Table 1. The organic matter content was determined by the method of potassium dichromate–sulfuric acid oxidation. Soil water content was determined gravimetrically by drying overnight at 110°C in a convection oven. The soil-water content referred to hydroscopic water, i.e. the rest of total water in soil subtracted by free water and chemical water. Soil pH was determined by placing a combination glass electrode in a mixture containing equal weights of soil and a 0.005 M calcium chloride solution.

The soil samples were sterilized by autoclaving to prevent the degradation of aldicarb by microorganism.

Procedures

Experiment of shaking sorption balance. The sorption isotherms of aldicarb and SDBS in soil were determined by the method of shaking balance. Forty-two aliquots of 5.0 g soil were weighed and divided into six groups, i.e. there are seven soil samples in each group. The right amount of standard solution of aldicarb was added to each group to give the concentration of aldicarb of 0.4, 0.8, 1.2, 1.6, 2.0, and 5.0 mg/kg dried soil, respectively. For seven soil samples in each group a right amount of SDBS standard solution was added to give the SDBS concentration of 0, 16, 50, 100, 200, 500 and 1000 mg/kg dried soil, respectively. Care should be taken so that the volume of aldicarb and SDBS standard solution added must be consistent with the soil: water proportion of 1 : 1, i.e. the total volume of standard solution added was 5 ml and distilled water was added when it is less than 5 ml. Then 10% acetic acid was added dropwise in each sample to make the mixture of soil and water weakly acidic. Later these samples were put into shaker to shake at 25°C. After 24 h these samples were taken out and centrifuged for 20 min at 5000 rpm (4500 g). Exactly, 2 ml of supernatant was transferred into a separatory, funnel and 5 ml of dichloromethane was added. The funnel was adequately shaken for 30 s, venting to release carbon dioxide pressure, and the lower solvent layer was flowed into 15 ml graduated test tube. The aqueous layer was additionally extracted once as above. The extracts were evaporated to 5 ml with a gentle stream of nitrogen for the GC–FPD analysis.

Determination of SDBS. Cationic dye methylene blue reacted with SDBS to give a product of blue ionic chemical. This blue chemical can be extracted with trichloromethane from aqueous phase and has a maximal absorbance at the wavelength of 652 nm (National Environmental Protection Bureau of China, 1989).



Two milliliters of supernatant mentioned previously was transferred into a separatory funnel and 10 ml distilled water was added. Two drops of 1% phenolphthalein solution were added as an indicator. Sodium hydroxide solution (4%) was added dropwise until the color of the solution just became violet. Vitriol aqueous solution (3%)

Table 1. Selected soil properties

Depth of sampling	pH	Organic matter content (%)	Organic carbon content (%)	Soil water content (%)
(0–30 cm)	7.93	4.20	2.47	3.66

was then dripped into funnel until the prunosus color disappeared exactly. Aqueous solution of 25 ml of methylene blue was added. After shaking adequately, 10 ml of trilchloromethane was added. The funnel was then shaken for 30 s, deflating off and on, and the lower solvent layer was flowed into 50 ml colorimetric tube. The aqueous layer was additionally extracted twice as above. After the third extraction, a right amount of trichloromethane was added into colorimetric tube to give a final volume of 50 ml. The absorbance of the sample was measured at 652 nm with a reference of trichloromethane. The concentration of SDBS in sample was calculated according to the standard curve.

RESULTS AND DISCUSSION

The influence of SDBS on sorption coefficient of aldicarb in soil/water system

There are three types of empirical equations describing the sorption behavior of organic pollutants in soil/water system: Freundlich, Langmuir, and linear sorption isotherm. Many studies have shown that linear and Freundlich isotherms were fitted for most pesticides (Liu and Ji, 1996).

Figure 1 is a plot of the solid versus solution-phase concentration of aldicarb after the sorption balance was reached. Each curve in Fig. 1 represents the sorption isothermal of aldicarb at certain concentration of SDBS, i.e. it was a plot of the solid versus solution-phase concentration of aldicarb at the same concentration of SDBS. From Fig. 1, the sorption data can be modeled with simple linear isotherm as follows

$$q = K_L C, \tag{1}$$

where q (mg/kg) is the solid-phase concentration and C (mg/l) is the solution-phase concentration, K_L (l/kg) is the linear isotherm sorption coefficient. The linear sorption coefficient, K_L, can be normalized to the soil organic carbon content, K_{OC}.

$$K_{OC} = K_L/\mathrm{OC}, \tag{2}$$

where OC is the organic carbon content in soil (see Table 1).

From Fig. 1, the values of K_L and K_{OC} of aldicarb in soil/water system at various concentrations of SDBS can be obtained. These values are listed in Table 2.

From Fig. 1 and Table 2, it was clear that the linear sorption coefficient of aldicarb in soil/water system decreased gradually with the increase of SDBS concentration. The linear isotherm sorption coefficient of aldicarb was 4.25 l/kg when no SDBS was added to soil/water system, but decreased to 3.94 l/kg when the concentration of SDBS was 16 mg/kg dried soil. When the concentration of SDBS reached to 1000 mg/kg dried soil, the sorption coefficient reduced to 2.32 l/kg, i.e., it decreased by 50% nearly. Corresponding with the reduction of sorption coefficient K_L the linear isotherm coefficient normalized per OC, K_{OC} also decreased from $10^{2.236}$ to $10^{1.973}$, which indicated that SDBS had a strong effect on sorption behavior of aldicarb in soil/water system.

In order to make the change of decreased sorption coefficient with increased SDBS concentration visualization, Fig. 2 was plotted by using the sorption coefficients, K_L and K_{OC}, as the y-axis and the

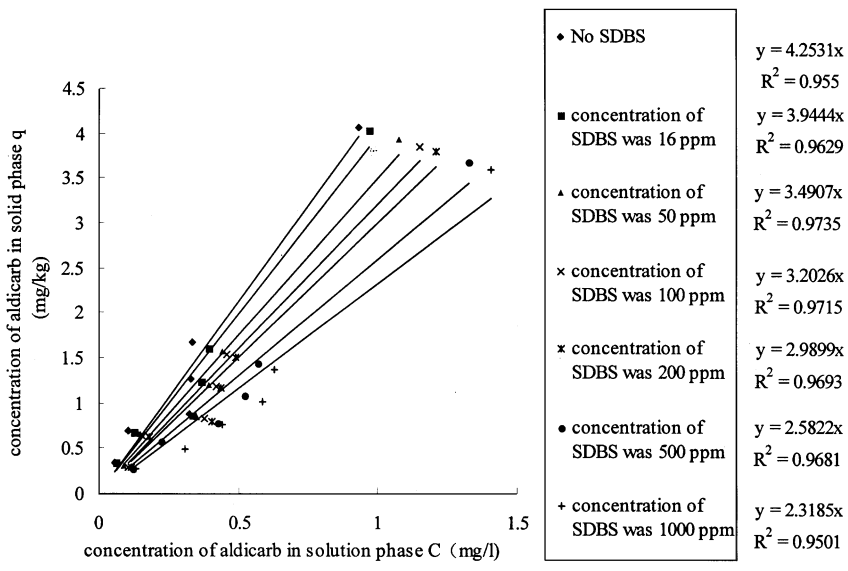


Fig. 1. The adsorption isotherm of aldicarb at various concentration of SDBS.

concentration of SDBS as x-axis. From Fig. 2, we can observe that the relationship between the concentration of SDBS and the sorption coefficient of aldicarb in soil is not linear. At initial stage (the concentration of SDBS was less than 200 mg/kg dried soil) the sorption coefficient of aldicarb decreased rapidly with the increase of SDBS concentration, but when the concentration of SDBS was less more than 200 mg/kg this reduction became slow and flat.

The influence of aldicarb on sorption of SDBS in soil

Being released into soil environment, surfactants also can enter into the interior of soil particles by sorption process. But there is a remarkable difference between various surfactants depending on the type of chemical. In general in most soils, anionic surfactants are poorly bound through adsorption process and a major amount remains in the liquid phase (Kuhnt, 1993). Dong (1999) determined that the sorption process of SDBS in soil/water system can be fitted by linear sorption isotherm ($q = 0.0136\ C + 0.304$, $R^2 = 0.9970$). In this experiment, the concentration of SDBS in solution phase was determined by colorimetry at aldicarb concentration of 1.2, 2.0, 5.0 mg/kg dried soil. Figure 3 was a plot of the solid versus solution-phase concentration of SDBS after sorption balance at the above aldicarb concentration. From Fig. 3, the sorption process of SDBS in soil can be simulated by linear isotherm similar to that of Dong's research. The effect of aldicarb on sorption behavior of SDBS was not observed in experiment. Probably the concentration of aldicarb varied so little that the influence of aldicarb on sorption of SDBS was not observed. Further studies should be done to lucubrate on this problem.

Table 2. The values of K_L and log (K_{OC}) of aldicarb in soil/water system at various concentration of SDBS

Concentration of SDBS (mg/kg)	0	16	50	100	200	500	1000
K_L (l/kg)	4.25	3.94	3.49	3.20	2.99	2.58	2.32
Log (K_{OC})	2.236	2.203	2.150	2.112	2.083	2.019	1.973

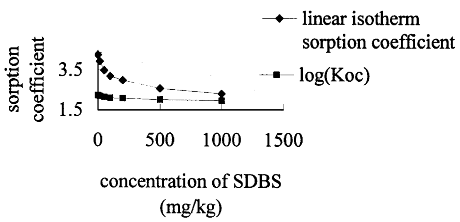


Fig. 2. Influence of SDBS on sorption coefficient of aldicarb.

Discussion on mechanism of effect of SDBS on sorption behavior of aldicarb

Usually even at very low concentration, surfactants can alter the physical, chemical and biological properties of soil remarkably. These properties include surface tension of soil water, water capacity, infiltration and percolation, permeability and capillary dispersion, soil structure such as porosity and aggregation, pH value, exchange capacity, redox potential, microorganisms and biological activity, and plant growth and cell activity, and so on. During this process, sorption behavior of surface active agents in soil played a dominant role (Kuhnt, 1993). Though sorption of anionic surfactants is much weaker than that of cationic and non-ionic surfactants is soil, a small amount of surfactants adsorbed into soil had a strong effect on soil properties. Law *et al.* (1966) discovered that even at low concentrations, surfactants could reduce the surface tension of soil water to a large extent, which would result in a higher wettability of soil particles. Therefore, the stability of soil aggregates was weakened and soil particles dispersed more rapidly and were translocated downward by percolating water. A higher wettability of soil particles would reduce the amount of other pollutants adsorbed by soil. On the other hand, the exchange of anionic surfactants with aquo-groups would decrease the positive charge of the soil colloid surface, which could increase the pH value of the soil solution and decrease sorption capacity of soil.

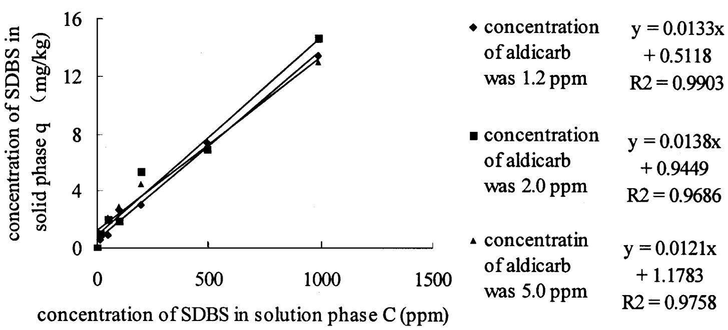


Fig. 3. The sorption isotherms of SDBS at various concentration of aldicarb.

Besides altering the soil properties as above, surfactants can also change physical and chemical properties of other pollutants directly and influence their environmental chemical behavior consequently. Due to its special surface properties surfactant could form micellar and microemulsion pseudophase which would increase the water solubility of some organic chemicals (Haigh, 1996; Edwards *et al.*, 1991). In our other experiment it has been testified that SDBS can increase the water solubility of aldicarb despite its strong hydrophilicity. At the concentration of 500 mg/l SDBS can increase the water solubility of aldicarb by one fold, i.e., it varied from 6000 to 12,000 mg/l. As a result, this solubilization of aldicarb in water must decrease the amount of aldicarb adsorbed onto soil.

In addition, competitive sorption may occur between surfactants and other chemicals. Many experiments had testified that sorption of a lot of organic chemicals in soil was competitive, especially when sorption occurred in soil organic matter (Jafvert and Heath, 1991; Scheunert and Korte, 1985; Xing *et al.*, 1996).

Summarizing briefly we could say that SDBS affected sorption behavior of aldicarb in three aspects as follows: (a) the sorption of SDBS increased wettability of soil particles and decreased the positive charge of the soil aggregates surface, which weakened the sorption action of aldicarb in soil; (b) SDBS-enhanced solubilization of aldicarb in water decreased the amount of aldicarb adsorbed into soil; and (c) competitive sorption occurred between SDBS and aldicarb. But this competition, may be, was very weak because aldicarb showed no effect on sorption of SDBS in this experiment.

Attention should be paid that soil can vary from region to region and with the season of the year. The soil used in this experiment was loam sand and collected in November. But another experiment showed that SDBS can decrease the sorption of aldicarb onto sandy soil collected from County Lulong, Hebei Province in May. The K_L values of aldicarb in soil containing 0, 500, 1000 mg/kg SDBS were 3.57, 2.31, 21.0 ml/g, respectively (Dai and Liu, 2000). Though sorption of aldicarb differed with the type of soil, the complex effect of SDBS on its sorption needs further research.

CONCLUSIONS

By altering physical, chemical and biological properties of soil, enhancing solubilization of aldicarb, and competing with aldicarb in sorption process, SDBS can reduce the amount of aldicarb adsorbed into soil evidently. In the range of concentrations of 0.4–5.0 and 0–1000 mg/kg of dried soil for aldicarb and SDBS, respectively, linear sorption isotherms were well fitted for these two chemicals. While the concentration of SDBS increased from 0 to 1000 mg/kg, the linear sorption coefficient of aldicarb can be decreased by 50%. But aldicarb showed no effect on the sorption of SDBS in experiment. The decreasing sorption of aldicarb would lead to enhancing movement either in horizontal direction or in vertical direction, which magnified the danger of aldicarb on environment. For this complex effect between various pollutants enough attention should be paid.

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