

Studied on the Sorption Behavior of Butachlor on Soil

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Abstract:In this paper, the Batch experiments methods were used to acquire the sorption isotherm, which were were conducted to quantify the contributions to adsorption and compare adsorption characteristics of butachlor with three kinds of soils. Through the experiments, the adsorption characteristic of butachlor in three types of soil contain different organic matter and the factors influencing butachlor adsorption by changing the factors such as quantity of soil, temperature and pH value of butachlor were studied. The result of the experiment indicates that the balance time of the adsorption of butachlor on three soils is about 12h. And the main one is celerity adsorption. The quantity of organic matter in soil is the most important factor influence the adsorption of butachlor, the quantity of organic matter in soil is positive correlation with the adsorption of pesticide on soil .The more soil it put the more quantity it adsorbed, the quantity of adsorption of pesticide on soil is decreased along with the temperature increased, but the infection is not evidence; Alkalescency is not good for adsorption.

Key words: butachlor organic matter of soil adsorption

1. Introduction

In the past few years, the ubiquitous presence of endocrine-disrupting chemicals (EDCs),and their respective metabolites in the urban aquatic environment has become a subject of growing concern. Example of EDCs include polychlorinated biphenyl's(PCBs), polychlorinated dibenao-p-dioxins and furans, polycyclic aromatic hydrocarbons (PAHs), and pesticides such as DDT, chlordane, and heptachlor. EDCs are introduced into the environment not only by direct release of effluents into waterways,but also by leaching from sludge and recycled water used in agriculture . Due to their widespread use and high consumption, pesticide and their degradation products have been detected at various concentrations in surface waters, sediments and sludge-amended soils [2,4].

As EDCs are known to accumulate in soils and sediments, character of sorption and desertion is crucial for understanding the eventual fate of these compounds. Although the impact of soil properties on the transformation and mobility of EDCs is poorly understood, we need to understand the distribution, behavior, fate and biological effects of these surfactants in the environment for assess their environmental risk[5,6,8,1,3].

Sorption is one of the major processes affecting the interactions among pesticides, soil water, and the immobile and mobile solid phases of soil(McCartly and Zacha-

ra,1989). The rates of pesticide degradation, volatilization, hydrolysis and photolysis are directly dependent upon the sorption process as it ultimately determines the pesticide concentration in the soil solution. Key factors governing pesticide sorption in soil include organic matter and clay contents, soil pH, soil water content and soil temperature but also the structure of the pesticide.

Herbicide, as a representative of EDCs ,was widespered use and high comsumption in agriculture. Butachlor is one of the most produce herbicide in China, out put is more than 1×104 , every year, and carry on increasing current.

2. materials and methods

2.1Soil sample

There are three soil samples ,they are No.1,No.2 and No.3 from nan tong. The sample has air-dry, and through 0.63mm bolt, standby. The content of organic matter in three soil are as follows: No.1:0.1671%,No.2:6.5200%, No.3:13.4310%.

2.2Sorption

Sorption experiments were conducted in triplicate and isotherms were measured using the standard batch equilibration method (OECD, 2000). Soil was sieved (<0.63 mm) and added to 30 ml centrifuge tubes. Twenty milliliter solutions of butachlor at different concentrations were prepared with the commercial product in 0.01 M CaCl2. The samples were agitated on a rotary shaker for 24 h at $20 \pm 1^{\circ}$ C in the dark to achieve equilibrium. Tubes were centrifuged for

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20 min and the supernatant liquid collected. Blanks without soil, prepared in the same way, showed no sorption of butachlor on the centrifuge tube wall.

3. Results and discussion

Sorption is one of the major processes affecting the interactions among pesticides, soil water, and the immobile and mobile solid phases of a soil (McCarthy and Zachara, 1989). The rates of pesticide degradation, volatilisation, hydrolysis and photolysis are directly dependent upon the sorption process as it ultimately determines the pesticide concentration in the soil solution. Key factors governing pesticide sorption in soil include organic matter and clay contents, soil pH, soil water content and soil temperature, but also the structure of the pesticide. Structural factors influencing the sorption process are the pesticide's molecular size, hydrophobicity, molecular charge, hydrogen bonding, arrangement and interactions of molecular fragments and its coordination (Dragun, 1998). The pesticide sorption process incorporates a wide range of different chemical mechanisms including ion exchange, cationbridging, ion-dipole interactions, ligand exchange, charge transfer, hydrogen bonding and van der Waals' forces (Bailey and White, 1970).

3.1 Sorption isotherms of butachlor

Sorption isotherms are important parameters in assessing the environmental fate of pesticides. The experiment determines the adsorption velocity curve of butachlor on different soils, the concentration of butachlor is 30mg/L at first ,pH is 7.0.Result is as fig3-1.(The data has been conversion to the quality of pesticide on unit mass of soil):





The picture shows that the curve of the adsorption on three soil is similate, the quantity is increased with the contact time prolong, they contact 60min when the quantity can arrive at 38.7%, 56.4% and 63.3% of the most quantity, and 240min can arrive at 83.8%, 82.1% and 90.8% of the most quantity. It indicates that the main adsorption of butachlor on three different soils is celerity adsorption, and slow adsorption is little. In this process, organic matter in soils have exerted mostly effect. The time of arriving at the most quantity is 24 hours. But after arriving at the most quantity, there is a release process, it results certain butachlor desorption, and dissolve in water, then adsorption quantity is decreased, so adsorption speed curve is not smooth enough.

A pilot kinetic study showed that sorption equilibrium was reached after 24h of shaking confirming the choice to use the methodology of Ahmad et al. (2001). Sorption isotherms were fit using the Freundlich equation and organic carbon sorption distribution coefficients (Koc) can be calculated (Bourg, 1989; Schiavon et al., 1990).In three soil, No.3 has the most organic matter, next is No.2 ,the last is No.1. The fig3-1shows that the adsorption quantity of buatchlor on No.3 is most ,next is No.2 ,and the last is No.1, this is the same as many results of research. This phenomenon testified that the quantity of organic matter in soil is positive correlation with the adsorption of pesticide on soil .

3.2. Influence of soil pH

The pH-changes can affect pesticide sorption processes due to impacts on the pH-dependent ion exchange capacities of the variable charge components such as organic matter and silicate clay minerals in soils.

Sorption of ionic solutes by variable charge components in soils is mainly due to active sites that terminate with non-bridging hydroxyls (M–OH) that are coordinated with Fe(III), Al, Mn(IV), Ti, or Si.

Non-bridging hydroxyls carry a partial negative charge and on protonation become surface water molecules (M– OH2) that carry a partial positive charge (Dragun, 1998; Lair and Sawhney, 2002).

pH not only influence the amount of electric charge of soil colloid ,but also influence the distributing form of con-



tamination; so it is an import factor of influencing the adsorption/ desorption of chemistry matter. Take different soil samples as objects, melody the pH in soil/ water environment to 2.0--10.0 separately, surge to balance and then sampling to mensurate the origination concentration of butachlor is 30mg/L.

Result is as fig3-4 (The data has been conversion to the quality of pesticide on unit mass of soil) :



Fig.3-2 Relationship between the adsorption of butachlor and the pH

From fig3-4, when the soil is in the range of acid ,the quantity of adsorption increase along with the increase of pH. The increase in soil pH may have a positive impact on the total number of available binding sites for butachlor. When the pH is about 6.0, the quantity is reaches maximum,because sorption of organic chemicals reaches maximum at pH-values around the pKa value of the compound (Barriuso et al., 1992).

With increasing soil pH higher than 7, butachlor ionise and become anions, thus repulsion to the mainly negatively charged soil surfaces increases and sorption decreases (Weber, 1993). That is ,when pH is in 7.0—10.0, when pH is increased, butachlor is released to solution by organic matter, so the quantity of butachlor on soil was decreased, besides, along with the increasing of pH, the solubility of butachlor is increased, it exists mainly as dissolve form. When its concentration increases to a certain value, the quantity of adsorption is increased along with the increasing of concentration. In another side, if the soil pH is higher than the pKa of butachlor , they exist as neutral species. In this case sorption is dominated by hydrogen bonding , van der Waals' forces and hydrophobic interactions, and organic carbon is the main sorbent.

3.3. Influence of dissolved organic matter

The addition of organic matter through effluent irrigation is a key factor for its effects on pesticide fate in soil (Fig.3-1). Addition of DOM affects pesticide sorption, degradation and transport. It can form complexes with pesticides and/or can compete with pesticides for sorption sites enhancing pesticide mobility. However, these two processes can be counteracted by co-adsorption of DOM– pesticide complexes onto the soil matrix and/or by DOM adsorption, which in turn leads to the formation of an additional domain for cumulative sorption. These two processes lead to reduced pesticide mobility. Various researchers have shown that different pesticides can form complexes with DOM .

Nature and source of DOM impact the degree of complex formation. DOM is composed of at least two fractions-a mobile hydrophilic and an immobile hydrophobic fraction. The mobile fraction showed the same transport behaviour (same retardation factor and dispersion length) as the non-reactive tracer, chloride. Also it has been shown that the effect of organic colloids on the complexation of pesticides depends on the molecular configuration and/or chemical fractions (soil organic humics/fulvics, aquatic organic humics/fulvics) of these colloids. Important DOM characteristics for its potential impact on pesticide sorption are its concentration, biodegradability and stability, size distribution, polarity and aromaticity and content of hydrophobic DOM fractions. Sorption of DOM in soils is not only dependent on the properties of the added DOM, but also on soil properties such as the amount and the nature of SOM, clays and Feoxides, pH and the ionic strength of the soil solution, and the concentration of metals. Mobile DOM serves as a sorbent for strongly hydrophobic non-ionic compounds, such as organochlorines, and compounds with high sorption coefficients.

3.4 The infection of temperature

The quantity of heat of the pesticide adsorption from solution to soil is more than it shrink in solution ,so the heat releases in the process of adsorb is used to repair the loss of entropy during the reaction, so it has prodigious connection with temperature[6,7]. The temperature infect the adsorption of pesticide by changing the water-solubility and surface adsorb alive of pesticide .Many research indicate that the adsorption of pesticide is a process of releasing heat. Commonly, the quantity of adsorption of pesticide on soil is decreased along with the temperature is increased. In order to review the infection of the temperature ,the experiment choose the sample A which has high content of organic matter ,determine the isotherm at 4°C, 15°C, 30°C, 45°C and 60°C separately. Result is as fig3-3 (The data has been conversion to the quality of pesticide on unit mass of soil):



Fig.3-3 Relationship between the adsorption of butachlor and the temperature

From fig 3-3, it can see that when the temperature is increased, the adsorption of quantity of butachlor on soil is increased and then decreased. When the temperature is exceed 30°C, because of its volatility, the higher the temperature is ,the more the pesticide is volatilization. So if the temperature is too high, the quantity of adsorption will decrease. But from the whole curve, the infection of temperature to adsorption is not evidence, the quantity of butachlor on soil is decreased with the temperature is increased; it indicates that the adsorption is a process of giving out heat.

4. Summary

(1)The adsorption velocity curve of butachlor on different soils was studied, the curve of the adsorption on three soil is similate, the main adsorption of butachlor on three different soils is speed-adsorption, and slow-speed adsorption is just little partion.

(2)The adsorption quantity is direct ratio with organic matter in soil, the more soils in it, the more organic matter in it, and the adsorption quantity is also increased, and the



effect of adsorption is better.

(3)Temperature has a certain infection to the adsorption of pesticide on solid, when the temperature is low, the quantity of adsorption is increased with the temperature is increased, but when the temperature is too high ,the pesticide volatilization easily, the higher the temperature, the more it volatilization, thereby it results that the effect of adsorption is low when the temperature is high. According to the fact complexion, the effect of adsorption is better when the temperature is lower.

(4)The action of soil and the pH of pesticide have a certain consanguineous connection, commonly, the ability of adsorption is stronger in acid solution, this due to the pesticide can form hydrogen bond with acid in acid solution and that will improve the ability of adsorption, but it will appear "mucus dissolve" and "desorption" phenomena in alkalescence solution, and dissolve the matter in soil to solution, thereby the organic matter in solution is increased.

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References (参考文献)

[1]Weiping Liu, Jin Ji. The main control factors of the end-result of pesticide in soil-water enviroment ——adsorption and desorption[J]. Environmental science of china, 1996, 16(1):25 - 30.

[2] Shicang Wu. Assemble of new pesticide[M]. Beijing: China agriculture science and technology publishing company, 1992: 206-207.

[3] Liqing Zheng, Na Fang, Qingxiang Zhou, etal. The adsorption of pesticide on soil and its infection factors. [S]0517 - 6611(2007) 21 - 06573 - 03

[4] Ateeq B, Farah M A, Ahmad W. Evidence of apoptotic effects of 2,4-D and butachlor on walking catfish, clarias batrachus, by transmission electron microscopy and DNA degradation studies [J]. Life Sciences, 2006,78(9):977-986.

[5] CAVANNA S ,GARATTI E,RASTELLI E,et al. Adsorption and desorption of bensulfuron2methyl on Italian paddy field soils[J]. Chemosphere ,1998 ,37(8) :1547 - 1555.

[6] PAUL CHENJ, SIMO O PEHKONEN, CHIA2CHIA CHIUN LAU. Phorate and terbufos adsorption onto four tropical soils[J]. Colloids and Surfaces A:Physic2 ochemical and Engineering Aspects ,2004 ,240(1/3) :55 - 61.

[7] PUSI P ,ARFAIOLIP C. Interactions of two acetanilide herbicides with clay surfaces modified with Fe (III) oxyhydroxides and hexadecytrimethyl ammonium [J]. Chemosphere , 1993 ,27(5) :765 - 771.

[8] SINTHALAPADI THULASIRAMARAJA MAHESWARI, ATMA-KURU RAMESH. Adsorption and degradation of sulfosulfuron in soils[J]. Environmental Monitoring and Assessment ,2007, 127(1/3):97 - 103.