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The synthesis of humic acids graft copolymer and its adsorption for organic pesticides

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ABSTRACT

humic acid graft copolymer (PSt-g-HA) was prepared by graft copolymerization of Humic acid (HA) with styrene and the sorption of three selected organic pesticides, parathion-methyl, carbaryl and carbofuran by PSt-g-HA acid and untreated humic were also examined, respectively. The PSt-g-HA had relatively high aromatic carbons content because the grafted copolymerization of polystyrene entered into condensed domains in HA, whereas the removal of the polar function groups, such as carboxyl and phenolic hydroxyl group, was performed. For above reasons, the sorption capacity of three organic pesticides (parathion-methyl, carbaryl and carbofuran) on PSt-g-HA increased by 64.1% to 95.2%.

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1. Introduction

Organic pesticides such as parathion-methyl, carbaryl and carbofuran are highly toxic organic pollutants, and are widely used in cotton, sugar cane, rice, citrus and other crops in China. Due to wide applications of these pesticides, they are often detected in fresh water exceeding permissible levels and impact on human health. In order to minimize the possible damages to human, various kinds of treatments technologies such as adsorption, chemical flocculation, chemical oxidation, ultra filtration and biological treatment technologies have been employed. Among these methods, adsorption is generally considered to be a simple, relatively low-cost and effective method in removing organic pesticides from water and wastewater. Meanwhile, it is an important task to research on selection in absorbent of these pesticides. Humic acid (HA) is a kind of natural mixture of organic macromolecule which contains both hydrophilic and hydrophobic molecules as well as phenolic, carboxyl and hydroxyl groups connected to the skeleton of aliphatic or aromatic units and has loose sponge texture, large surface area and surface energy [1], thereby, HA has highly potential for treatment of heavy metals or organic contaminant from wastewater with adsorption method. Recently, more attention has been paid to interaction between HAs and organic contaminant. The studies suggested that the adsorption activity of organic contaminant were significantly affected by the chemical structure of HA [2]. Thus, there is a need to identify the overall chemical structure of HA in adsorption processes so that a significant theoretical basis could be provided to treatment techniques of organic contaminant from wastewater with HA adsorption.

Many studies reported that the adsorption process of hydrophobic organic chemicals (HOCs) could be related to different content and chemical structure of HA. For instance, Gauthier et al. [3] reported that the binding of pyrene to humic and fulvic acids was modified to a significant extent by the degree of aromaticity in the humic material. Xing et al. [4] observed that isotherm nonlinearity increased with the increase of aromatic carbon in adsorption of two HOCs, naphthalene and phenanthrene, by six pedogenetically related HAs. Besides, another group of authors investigated that aromatic carbon content influenced the adsorption of contaminant in HA [5–8]. Aromatic components also were recognized as condensed domain in soil organic matter (SOM) dominating the adsorption of HOCs in soils and sediments [9,10].

However, several contradictory arguments about the positive correlation between K_f (or K_{oc}) and aliphatic content were reported. Some investigations revealed that the aliphatic carbon was the most important factor which could lead to changes in adsorption coefficient, instead of the aromatic carbon [12,13]. With pyrene adsorption to natural organic matter varying in chemical composition (e.g., high aliphaticity or aromaticity),

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Chefetz observed a positive trend between the K_{oc} and the aliphaticity of sorbent [11].

Since structure and contents of chemical groups in humic materials, especially those of polar functional group, were recognized as the most important factors that affected the isotherm nonlinearity and adsorption capacity, further process has been conducted by various methods of sorbent modification to determine the change of structure in HA and its consequent results on adsorbing soil contaminant. Sachs et al. identified the changes in organic matter chemistry due to structural modification by combining the Nuclear Magnetic Resonance (NMR) spectra [12]. Witte et al. studied binding behavior of the metabolites 2-aminobenzothiazole (ABT) and 2-(methylamino) benzothiazole (MABT) toward to humic acids in oxidative atmosphere and argon atmosphere [1].

However, modifying chemical structure of the humic acid with polystyrene has not been investigated before. To the best of our knowledge, this will be the first study that identifies the chemical and structural heterogeneity of polystyrened-HA and unmodified HA by element analysis, potentiometric titration, Fourier-Transform Infrared (FT-IR) spectroscopy, and cross polarization magic angle spinning carbon-13 nuclear magnetic resonance (CPMAS ^{13}C NMR) spectroscopy. In addition, no previous reports have examined the adsorption behavior of three selected organic pesticides, parathion-methyl, carbaryl, and carbofuran, using structurally modified HA. The results will help us determine the chemical groups of the adsorption domains and their contributions to adsorption of organic pesticides.

2. Materials and methods

2.1. Structural modification

The humic acid used in the study was purchased from JingKe Precise Chemical Academy in Tianjin, China. Structural modification was performed by mixing 5 g of HA with 200 ml of dimethyl sulfoxide (DMOS) in a 500 ml beaker and the mixture was washed with 50 ml of dimethyl sulfoxide three times. The solution was heated in a temperature controlled water bath shaker at temperatures varying between 70 and 80 °C. 20 min later, 30 ml of fluid polystyrene, 5 mmol $FeCl_2$ and 15 mmol H_2O_2 (30%) were added to the suspension by shaken 30 min. After cooling to room temperature, this solution was precipitated with methanol and concentrated hydrochloric acid, and then centrifugated at 4000 *g* for 20 min. After removal supernatant fluid of the mixture, the precipitate was washed with dilute hydrochloric acid and deionized distilled water to neutral, freeze-dried, ground, and stored for their characterization and adsorption work.

2.2. Chemical characterization of HAs

The C, H, and N contents of HAs were determined on an Elemental Analyzer (Elementar Vario EL, Germany). The content of Oxygen was calculated according to the mass difference and the atomic ratios of H to C, O to C were calculated consequently.

2.3. Potentimetric titration of HAs

0.20 g of each of HA sample was added to 75 ml of 0.10 M NaCl solution in auto-controlled temperature cabinet at a temperature of 25 ± 0.2 °C. After reaching equilibrium by bubbling N_2 for 20 min, the solution was titrated with 0.05 mol/L HCl until the pH was 2.5, and then was titrated with 0.10 M NaOH solution until the pH increased to 9.0. Details were reported in elsewhere [14]. The carboxyl and phenolic hydroxyl group were neutralized by alkaline solution.

2.4. Spectroscopic characterization of HAs

Fourier-Transform Infrared (FT-IR) spectra were recorded on an FT-IR spectrophotometer (NEXUS 670X, Perkin Elmer). Samples were prepared in the form of KBr pellets by mixing 1 mg of HA and 400 mg of KBr at 10,000 kg/cm^2 pressure for 30 min. Details of this procedure were described elsewhere [15].

Two HAs samples were subjected to ^{13}C NMR analysis to acquire their chemical group distribution. Spectra were run on a Bruker DSX-300 operating at a 75 MHz for ^{13}C and 300 MHz for ^{1}H observation frequency, MAS spinning rate of 5 KHz, contact time of 1 ms, 4 s recycle delay, approximately 10,000 scans per sample, using a ramp cross-polarization pulse program with magic angle spinning. Structural carbons determined were alky carbon (0–50 ppm), oxygen-alky carbon (50–108 ppm), aromatic carbon (108–168 ppm), carboxyl carbon (168–192 ppm), and carbonyl carbon (192–220 ppm).

2.5. Adsorption experiments

Parathion-methyl, carbaryl and carbofuran (>99.5% purity), were purchased from Drug Control Institution of the Ministry of Agriculture of China and used without further purification, and their solubility in water at 20 °C were 55 mg/L, 120 mg/L and 250 mg/L, respectively. These pesticides were chosen because they are common organic pollutants in soil and sediment and have often been used in environmental research. All adsorption isotherms were obtained by adding 0.1 g of each HA sample in three flasks, respectively, at room temperature based on a batch of equilibration technique [12]. Preliminary experiments with UV-visible spectroscopy showed little difference (if any) between 0.01 M $CaCl_2$-$NaNO_3$ solution and the same solution mixed with HAs after 7-d equilibration and centrifugation, due to the effective flocculation by the $CaCl_2$ and low pH [16]. 20 ml of varying concentration of these three pesticides and 5 ml of 0.025 mol/L $CaCl_2$ solution were added into the 50 ml flasks which contained 0.1 g of HA sample, respectively. Isotherms consisted of ten varying concentration points; each point, including the blank, was run in duplicate. After 24 h of vibration and equilibrium, partial of each solution was distracted to a 10 ml centrifugal tube and centrifuged at 3000 r/min for 20 min, and then the pesticides tested in supernatant solutions were separated and purified by using solid phase extraction (SPE) technique and analyzed by gas chromatography [17,18]. Because of little adsorption by flasks and no biodegradation, adsorbed pesticides by the sorbents were calculated by mass difference. The other experimental details were reported elsewhere [19].

All adsorption data were fitted to the logarithmic form of the Freundlich equation:

$$\log S = \log K_f + N \log C_e$$

where S is the solid-phase concentration (μg/g) and C_e is the liquid-phase equilibrium concentration (μg/ml), K_f for adsorption capacity coefficient [(μg/g)(μg/ml)$^{-N}$] and N are constants with $N < 1$. The parameters, K_f and N (dimensionless) indicating isotherm nonlinearity were determined by linear regression of log-transformed data. Linear fitting of log-transformed data was justified over direct nonlinear curve fitting in this paper for two reasons: (i) concentrations spread evenly over the log scale, thus, nonlinear curve fitting would underestimate the importance of the low concentration data, and (ii) the relative uncertainty in the measurement was not greatly dependent on concentration [9].

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