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A biomimetic absorbent for removal of trace level persistent organic pollutants from water

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Triolein-embedded absorbent was developed and it could remove lipophilic pollutants from water effectively.

Abstract

A novel biomimetic absorbent containing the lipid triolein was developed for removing persistent organic pollutants (POPs) from water. The structural characteristics of the absorbent were obtained by SEM and a photoluminescence method. Under optimum preparation conditions, triolein was perfectly embedded in the cellulose acetate (CA) spheres, the absorbent was stable and no triolein leaked into the water. Dieldrin, endrin, aldrin and heptachlor epoxide were effectively removed by the CA–triolein absorbent in laboratory batch experiments. This suggests that CA–triolein absorbent may serve as a good absorbent for those selected POPs. Triolein in the absorbent significantly increased the absorption capacity, and lower residual concentrations of POPs were achieved when compared to the use of cellulose acetate absorbent. The absorption rate for lipophilic pollutants was very fast and exhibited some relationship with the octanol–water partition coefficient of the analyte. The absorption mechanism is discussed in detail.

Keywords: Biomimetic absorbent; Triolein; Organic pollutants; Water treatment

1. Introduction

The problem of persistent organic pollutants (POPs) is an urgent global issue requiring immediate attention. These compounds share unique physicochemical characteristics that make them highly mobile and capable of long-range atmospheric transport (Xu et al., 2004). Due to their persistent and lipophilic nature, POPs tend to bioaccumulate in aquatic organisms such as fish and whales and ultimately in humans (Petty et al., 1995). Methods to remove residual POPs that have been released into the environment have attracted increasing attention in recent years (Jones and Voogt, 1999). Most POPs are lipophilic chemicals and this explains their low concentrations in water, usually varying between nanogram and picogram quantities per liter (Peter and Della, 2003; Zhang et al., 2003). Therefore, POPs are especially difficult to remove from water.

The photocatalytic oxidation of POPs on semiconductor surfaces of compounds such as TiO_2 and WO_3 has recently attracted widespread interest (Balasubramanian et al., 2004) and ozonation has been proposed as a potential alternative. These latest methods were shown to be effective in eliminating POPs from water. However, the cost of photocatalytic oxidation and ozonation for such purposes, especially for removing trace levels of POPs from water, needs to be further ascertained to ensure their competitiveness. Adsorption by activated carbon is widely used in removing organic pollutants from water as shown in many relevant studies (Urano et al., 1999; Miyake et al., 2003; Bembnowska et al., 2003). However, due to the non-selectivity of activated carbon to all organic pollutants and its tendency to desorption after saturation, it is difficult to remove trace or ultratrace POPs near the

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environmental levels by adsorption on active carbon. Some studies have shown that activated carbon is not useful for organic halogens with a concentration below 5 μg L^{-1} (Wang and Liu, 2001). This has stimulated interest in the development of new adsorbents to remove low concentrations of organic contaminants from water.

Even at trace concentrations in water, POPs can accumulate in organisms. Many studies have been carried out on bioaccumulation in diverse organisms such as white whales (Andersen et al., 2001), arctic wolves (Mary and Birgit, 1999), South African fur seals (Walter et al., 1999), marketable fish (Ahmed and Aly, 2004) and mussels (Azza et al., 2004; Perihan and Hulya, 2004). Semipermeable membrane devices (SPMD), which are also based on the diffusion of hydrophobic substances from water to membrane bags filled with lipophilic phases, are widely used for monitoring organic contaminants in water (Huckins et al., 1990; Frank, 2005; Lu and Wang, 2003; Lu et al., 2002).

Using the concept of bioaccumulation, a novel composite absorbent containing the lipid triolein is proposed to remove trace POPs from water. The absorbent was prepared by embedding triolein into cellulose acetate (CA) spheres. Triolein has a high accumulation capacity (10^5–10^7) for trace concentrations of POPs in water (Chiou, 1985) and it exhibits low membrane solubility and permeability because of its large molecular mass of 885.45 Da (Huckins et al., 1990). A cellulose acetate (CA) polymer was chosen for preparing hybrid materials because it can be easily molded into different forms such as membranes, fibers and spheres. Furthermore, its hydrophilicity improves the accessibility of aqueous solutions to the surface of the film. The biomimetic absorbent was prepared with these pollution-free and environmentally friendly raw materials and the spherical absorbent was easy to use in water treatment processes.

This paper addresses the optimum preparation method, the characteristics of the absorbent and the efficient removal of some representative POPs from water. The absorption mechanism is also discussed.

2. Experimental section

2.1. Materials

Cellulose acetate was purchased from the Chemical Reagent Corporation (Shanghai, China), Triolein (98% purity) was purchased from the Jinlong Chemical Reagent Corporation (Beijing, China), and Tween 80 (A.R.), acetone (A.R.), $Mg(ClO_4)_2$ (A.R.) and liquid olefin were purchased from the Chemical Reagent Corporation (Beijing, China).

The reagents n-hexane, dichloromethane and methanol, purchased from Fisher Scientific Company (USA), were all pesticide grade. The target analytes dieldrin, aldrin, endrin and heptachlor epoxide (99.0% purity) were purchased from the Environmental Protection Center of the Chinese Department of Agriculture. An SPE-filtration device with a vacuum pump and ten connectors, SPE units, and 500-mg C18 cartridges were supplied by Agilent Corporation (USA).

2.2. Preparation of absorbent

The preparation method is presented in a patent (Liu et al., 2004) and briefly described here. A solution of CA in acetone was prepared and varying amounts of triolein, water, $Mg(ClO_4)_2$ and Tween 80 were then added to the solution. The mixtures were kept at 35 °C for 2 days and stirred in order to admix uniformly. Thus, viscous syrups with different triolein loadings were carefully prepared and homogeneous phases were obtained. Each viscous syrup was added drop by drop to a glass tube containing the liquid olefin (about 2/3 of the volume). The temperature ranges of the CA solution and liquid olefin were kept at 30–35 °C and 15–20 °C respectively. During the process of the viscous syrup dripping through the air to the column of liquid olefin and through the action of surface tension, a white, spherical absorbent was formed which collected at the bottom of the glass tube. Finally, composite absorbents were washed with distilled water to remove all soluble impurities. The TOC of the leachate was determined using a Phoenix 8000 Total Organic Carbon Analyzer (Tekmar-Dohrmann Co., USA). After changing the water up to 10 times over a 3-day period, the TOC level of the leachate was near that of distilled water.

The water, dissolved in the casting solution, was used as a pore forming agent. As mentioned previously by Meier et al. (2004), water acts as a non-solvent but it can form porous membranes. An additional advantage of adding water is to enhance the density of the casting solution so that it can drop into liquid olefin and form spheres. In the present study the influence of water on the absorbent was followed in detail. Optimum results were obtained with 12–14% (w/w) water in the casting solution. Under these conditions the spheres of absorbent are readily formed in liquid olefin. The amount of triolein was another important factor affecting the formation of spheres in liquid olefin because the triolein had an oily consistency. A 2–5% (w/w) triolein concentration in the casting solution was found to be an appropriate range. Under these conditions a smooth surface absorbent was easily prepared.

Cellulose acetate spheres were also prepared using the above method but without adding triolein. All of the absorbents were stored in distilled water before use.

2.3. Analytical methods

Scanning electron micrographs (SEM) of the surface and the cross sections of freeze-dried absorbents were obtained using a Hitachi S-3000N scanning electron microscope. Samples were prepared, frozen in liquid nitrogen and then coated with gold. The triolein concentration in the water that leaked out from the CA–triolein absorbent was analyzed using a Hitachi F-3000 fluorescence spectrometer.

A gas chromatograph (HP-6890N) equipped with a ^{63}Ni electron capture detector (GC-ECD) and a HP-5 fused silica capillary column (30 m × 0.32 mm × 0.25 μm) was used to determine the residual concentration of the studied POPs. The temperature of the injector and the detector was kept at 250 °C and 300 °C, respectively. Column temperature was programmed at 85 °C, increasing at 10 °C min^{-1} to 180 °C, and then increasing at 20 °C min^{-1} to 280 °C, and held for 20 min at 280 °C. Nitrogen of extra purity (>99.999%) was used as the carrier gas. The flow rate was 2.5 mL min^{-1} and the pressure was kept at 20 psi. Data were collected and analyzed with Agilent Chem-Station.

2.4. Absorption experiment

The four organics selected to test the effectiveness of the novel absorbent were dieldrin, aldrin, endrin and heptachlor epoxide. Absorption experiments were carried out in triplicate with two types of absorbents (CA absorbent and CA–triolein absorbent) in batch mode. A fresh solution was prepared with distilled water free of the detectable analytes listed above throughout the course of the absorption experiment. Distilled water (100 mL) in conical flasks was spiked with an organic standard and agitated for 8 h using a horizontal shaker operated 170 rpm at 25 °C to dissolve the organics in water homogeneously. One gram of absorbent was employed in contact with a solution of 100 mL. The absorption experiments were carried out in conical flasks with agitation provided by a shaker at 170 rpm. The temperature was controlled at 25 °C by an air bath. The initial concentration of selected organics was 10 μg L^{-1}. Samples were withdrawn at regular intervals for analysis. Finally, the water samples were concentrated by SPE (C-18) and analyzed by gas chromatography for residual organics in the samples.