ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Separation and Purification Technology 44 (2005) 37–43

Separation and Purification Technology

www.elsevier.com/locate/seppur

Preparation and characteristic of triolein-embedded composite sorbents for water purification

Jinxian Huo, Huijuan Liu, Jiuhui Qu*, Zijian Wang, Jiantuan Ge, Haining Liu

State Key Laboratory for Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences Beijing 100085, PR China

Received 5 September 2004; received in revised form 2 December 2004; accepted 7 December 2004

Abstract

The novel triolein-embedded composite sorbents for removing persistent organic pollutants (POPs) in water were developed. Comprehensive structural characteristics of the composite sorbents were characterized using scanning electron microscope (SEM), fourier transform infrared spectrum (FT-IR) and X-ray photoelectron spectrum (XPS). It is suggested that triolein/cellulose acetate (CA) viscous syrup can be deposited on the surface of silica gel granules, because the silica gel granules have the large enough aperture to make the polymer penetrate into. Triolein is also embedded into a hybrid membrane perfectly. Dieldrin is regarded as a representative compound of POPs. Sorption experiments in solutions with constant concentrations show that adsorption capacity increased with increased triolein content in composite adorbents. Dieldrin removal could reach 80% at 50 ng/l initial concentration, which is near the environmental level.

Keywords: Triolein; Cellulose acetate (CA); Composite sorbent; Persistent organic pollutants (POPs); Dieldrin

1. Introduction

Persistent organic pollutants (POPs) as a set of organic compounds possess toxic characteristics. They are also persistent, liable to bioaccumulation and prone to long-range atmospheric transport. Moreover, they can result in adverse environmental and human health effects in locations near and far from their sources [1]. POPs released to the environment can travel through air and water to regions far from their original sources. In these distant regions, POPs can concentrate in living organisms, including humans, to levels that have the potential to injure the human health and/or the environment. The most common contaminated media of POPs include sediment, air and water [2]. Due to their lower concentration in water, from nanogram per litre to picogram per litre [3,4], POPs are especially difficult to be removed from water.

The most prevalent techniques in water treatment, such as photocatalysis [5], ozone-oxidation [6], biological degradation [7] do a poor job in removing POPs from aqueous solutions because POPs resist photocatalysed, chemical and biological degradation. Sorption is a dominant and effective technique in removing organic pollutants from aqueous solutions, but its continued viability is greatly dependent on the development of novel sorptive materials [8]. Currently, active carbon adsorption is extensively used to remove organic pollutants from water [9]. Due to nonselectivity of active carbon to all organic pollutants and its tendency to desorption after saturation, however, it is difficult to remove trace or ultratrace POPs near the environmental level by sorption of active carbon. Activated carbon cannot adsorb organic halogen whose concentration is below 5 μg/l [10].

Current research is limited to analysis and identification, ecological effect, environmental monitoring, impact on human health and reproduction [11–16]. There are very little researches on the removal of trace POPs from water, especially on the developing of purificatory materials for POPs in water. Recent developed composite adsorbents have nothing to do with POPs, such as cationic MCM-41 for aromatic compounds [17], macroporous silica-based polymeric ma-

---

* Corresponding author. Tel.: +86 10 62849151; fax: +86 10 62923558.
E-mail address: jhqu@mail.rcees.ac.cn (J. Qu).

1383-5866/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.seppur.2004.12.001

terial for strontium [18], polyacrylic acid-bound iron oxide magnetic nanoparticles for methylene blue [19]. Therefore, the development of novel materials is urgent in order to improve water quality.

The object of this study is aimed at developing a novel composite sorbent for the removal of trace POPs in water. Triolein has a high accumulating capacity (10^5–10^7) for trace POPs in water [20,21]. Cellulose acetate (CA) is a particularly useful polymer for preparing hybrid materials because it can be easily molded into different forms, such as membranes, fibers and spheres [22]. Furthermore, its hydrophilicity improves accessibility of aqueous solutions to the surface of the film. Mesoporous silica gel granules were selected as a supporter because mesoporous materials possess pores large enough to readily allow the penetration of polymer chains [23]. Furthermore, silica gel is prone to be chemically and physically modified. The novel composite sorbents were prepared with these pollution-free and environmental-friendly raw materials.

In this study, dieldrin was taken as a representative POPs because of its common characteristics of POPs, such as low solubility in water, nonpolarity and lipophilia. Sorption experiments were carried out in order to test adsorption capacity of three composite adsorbents. Sorption experiments at nanogram level were set to test the removal capacity for dieldrin dissolved in water at concentrations similar to those found in actual water bodies.

2. Experimental section

2.1. Materials

The FNG-II type water-tolerant silica gel with 2–4 mm diameter was obtained from Special Silica Gel Factory (Qingdao, China). Cellulose acetate (2.5 degree of acetylation) was purchased from Chemical Reagent Corporation (Shanghai, China). Triolein (purity, 99%) was purchased from Sigma (St. Louis, MO, USA). Materials for the preparation of the composite sorbents also included 1,4-dioxane (A.R.) and acetone (A.R.). Dieldrin (purity, 98.6%) was purchased from Accustandard Inc. (125 Market Street, New Haven, CT 06513).

2.2. Instrumentations

Scanning electron microscope (SEM) images were acquired using a HITACHI S-450 scanning electron microscope. The cross-section of the sample was prepared by freezing–fracturing in liquid nitrogen. A GIKOIB-3 sputter coater with a gold–palladium target was used for coating gold on the surface of samples.

The IR spectrum was obtained using a Spectrum GX FT-IR system from Perkin-Elmer. The attenuated total reflectance technique was used in the sample analysis. The wave number was between 4000 cm^{-1} and 650 cm^{-1} and scanning times were 16.

Specific surface area, pore volume and pore diameter were obtained by an ASAP 2000 surface analyzer (Micromeritics Co., USA) and liquid N_2 was used as sorbate.

The X-ray photoelectron spectra (XPS) were recorded by the Japan Rigaku Dmax/gA diffractometer using an X-ray source (Al Kα, 1486.6 eV) with a 45.0 source analyzer angle. Samples for XPS analysis were prepared by freezing–desiccation for 3 days.

HITACHI F-3000 (Japan) was used to measure the triolein content in water that leaked out from composite adsorbents.

2.3. Preparation of the composite sorbents

The composite sorbents were prepared according to the following steps:

(1) First, the oxygen within acetone was removed by using nitrogen. Next 17 g of CA, different triolein contents (triolein versus CA) and other additives, such as 1,4-dioxane, were added together in 80 ml of acetone. The mixture was kept at 35 °C for 2 days and stirred in order to admix uniformly. Finally, viscous syrups were sonicated for 30 min in order to enhance triolein dispersion [24]. Thus, viscous syrups with different triolein loadings were well prepared and homogeneous phases were obtained. Miscibility and solid-state structure for blends of triolein and CA were observed through SEM images (Figs. 1 and 2). Hybrid plat membranes were prepared as analytic samples. ATR-FTIR spectra (Fig. 3) were also obtained to identify the miscibility of triolein and CA.

(2) Silica gel granules were modified in order to enhance cementation between silica gel granules and the hybrid membranes. In a conical flask, 2 g CA was dissolved into 100 ml acetone. Silica gel was added to the CA/acetone solution. After excessive solution was spilled out, acetone in the silica gel evaporated, and the modified silica gel desiccated in a freezing and vacuum manner for 3 days. In order to find out the optimum modified conditions, different dipping time and sonication time were considered. Subsequently, aperture analysis by BET and element analysis by X-ray photoelectron spectrum (XPS) were carried out. XPS results are shown in Table 1.

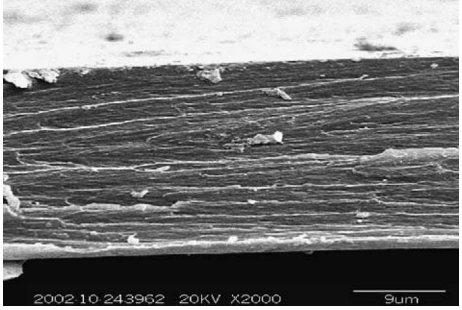

Fig. 1. SEM image of a pure CA membrane cross-section.