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Bromopropyl functionalized silica nanofibers for effective removal of trace level dieldrin from water

Xiuli Yue[a,b,*], Shanshan Feng[b], Shouzhu Li[b], Yuanmiao Jing[b], Changlu Shao[c]

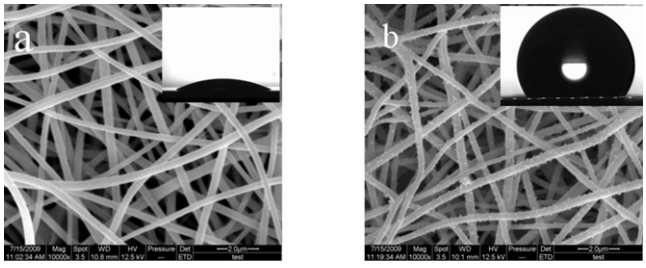
[a] College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China
[b] State Key Laboratory of Urban Water Resources and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150001, China
[c] Center for Advanced Optoelectronic Functional Materials Research, Northeast Normal University, Changchun 130024, China

HIGHLIGHTS

- Bromopropyl modified silica nanofibers were fabricated by calcination of electrospun PVA/TEOS fibers and subsequent surface modification with 3-bromopropyltrichlorosilane.
- The prepared bromopropyl-silica nanofibers possessed specific surface area and pores beneficial for removal of hydrophobic POPs.
- A maximum removal rate was evaluated to be 91.02% for such nanofibers, much higher than the commercially available granular activated carbon (38.65%).

GRAPHICAL ABSTRACT

Novel bromopropyl functionalized silica nanofiber films were fabricated by electrospinning the mixture of tetraethylorthosilicate (TEOS) and polyvinyl alcohol (PVA), followed by calcination and subsequent surface modification with 3-bromopropyl trichlorosilane (BPTCS). A polychlorinated chemical of dieldrin detected from the surface water frequently was selected as a model pollutant to test the removal efficiency of persistent organic pollutants (POPs) by bromopropyl modified silica nanofibers. Strong hydrophobic interaction between dieldrin and bromopropyl groups on the surface of the fibers based on the principle of "like prefers like". (a) SiO_2 fibers; (b) SiO_2 fibers modified with 3-bromopropyltrichlorosilane. Insets: contact angles of the corresponding fibrous films.



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ABSTRACT

Novel bromopropyl functionalized silica nanofiber films were successfully fabricated by electrospinning the mixture of tetraethylorthosilicate (TEOS) and polyvinyl alcohol (PVA), followed by calcination and subsequent surface modification with 3-bromopropyl trichlorosilane (BPTCS). A polychlorinated chemical of dieldrin detected from the surface water frequently was selected as a model pollutant to test the removal efficiency of persistent organic pollutants (POPs) by bromopropyl modified silica nanofiber films. Because of larger specific surface area and large amount of pores, the bromopropyl modified silica nanofibers were found to be highly effective for the removal of hydrophobic POPs from micro-polluted water, especially at low concentrations. Its removal rate was evaluated to be 91.02%, much higher than that of the unmodified silica nanofibers (20.93%) and the commercially used granular activated carbon (38.65%). The higher adsorption efficiency of the bromopropyl silica nanofibers was assumed to be the accumulating effect of the bromopropyl groups on hydrophobic dieldrin due to strong hydrophobic interaction between dieldrin and bromopropyl groups on the surface of the fibers based on the principle of "like prefers like".

* Corresponding author. Tel.: +86 451 86402692; fax: +86 451 86403192.
E-mail address: Xiulidx@yahoo.com.cn (X. Yue).

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1. Introduction

Persistent organic pollutants (POPs) act as environmental hormone that adversely affect human health and the environment around the world [1–3]. Most POPs are lipophilic and have extremely low concentrations in water [4–6]. However, POPs tend to bioaccumulate in aquatic organisms such as fish and ultimately in humans even at trace level. Because of the characteristics of bioaccumulation, persistence, sub-chronic toxicity and long-range transport, the methods to remove POPs from the environment have been taking on increasing international attention.

Adsorption has been widely used as an effective method for the removal of organic pollutants from water. Various adsorbents, such as activated carbon, chitosan and organoclays, have been investigated for POPs removal. But, the experimental results demonstrate that it is difficult to remove trace level POPs near the environmental levels by these adsorbents. Due to a high degree of porosity and an extensive surface area, activated carbon is an effective adsorbent for several compounds of concern in water and wastewater treatment [7,8]. Nevertheless, some studies have shown that activated carbon is not useful for organic halogens with a concentration below 5 μg/L. Attacking this problem head on, investigators are developing innovative techniques and new adsorbents for the removal of trace or ultratrace POPs from water for the remediation.

Electrospinning is a cutting edge technique that allows producing conveniently continuous fibers with diameters ranging from 10 to 1000 nm [9,10]. Electrospun nanofiber membrane offers unique properties like high specific surface area, low basis weight, high permeability, small pore size, good interconnectivity of pores and potential to incorporate active chemistry or functionality on nanoscale. Also, the possibility of large scale production combined with the simplicity of the process makes this technique very attractive for many different applications. Compared with powder materials and even granular materials, electrospun nanofiber films can be a good candidate for organic pollutants adsorption from an aqueous solution because of their high permeability and small pore size that makes them appropriate for a wide range of filtration applications [11,12]. Herein, we reported for the first time the fabrication of novel bromopropyl functionalized silica nanofiber membranes for the efficient removal of hydrophobic POPs at trace level from water. A polychlorinated chemical of dieldrin detected from the surface water frequently was selected as a model pollutant.

In this work, bromopropyl modified silica nanofiber films were fabricated by calcination of electrospun PVA/TEOS fibers and subsequent surface modification with 3-bromopropyltrichlorosilane. The morphology and chemical composition of bromopropyl modified silica nanofiber films were characterized by scanning electron microscope, atomic force microscope, water contact angle, X-ray diffraction, X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy, respectively. The adsorption behavior of dieldrin on the bromopropyl modified silica nanofiber films was studied by liquid-phase adsorption experiments.

2. Experimental

2.1. Materials

Tetraethylorthosilicate (TEOS, $Si(OC_2H_5)_4$, >99%) and 3-bromopropyl trichlorosilane (BPTCS, $Br(CH_2)_3SiCl_3$, >96%) were obtained from Aldrich Company. Polyvinyl alcohol (PVA, Mn = 80,000) was supplied by Shanxi Chemical Co. Ltd., Shanxi, China. Granular activated carbon ZJ-15 (GAC) was supplied by Xinhua Activated Carbon Co. Ltd., Shanxi, China. Dieldrin ($C_{12}H_8Cl_6O$, 99.0% purity, in acetone) was obtained by Environmental Quality Supervision and Testing Center of Ministry of Agriculture, Tianjin, China. Millipore water was used as solvent.

2.2. Preparation of SiO_2 nanofibers

PVA solution (8.0%) was firstly prepared by dissolving PVA powder in water and heating at 96 °C. After cooling to room temperature, 30.0 mL PVA solution was dropped slowly into a mixture solution of 2.0 mL TEOS, 3.0 mL ethanol and 1.0 mL acetic acid. Thus, a viscous solution containing PVA/TEOS composite was obtained.

Then, the viscous solution of PVA/TEOS composite was contained in a plastic capillary for electrospinning. A copper pin connected to a DC high-voltage generator was placed in the solution, and the solution was kept in the capillary by adjusting the angle between capillary and the fixing bar. An aluminum foil served as counter electrode. A voltage of 10 kV was applied to the solution and a sprayed dense web of fibers was collected on the aluminum foil. During the course of electrospinning, the traveling jets of polymeric solution that carry abundant charges solidify through evaporation of solvents in the high electrostatic field, then the solidified jets turn into nanofibers. The web of fibers were dried initially for 12 h at room temperature under vacuum, and then calcined at 600 °C with a rising rate of 20 °C/h.

2.3. Modification of silica nanofibers using BPTCS

The 0.10 g silica nanofibers were immersed in 15.0 mL petroleum ether containing 0.32 g BPTCS at room temperature for 2 h. After reaction, the modified silica nanofibers were washed by petroleum ether three times to remove the unreacted BPTCS. These fibers were dried for 5 h at room temperature under vacuum. Thus, bromopropyl functionalized silica nanofibers were obtained.

2.4. Characterization

The samples were gold-sputtered before being imaged by SEM (FEI Quanta 200). EDX was recorded by EDAX Genesis 2000. Diameter distribution and average diameter were determined by measuring at least 100 random nanofibers in the SEM images. The diameters of nanofibers were analyzed using software Image J 1.3s. Morphological changes before and after bromopropyl modification of the fibers were analyzed using an AFM (BioScope Catalyst, USA) in the tapping mode and expressed as height and phase image. FT-IR spectra were acquired using a Varian resolution Fourier transform infrared spectrometer (Varian FTS 3100, USA). For each spectrum, a 128-scan interferogram was collected with a 4 cm^{-1} resolution from the 4000 to 400 cm^{-1} region at room temperature. The crystal phase of nanofibers was analyzed using X-ray diffraction (D/MAX-2500, Rigaku, Japan). The fiber's surface element binding energy and chemical composition were characterized by XPS (Perkin-Elmer PHI 5000C XPS system with an Al source). Contact angles on the nanofiber membranes were detected employing drops of deionized water using the contact angle and surface tension meter (KAM101, KSV).

2.5. Removal of dieldrin by bromopropyl functionalized silica nanofibers

Stock solution was prepared by dissolving appropriate amount of dieldrin in hexane, which was refrigerated for use. Dieldrin solution was prepared by adding the dieldrin stock solution to conical flasks. After removal of organic solvent under N_2, 50 mL deionized water was added followed by mechanical agitation for 2 h. Then in batch adsorption experiments, accurately weighted 5 ± 0.1 mg of Br-silica fibers, SiO_2 fibers and GAC were added to 50 mL aqueous solutions of dieldrin containing various initial concentrations.