



Research article

Carbon-cryogel hierarchical composites as effective and scalable filters for removal of trace organic pollutants from water



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ABSTRACT

Effective technologies are required to remove organic micropollutants from large fluid volumes to overcome present and future challenges in water and effluent treatment. A novel hierarchical composite filter material for rapid and effective removal of polar organic contaminants from water was developed. The composite is fabricated from phenolic resin-derived carbon microbeads with controllable porous structure and specific surface area embedded in a monolithic, flow permeable, poly(vinyl alcohol) cryogel. The bead-embedded monolithic composite filter retains the bulk of the high adsorptive capacity of the carbon microbeads while improving pore diffusion rates of organic pollutants. Water spiked with organic contaminants, both at environmentally relevant concentrations and at high levels of contamination, was used to determine the purification limits of the filter. Flow through tests using water spiked with the pesticides atrazine (32 mg/L) and malathion (16 mg/L) indicated maximum adsorptive capacities of 641 and 591 mg pollutant/g carbon, respectively. Over 400 bed volumes of water contaminated with 32 mg atrazine/L, and over 27,400 bed volumes of water contaminated with 2 µg atrazine/L, were treated before pesticide guideline values of 0.1 µg/L were exceeded. High adsorptive capacity was maintained when using water with high total organic carbon (TOC) levels and high salinity. The toxicity of water filtrates was tested *in vitro* with human epithelial cells with no evidence of cytotoxicity after initial washing.

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1. Introduction

A wide range of contaminants are continuously released into waterways as a result of anthropogenic activity, many of which are not effectively removed by current waste water treatment processes (Wilkinson et al., 2016; Loos et al., 2013). Problem

contaminants commonly comprise agrochemicals, pharmaceuticals, hormones, plasticisers, flame retardants, personal care products and food additives (Homem et al., 2015; Kokotou et al., 2012; Richardson and Ternes, 2014). These organic compounds are distributed across different environmental systems (e.g. soils, sediments, surface and ground waters), and the most polar (e.g. amines, alcohols or carboxylic acids and derivatives with small hydrocarbon skeletons and low partition coefficients) are bioavailable and may persist in the aqueous phase. These contaminants are now ubiquitous, and even at very low environmental concentrations (e.g. below 0.5 µg/L in surface and ground water, Cabezam et al., 2012; Loos et al., 2013; Sorensen et al., 2015) can potentially cause ecological changes and contaminate water

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supplies with (in some cases) unknown consequences for human health (Fent et al., 2006; Jeong et al., 2012). There is therefore a pressing need to purify water to safe (i.e. sub-ppb or ppt) levels. A range of technologies have been proposed to remove trace organic contaminants from waste and other waters, including chemical oxidation and improved adsorption methods, often using activated carbons. Indeed, in advanced waste water treatment processes, Granulated Activated Carbon (GAC) is used as a relatively low cost bulk adsorbent and is recognised as an industry standard. However, the adsorptive capacity of GAC diminishes over time, and it shows relatively poor adsorptive uptake for a range of more polar organic contaminants such as estrogens, pharmaceuticals and some pesticides (Busquets et al., 2014; Cabezam et al., 2012; Ifelebugu, 2011). This has led to a number of studies examining the potential of “designer” activated carbons, where control over the pore architecture is attempted to target particular dissolved species, to improve polar contaminant removal (Busquets et al., 2014; Gueudré et al., 2014; Ji et al., 2010; Unur, 2013; Zhang et al., 2011). In addition, use of hierarchical porous materials has been suggested to enhance mass transfer properties (Gueudré et al., 2014) and provide more effective adsorption of trace contaminants from water.

The present work explores the design of a flexible and scalable hierarchical composite filter comprised of phenolic resin-derived carbon microbeads with optimised micro-, meso- and macroporous structure embedded in a monolithic, flow permeable poly(vinyl alcohol) cryogel for the removal of small size, polar pesticides. Atrazine, (a herbicide of the triazine class, 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine, $\log K_{ow}$ 2.75; US EPA, 2006), and malathion, (an organophosphate insecticide, diethyl[(dimethoxyphosphinothioyl)thio]butanedioate, $\log K_{ow}$ 2.36–2.89; WHO, 2004), which enter waterways via runoff from agricultural land and have been frequently detected in surface or ground water (Fadaei et al., 2012; Nogueira et al., 2012; Sorensen et al., 2015; Varca, 2012), are used as model compounds to assess and optimise the water filters. Application and scalability are also discussed.

2. Materials and methods

2.1. Materials

The sources and purities of the chemicals used are provided in the Supporting Information S1. GAC was kindly provided by a UK water company.

2.2. Synthesis of carbon microbeads

Spherical activated carbon microbeads were obtained from Novolac phenol-formaldehyde resin with an average molecular weight 700–800 D (Hexion Specialty Chemicals Ltd., UK) following the technology patented by Tennison et al. (Tennison et al., 2000). Briefly, micro-, meso- and macroporous phenolic resin-derived carbon beads were prepared by pyrolysis and physical activation in carbon dioxide. Beads were tailored by dissolving Novolac resin (100 weight parts) and cross-linking agent hexamethylenetetramine (20 weight parts) in varying quantities of ethylene glycol (180–300 weight parts for micro-, meso- (TE3), and macroporous (TE7) resins respectively). The resin suspension was then heat-cured in mineral oil. After removing the ethylene glycol (which acts as a solvent and pore former) by hot water washing or vacuum drying, the resin beads were ready for processing into carbons. The amount of carbon loss (burn-off) during activation with CO₂ was 34% and 55% in carbon beads denoted in this work as TE3 and TE7, respectively and the particle size studied ranged from 40 to 250 μm.

The structural features of the carbon beads are summarised in Supporting information S2.

2.3. Preparation of polymer scaffold and composite filter

Monolithic macroporous polymer “scaffolds” (Macroporous Polymer Structures (MPPS^(TM)) produced by the authors (Protista), also referred to as cryogels, were prepared by chemical cross-linking of polyvinyl alcohol (PVA) at –12 °C and used to support the carbon beads. PVA was dissolved at a concentration of 5% w/v in boiling water and cooled to room temperature. Hydrochloric acid (1 M, 0.8 mL) was mixed with the PVA solution (7.2 mL) and kept in an ice bath for 30 min. Glutaraldehyde solution (75 μL, glutaraldehyde: water 50:50 v/v) and carbon beads (40–60 μm diameter, 320 mg) were added to the cooled PVA solution with stirring. The mixture was poured into $\varnothing 3 \times 100$ mm glass tubes. The sealed tubes were placed into a cryostat (Arctest, Finland) at –12 °C overnight. The cryogels were rinsed with water, then placed in sodium cyanoborohydride solution (0.1 M, pH 9.2) overnight to reduce the residual aldehyde groups, and finally rinsed with 4 bed volumes of water. The cryogels containing carbon beads were $\varnothing 3 \times 85$ mm (0.6 mL) in size when non-hydrated and were used in this configuration for flow through studies.

2.4. Structural characterisation

The structure of the prototypes and GAC was analyzed using low temperature nitrogen adsorption-desorption isotherms and scanning electron microscopy (Supporting Information S2, 3). The mechanical properties of the composites were tested with a T.A. XTPlus texture analyser equipped with a 1 cm diameter cylindrical probe (Stable Micro Systems, UK). The composite samples were compressed with steadily increasing force of 5 N/min from 0.01 N to 20 N at room temperature. The stiffness was assessed as the stress necessary to achieve 75% compression. The Young’s modulus of elasticity E , which is the slope of the stress-strain curve in the range of linear proportionality of stress to strain, has been calculated using equation (1), where F is the applied force; A , the cross-sectional area; L , the unstressed height; and ΔL , the change in height due to F ; F/A (in compression or tension) is the stress and $\Delta L/L$ is the strain.

$$E = (F/A)/(\Delta L/L) \quad (1)$$

The stress-strain curve obtained for the composite carried out immediately after a filtration test is shown in Supporting Information S4.

2.5. Adsorption experiments

Adsorption tests were carried out in batch mode under equilibrium conditions using an orbital shaker at 90 rpm, 25 °C for 48 h or magnetic stirring. To assess breakthrough curves in the high capacity carbon-cryogel prototypes using realistic volumes of water at laboratory scale, it was necessary to filter highly contaminated water. Hence, pesticides concentrations were high (32 mg atrazine and 16 mg malathion per L) relative to environmental concentrations. Ethanol (1.4%) was added to stabilise the contaminants in aqueous solution and prevent their precipitation, which would cause overestimation of the removal capacity of the developed prototypes. Batch adsorption tests were also carried out at more environmentally relevant contamination levels of 2 μg atrazine/L. For determination of the diffusion coefficient of atrazine and kinetics of its uptake, carbon beads (15 mg), or carbon-cryogel composites cut into cubes of 2 mm sides containing an equivalent

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