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Use of sub-micron sized resin particles for removal of endocrine disrupting compounds and pharmaceuticals from water and wastewater

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ABSTRACT

Endocrine disrupting compounds (EDCs) and pharmaceuticals pose a challenge for water and wastewater treatment because they exist at very low concentrations in the presence of substances at much higher concentrations competing for adsorption sites. Sub-micron sized resin particles (approximately 300 nm in diameter) (SMR) were tested to evaluate their potential as a treatment for EDCs including: 17-β estradiol (E2), 17-α ethinylestradiol (EE2), estrone (E1), bisphenol A (BPA), and diethylstilbestrol (DES) as well as 12 pharmaceuticals. SMR were able to remove 98% of spiked E2, 80% of EE2, 87% of BPA, and up to 97% of DES from water. For a 0.5 ppm mixture of E2, EE2, E1, BPA and DES, the minimum removal was 24% (E2) and the maximum was 49% (DES). They were also able to remove the pharmaceuticals from deionized water and wastewater. Overall, SMR are a promising advanced treatment for removal of both EDCs and pharmaceuticals.

Introduction

Micropollutants are organic substances whose toxic, persistent and bioaccumulative properties may have a negative impact on organisms in the aquatic environment. They encompass a large group of pollutants of varying chemical characteristics that can be found ubiquitously in water and wastewater. Both endocrine disrupting compounds (EDCs) and pharmaceuticals are considered micropollutants. Although they exist at very low concentrations, they can be harmful to the health of living organisms, wildlife and humans (Ashby et al., 1997; Bergman et al., 2013; Bögi et al., 2003; Evgenidou et al., 2015; Helfman, 2007; Kuzmanović et al., 2014; Rochester, 2013; Segner et al., 2003). Additionally, removal of micropollutants can be difficult because other substances, present at much higher concentrations, may interfere with treatment (Li et al., 2003; Pelekani and Snoeyink, 1999, 2001, 2000; Quinlivan et al., 2005).

EDCs are capable of interfering with the natural hormonal systems of animals. Suspected health effects include an increased risk of breast, testicular, and prostate cancers, reproductive disorders, immune and hormonal disorders, obesity, fewer male offspring, diabetes, metabolic disorders, and cardiovascular disease (Ashby et al., 1997; Bergman et al., 2013; Rochester, 2013). Evidence of these health effects comes from correlations between the prevalence of EDCs and increasing incidence of the disorder, observations of these effects in animal populations, and laboratory studies. It is possible that the risk of illness from EDCs has been

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underestimated because most of these studies link a single EDC to a corresponding negative health outcome, but humans, animals, and fish are exposed to a mixture of EDCs with unknown interactions (Bergman et al., 2013).

Pharmaceuticals represent a diverse category of substances with different pharmaceuticals causing different negative health effects when consumed inadvertently. The transformation products of pharmaceuticals, and effects of mixtures of pharmaceuticals remain largely unknown and also pose a risk (Evgenidou et al., 2015; Kuzmanović et al., 2014).

Water and wastewater treatment plants have historically been designed to remove particles, organic matter and nutrients, but they are not very effective in removing micropollutants (Snyder et al., 2007; Vieno et al., 2006). Adsorption is one method commonly employed to remove micropollutants (Ben et al., 2014; Ma et al., 2015). Micropollutants pose a challenge for adsorptive treatments because of competition from other substances present at much higher concentrations. A sizeable portion of the capacity of adsorptive treatment processes can be consumed treating these higher concentration pollutants in addition to the target micropollutants (Liao et al., 2007; Pelekani and Snoeyink, 1999, 2001, 2000; Quinlivan et al., 2005).

Porous polymer resins have long been used for the removal of organic contaminants from industrial wastewaters. They are chemically stable adsorbents, and their pore structure and surface chemistry can be controlled to target specific water treatment challenges (Xu et al., 2003). Additionally, they can be designed with magnetic cores, or on structural supports, making their application in full-scale treatment flexible (Jiang et al., 2015; Le Noir et al., 2007; Li et al., 2010; Luo et al., 2011; Xia et al., 2012a, 2012b). One such challenge is the treatment of micropollutants in the presence of natural organic matter (NOM) at much higher concentrations.

Sub-micron sized resin (SMR) were chosen to target micropollutants in this study because previous studies in the literature with superfine activated carbon showed better adsorption in the presence of competing substances in comparison to conventionally sized powder activated carbon. Some literature showed the removal of 2-methylisoborneo (Matsui et al., 2012, 2010) and geosmin (Matsui et al., 2010, 2009, 2007) using super fine powdered activated carbon. They found that the small particle size of superfine Powdered activated carbon (PAC) increased external surface area and the superfine PAC adsorbed more NOM without a reduction in adsorption of 2-methylisoborneo or geosmin. Additionally, 75% less superfine powdered activated carbon was required in comparison to normal sized powdered activated carbon.

Since SMR particles can be designed for specific applications, they are ideal candidates for the rapid removal of EDCs and pharmaceuticals in water treatment. The SMR particles used in this study had an average diameter of (333 ± 76) nm, determined from scanning electron microscope images. SMR were evaluated for their ability to remove several EDCs: 17-β estradiol (E2), 17-α ethinylestradiol (EE2), estrone (E1), diethylstilbestrol (DES) and bisphenol A (BPA) from water. Experiments were conducted with EDCs individually and in mixture. Additionally, a mixture of 12 pharmaceuticals: acetaminophen, caffeine, carbamazepine, cloxacillin, diphenhydramine, enrofloxacin, lincomycin, oxacillin, sulfadiazine, sulfamethizole, sulfanilamide, and sulfathiazole was studied in both water and wastewater.

1. Experimental

1.1. SMR synthesis

Functional monomer methacrylic acid (MAA) (99%) (Sigma-Aldrich; Oakville, Canada) and cross-linker ethylene glycol dimethacrylate (EGDMA) (98%) (Sigma-Aldrich, Oakville, Canada) were dissolved in a porogen with a molar ratio of 8 mmol:6.7 mmol (Wei et al., 2006). The porogen was composed of 40 mL of 1:3 (V/V) acetone (99.5%) (Fisher Scientific, Ottawa, Canada), and acetonitrile (99.9%) (Fisher Scientific, Ottawa, Canada). The 2% (W/W) of 2-isobutyronitrile (99%) (AIBN) was added as the initiator (Sigma-Aldrich, Oakville, Canada). The mixture was mixed with a vortex mixer (Fisher Scientific Vortex Mixer, USA), deoxygenated with nitrogen for 5 min, and then placed in a 60°C hot water bath for 24 hr (Isotemp 220, Fisher, USA). The resulting polymer particles were dewatered using a centrifuge (Thermo Scientific Sorval Legend RT$^+$, Fisher Scientific) at 10,000 r/min, rinsed with deionized water, air dried at room temperature, and ground manually.

1.2. Micropollutants

EDCs and pharmaceuticals: E2 (≥98%), EE2 (≥98%), E1 (≥99%), DES (≥99%), BPA (≥99%), acetaminophen (≥99%), caffeine (≥99%), carbamazepine (≥98%), cloxacillin (≥97%), diphenhydramine (≥98%), enrofloxacin (≥98%), lincomycin (≥95%), oxacillin (95%), sulfadiazine (≥99%), sulfamethizole (≥99%), sulfanilamide (≥99%), and sulfathiazole (≥98%) were all purchased from Sigma-Aldrich (St. Louis, Missouri, USA). The 1 mg/mL stock solutions were prepared in methanol and stored in the freezer.

1.3. SMR characterization

Brunauer–Emmett–Teller (BET) surface area, average pore size, pore volume, and mesopore volume were measured by Engineering Performance Solutions (Jacksonville, FL, United States). Barret–Joyner–Halenda (BJH) and Quenched Solid Density Functional Theory (QSDFT) analyses were performed using a NOVA BET surface analyzer (Quantachrome Instruments, Boyton Beach, United States). The NOVA BET surface analyzer measures the pore volume of the adsorbent as a function of the partial pressure of nitrogen. A sample cell was submerged in liquid nitrogen to maintain a constant temperature of 273 K. The sample cell was slowly filled with nitrogen gas, and the volume of gas was recorded for several pressure intervals to create isotherms. From the isotherm data, the BET surface area, pore volume, average pore size, and mesopore volumes were calculated. The micropore volume was then calculated by subtracting the mesopore volume from the total pore volume, and the ratio of the micropore volume to the mesopore volume was calculated by dividing these two values.

1.4. Analytical measurements

1.4.1. Single EDC analysis

Analysis was conducted using high-performance liquid chromatography (HPLC) with a Phenomenex 50 × 2.00 mm PFP column and a mobile phase with 55:45 (V/V) methanol:deionized

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