JOURNAL OF ENVIRONMENTAL SCIENCES 51 (2017) 256–264

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES JOURNAL OF ENVIRONMENTAL SCIENCES

www.jesc.ac.cn

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

Audrey Murray[1], *Banu Örmeci*[1,*], *Edward P.C. Lai*[2]

1. *Department of Civil and Environmental Engineering, Carleton University, 1125 Colonel ByDrive, Ottawa, ON K1S 5B6, Canada. E-mail: amurray3@connect.carleton.ca*

2. *Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, ON K1S 5B6, Canada*

ARTICLE INFO

Article history:
Received 1 December 2015
Revised 19 April 2016
Accepted 6 May 2016
Available online 25 July 2016

Keywords:
Water treatment
Wastewater treatment
Pharmaceuticals
Endocrine disrupting compounds
Micropollutants
Adsorption

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

* *Corresponding author*. E-mail: banu.ormeci@carleton.ca (Banu Örmeci).

http://dx.doi.org/10.1016/j.jes.2016.05.033

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

water. A Shimadzu LC 20 AD HPLC with a Sil 20A autosampler (Shimadzu, Kyoto, Japan) was used for all analysis. Fluorescence detection (FD) with a RF-10AXL detector (Shimadzu; Kyoto, Japan) was used for E2, EE2 and BPA, and photo diode array (PDA) detection with a SPD-M20A detector (Shimadzu, Kyoto, Japan) was used for DES. Sample blanks consisting of water exposed to SMR particles and then centrifuged exhibited no peaks, indicating that the SMR did not leach into solution in a way that interfered with the analysis.

1.4.2. Treatment of water with a mixture of EDCs and removal kinetics

Analysis was conducted using high performance liquid chromatography tandem mass spectrometry (LC/MS/MS) in multiple reaction monitoring (MRM) mode. A Shimadzu HPLC (LC 20AD) was used in conjunction with an AB Sciex API 2000 triple quadrupole tandem mass spectrometer (Framingham, Massachusetts, United States). The HPLC column used was a Phenomenex Kinetex 2.6 μm PFP column. Electrospray ionization was applied in negative mode for the mass spectrometer.

1.4.3. Removal of pharmaceuticals

Analysis was conducted by Axys Analytical Services (Sidney, BC, Canada) using LC/MS/MS (Axys Method MLA-075 Rev 5).

1.5. Treatment of water with a single EDC

SMR were tested for their ability to remove E2, EE2, DES, and BPA from deionized water through a series of batch tests each with a single solute. For each sample, 5 mg of SMR were weighed into a 1.5 mL centrifuge tube, and 1 mL of deionized water spiked with the relevant concentration of E2, EE2, DES, or BPA was added. This was a high dose of SMR used to test high concentrations of a variety of EDCs. The tubes were sonicated for 5 min to disperse the SMR before centrifugation at 10,000 r/min for 5 min. Sonication was used for experimental purposed only to ensure a uniform distribution of particles. In practice, different distribution and application methods need to be investigated prior to full-scale application. The centrate was analyzed with HPLC as previously described. Three experimental replicates each consisting of two analytical replicates were analyzed. For E2, EE2 and BPA, concentrations were varied between 2 and 14 ppb, and for DES, concentrations of 5–20 ppm were tested.

1.6. Treatment of water with a mixture of EDCs

SMR were also tested for treatment of a mixture of EDCs consisting of 0.5 ppm each of E2, EE2, E1, BPA, and DES in deionized water over a 24 hr contact time. SMR concentrations of 0.1, 1, 10, 100, and 1000 mg/L were tested to establish the range over which SMR were effective for treatment of water containing 0.5 ppm for each EDC. The bottles were placed on a shaker table (Excella E1 Platform Shaker; New Brunswick Scientific Inc.; Enfield, Connecticut, United States) for 24 hr. The following day, the samples were centrifuged at 10,000 r/min (670,800 g) for 1 hr (Sorval Legend RT+; Thermo Scientific/Fisher Scientific; Waltham, Massachusetts, United States), and the centrate was analyzed with LC/MS/MS as previously described. Three experimental replicates, each consisting of 6 injection replicates, were conducted for each sample.

1.7. Establishing the kinetics of removal

The kinetics of removal were analyzed using a 0.5 ppm mixture of E2, EE2, E1, BPA, and DES following the same procedure as that outlined above for treatment of water with a mixture of EDCs. SMR concentrations of 50 and 500 mg/L were tested for contact times of 10 min, 30 min, 1 hr, 2 hr, 5 hr, 1 day, and 4 days.

1.8. Removal of pharmaceuticals

Tests were conducted with 12 pharmaceuticals: acetaminophen, caffeine, carbamazepine, cloxacillin, diphenhydramine, enrofloxacin, lincomycin, oxacillin, sulfadiazine, sulfamethizole, sulfanilamide, and sulfathiazole in deionized water and wastewater. Secondary wastewater effluent samples were collected from the Robert O. Pickard Environmental Centre in Ottawa, Ontario. The 200 ng/L of acetaminophen, 50 ng/L of sulfathiazole, and 100 ng/L of the remaining pharmaceuticals were spiked into 2.5 L each of deionized water and wastewater. A 100 g/L solution of SMR was created and sonicated to disperse the SMR. The 1 L of each of the spiked solutions was treated by adding 10 mL of the concentrated SMR solution to give a final concentration of 1 g SMR/L. The samples were mixed for 24 hr on a shaker table before being centrifuged at 10,000 r/min for 1 hr to remove the SMR. The centrate was poured into sample bottles, which were packed in a cooler and shipped to Axys Analytical Services for analysis (Sidney, BC, Canada).

2. Results and discussion

2.1. SMR characterization

BET surface area, average pore size, total pore volume, micropore volume, mesopore volume, and ratio of micropore volume to mesopore volume were measured for SMR and are provided in Table 1. SMR had a low BET surface area of 3.4 m^2/g, and a low pore volume of 0.0125 cm^3/g. Optimizing the surface area and micropore volume of the SMR could enhance adsorption. Additionally, the SMR had a relatively low ratio of micropores to mesopores as evidenced by the low micropore volume to mesopore volume ratio. Generally, a higher micropore volume is favorable for adsorption of micropollutants because micropollutants preferentially adsorb in smaller pores (Newcombe et al., 1997, 2002; Pelekani and Snoeyink, 1999, 2000; Ding et al., 2008; Redding and Cannon, 2014). Increasing the ratio of micropores to mesopores could also potentially improve adsorption of micropollutants.

2.2. Treatment of water with a single EDC

SMR were tested for treatment of a range of EDCs including: E2, EE2, BPA, and DES each in single solute solutions in deionized water. Fig. 1 shows the removal of E2, EE2, and BPA with SMR for initial EDC concentrations varying between 2 and 14 ppb for a 5 min contact time.

Table 1 – SMR characterization.

Characterization	Value
BET surface area (m^2/g)	3.4
Pore size (Å)	73.06
Pore volume (cm^3/g)	0.0125
Mesopore volume (cm^3/g)	0.0112
Micropore volume (cm^3/g)	0.0013
Micropore volume/mesopore volume	0.12

SMR: sub-micron sized resin; BET: Brunauer–Emmett–Teller.

For E2, error bars are shown, but are very small and therefore not visible. The error bars represent the standard deviation of the three experimental replicates. The SMR exhibited a high binding efficiency greater than 98% for all of the E2 concentrations studied. The high removal efficiency is also related to the SMR concentration used, and can be lower at lower SMR concentrations. The results show that SMR have an excellent ability to remove E2 from water within a very short contact time.

For EE2, Fig. 1 shows an increase in efficiency with increasing EE2 concentration, up to (80 ± 0.6)% removal for an initial EE2 concentration of 6 ppb compared to (19 ± 14)% at 2 ppb. This was followed by an area of uniform removal (80%) with increasing concentration. For the lowest concentration tested, 2 ppb EE2, 19% removal was measured but the data point also had larger error bars compared to the other points. The concentration of the final sample, measured after some removal of the 2 ppb initial concentration, was approaching the detection limit of the instrument. The low adsorption for lower EE2 concentrations may have been due to the short contact time and adsorption may have been limited by diffusion of EE2. However, it is common for adsorption efficiency to increase with increasing concentrations of adsorbents as evidenced by positive slopes for both Freundlich and Langmuir isotherms correlating increased removal with increased equilibrium concentrations (Crittenden et al., 2005). This is a challenge for removal of micropollutants that is not unique to SMR.

For BPA, the percent removal increased from (62 ± 13)% for 2 ppb to (87 ± 0.6)% for 10 ppm before leveling off. Again, the lower removal efficiencies for very low concentrations may have been due to the short contact time. Larger uncertainty for very low concentrations also occurred due to difficulties measuring concentrations close to the detection limit.

Fig. 2 shows the percent removal for DES with 5 mg/mL of SMR for a contact time of 5 min. The error bars represent the standard deviation of the three experimental replicates. For DES, the initial concentrations tested were in the range of 5–20 ppm instead of 2–14 ppb because DES had a much higher detection limit. The percent removal for DES decreased through this range from (97 ± 2)% for 5 ppm to (78 ± 0.75)% for 20 ppm. The decrease in efficiency for high DES concentrations likely occurred because the SMR were approaching saturation, but the quantity of DES adsorbed/mass of SMR increased from 15 ppm (2.4 ± 0.2) mg/g to 20 ppm (3.1 ± 0.03) mg/g, indicating that the SMR had not reached saturation yet. Overall, these results demonstrate excellent potential for use of SMR to remove DES, because the concentrations tested were more than a thousand times those tested for E2, EE2, and BPA; yet, up to 97% removal was achieved.

For 2–14 ppb of E2, EE2, and BPA, the maximum percent removals achieved after 5 min were 98%, 80%, and 87%, respectively. Therefore, the SMR did show a preference for E2 followed by BPA, and then EE2. For SMR, the mechanism for adsorption is non-specific and occurs through van der Waals forces and hydrogen bonds (Pichon and Chapuis-Hugon, 2008). The order of preference is expected to be inversely related to the solubility of the molecules, leading to an order of E2 > EE2 > BPA. This accurately predicts the preference for E2 over EE2 and BPA, but not for BPA over EE2. However, it is important to note that the contact time was relatively short and the order of removal may change with increased contact time. In general, the SMR showed an excellent potential for removal of E2, EE2, BPA, and DES.

2.3. Treatment of water with a mixture of EDCs

One challenge posed by EDCs in water and wastewater streams is that they exist as complex mixtures. SMR were tested for their ability to meet this challenge with a mixture of E2, EE2, estrone (E1), BPA, and DES. Removal efficiencies in the presence of competing compounds were tested and compared to the removal efficiencies measured in the previous section when there was no competing compound.

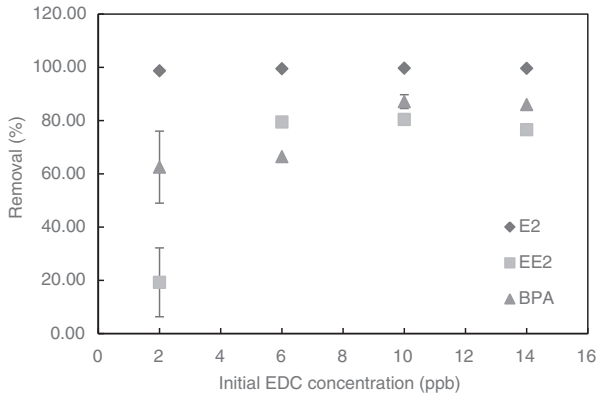

Fig. 1 – Removal of E2, EE2, and BPA (2–14 ppb) with SMR from deionized water. Error bars represent the standard deviation of three experimental replicates. E2: 17-β estradiol; EE2: 17-α ethinylestradiol; BPA: bisphenol A.

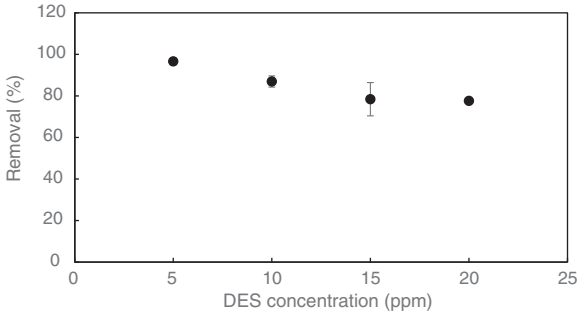

Fig. 2 – Removal of DES (5–20 ppm) with SMR from deionized water. Error bars represent the standard deviation of three experimental replicates. DES: diethylstilbestrol.

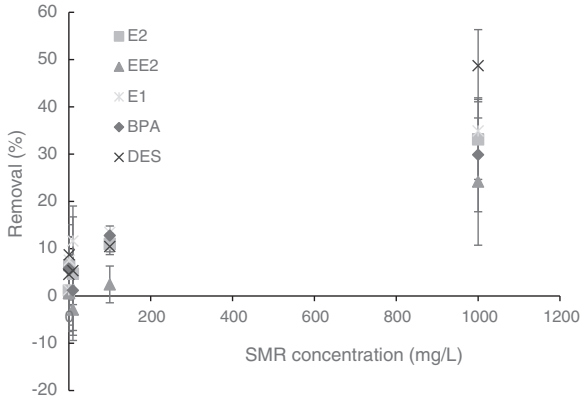

Fig. 3 – Treatment of a mixture of EDCs with SMR from deionized water. Error bars represent the standard deviation of three experimental replicates. EDCs: endocrine disrupting compounds.

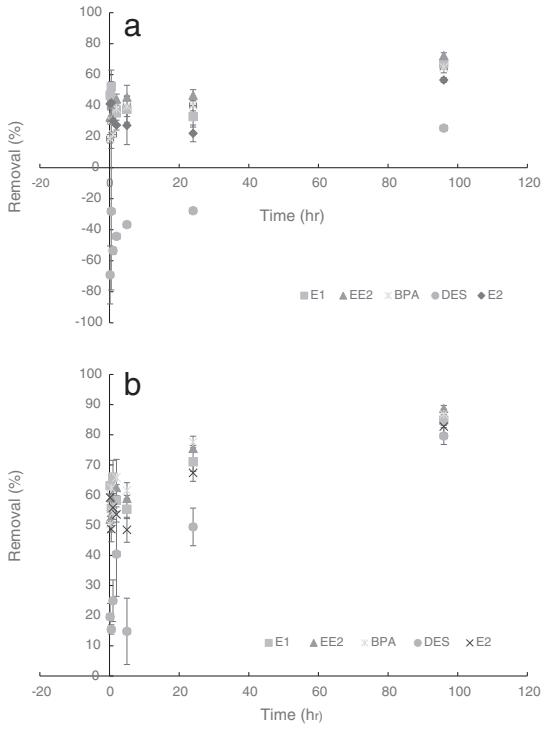

Fig. 4 – Kinetics of removal for a mixture of 5 EDCs with 50 mg/L (a) and 500 mg/L (b) of SMR from deionized water over a 4-day period. Error bars represent the standard deviation of three experimental replicates.

The capacity of the SMR was tested over a wide range of concentrations to determine the working range for the SMR. As seen in Fig. 2 for DES, a DES concentration more than a thousand times higher than the concentrations tested for E2, EE2, and BPA, exhibited a very high removal (97%), and the SMR appear to work effectively over a wide range of concentrations. Fig. 3 shows the results obtained, with percent removal on the *y*-axis, and SMR concentration on the *x*-axis. The results provided are averages of 3 experimental replicates, each of which represents the average of 6 analytical replicates. The error bars represent the standard deviations of the experimental replicates. Referring to Fig. 3, 0% removal was within 1 standard deviation of the mean percent removal for all 5 EDCs for SMR concentrations less than 100 mg/L, indicating negligible removal. For EE2, addition of 100 mg/L of SMR also led to negligible removal. Percent removal values for E1, E2, BPA, and DES were low for 100 mg/L of SMR and ranged from (10 ± 3)% for DES to (13 ± 1)% for E1. For 1000 mg/L of SMR, (30 ± 12)% of BPA, (33 ± 8)% of E2, (24 ± 13)% of EE2, (49 ± 6)% of DES, and (35 ± 8)% of E2 were removed from a 0.5 ppm mixture. Overall, SMR were able to remove a range of EDCs from water. Further testing should be completed with higher SMR to EDC ratios to achieve the near-complete removal seen in Figs. 1 and 2, and to determine the optimum SMR concentration.

2.4. *Establishing the kinetics of removal*

Removal kinetics were studied for the 0.5 ppm mixture of E2, EE2, E1, BPA, and DES in deionized water over a four-day period. A standard solution with 0.5 ppm each of E2, EE2, E1, BPA, and DES was treated with either 50 or 500 mg/L of SMR. Samples were taken after 10 min, 30 min, 1 hr, 2 hr, 5 hr, 1 day, and 4 days. The results, shown in Figs. 4a and b, are averages of three experimental replicates, each of which is the average of six analytical replicates.

For adsorption of E2 onto 50 mg/L of SMR shown in Fig. 4a, there were some initial fluctuations in the percent removal. After 10 min, (41 ± 2)% of the E2 had been removed, but this decreased to (22 ± 5)% after 1 day, before increasing to (57 ± 2)% after 4 days. These fluctuations may have been caused by competitive NOM and heavy metal complexation, adsorption to the bottle, or competition with other EDCs for adsorption sites. For E2 with 500 mg/L of SMR shown in Fig. 4b, the percent removal fluctuated during the first 24 hr, before increasing from (67 ± 3)% to (83 ± 25)% between 1 and 4 days.

For adsorption of EE2 onto 50 mg/L of SMR shown in Fig. 4a, the percent removal generally increased with increasing contact time, although a dip in the percent removal was observed after 1 hr. Overall, the removal of EE2 increased from (33 ± 0.5)% after 10 min to (72 ± 2)% after 4 days. It is interesting to compare these results with those for E2. After 10 min, the percent removal was higher for E2, (41 ± 2)% for E2 *vs.* (33 ± 5)% for EE2, but after 2 days, the percent removal was higher for EE2, (72 ± 2)% for EE2 *vs.* (57 ± 2)% for E2. This indicates that although the removal kinetics may have been faster for E2, but the final amount adsorbed was higher for EE2. For adsorption of EE2 with 500 mg/L of SMR, similar trends to those shown in Fig. 4a were seen. The amount of EE2 adsorbed increased from (52 ± 2)% after 10 min to (84 ± 2)% after 4 days. Also, similar to the 50 mg/L SMR results, the amount adsorbed after 10 min was higher for E2 ((59 ± 1)% for E2 *vs.* (52 ± 2)% for EE2), but after 4 days, more EE2 was adsorbed ((89 ± 2)% for EE2 *vs.* (83 ± 2)% for E2). The magnitude of the difference was less than that for 50 mg/L of SMR; however, probably because there was less competition for adsorption sites due to a greater availability of SMR.

For E1, Fig. 4a shows that the amount adsorbed with 50 mg/L of SMR initially decreased from (47 ± 2)% after 10 min to (33 ± 7)% after 1 day, before increasing to a final percent

removal of (67 ± 4)% after 4 days. For E1, the amount adsorbed after 10 min, was higher than that for E2 and EE2. However, after 10 days, the percent removal was higher for EE2. This can be explained by looking at the molecular weights of E1, E2, and EE2, which are 270, 272, and 296 g/mol, respectively. Smaller molecules can be expected to diffuse more quickly through solution, and adsorb more quickly (Crittenden et al., 2005). Therefore the kinetics of adsorption for E1 can be expected to be faster than that for EE2. For adsorption of E1 with 500 mg/L of SMR shown in Fig. 4b, the amount adsorbed fluctuated before increasing from (71 ± 3)% after 1 day to (85 ± 2)% after 4 days. Similar to the results shown in Fig. 4a, the amount adsorbed after 10 min, was higher than that for E2 and EE2. However, after 10 days, the percent removal was higher for EE2. This can be explained by the molecular weight of EE2, which is larger than that of E1 and E2, decreasing the rate of adsorption.

For BPA, the amount adsorbed increased from (19 ± 3)% after 10 min to (65 ± 3)% after 4 days for 50 mg/L of SMR, as shown in Fig. 4a. For 500 mg/L of SMR, the percent removal fluctuated, but generally increased from (63 ± 1)% after 10 min to (85 ± 2)% after 4 days. After 10 min the percent removal of BPA was lower than that for E2, EE2, and E1. After 4 days, it was higher than E2 for both 50 mg/L and both E2 and E1 for 500 mg/L. This was unexpected, because the molecular weight of BPA was 228 g/mol, which was the lowest of the 5 EDCs studied, so BPA was expected to have the fastest adsorption kinetics.

For DES with 50 mg/L of SMR shown in Fig. 4a, negative percent removal values were recorded for sample times less than 4 days. This was likely due to a source of DES contamination or due to the concentration of the controls used in the calculations. Further experiments, with a larger number of samples, and more measurements of the control sample might lead to an improvement in DES removal for future work. The concentrations of the controls were not measured for each sampling time and were only measured once after 4 days. If a significant portion of the DES was adsorbed to the bottle between 1 and 4 days, this could lead to falsely low or negative percent removal values. After 4 days, (26 ± 6)% of the DES was removed, which was lower than all the other EDCs tested. For adsorption of DES with 500 mg/L of SMR shown in Fig. 4b, the amount removed with time fluctuated, but generally increased from (20 ± 4)% after 10 min to (80 ± 3)% after 4 days, which, again, was lower than the removal of any other EDCs.

For a mixture of E2, EE2, E1, BPA, and DES in water at 0.5 ppm, equilibrium was not reached after 4 days. However, high removals of 80% or greater were achieved for all five of these EDCs with 500 mg/L of SMR.

2.5. *Removal of pharmaceuticals*

To further test the potential for SMR to treat a wide variety of micropollutants, the SMR were tested for their ability to remove a range of pharmaceuticals from both deionized water and wastewater. Acetaminophen, caffeine, carbamazepine, cloxacillin, diphenhydramine, enrofloxacin, lincomycin, oxacillin, sulfadiazine, sulfamethizole, sulfanilamide, and sulfathiazole were all spiked into both deionized water and wastewater in concentrations ranging from 50 to 200 ng/L. An SMR concentration of 1 g/L was used to treat the pharmaceuticals over a 24 hr contact time. This is a high concentration of SMR particles used to evaluate the potential of the particles. Further tests are required to optimize the synthesis of the particles as well as the required dose.

Fig. 5a provides the results for treatment of the pharmaceuticals in deionized water. The spiked concentration, untreated concentration, and treated concentrations are shown for each of the 12 pharmaceuticals. All analysis was conducted with LC–MS. The untreated samples were handled using exactly the same procedure as the treated samples, but SMR were not added. This was done to account for any effects of adsorption to the bottle, dilution errors, or contamination. Ionization due to ions released into solution by the SMR could not be accounted for with the controls. The pharmaceuticals were tested at very low concentrations, and avoiding contamination or dilution errors at these concentrations can be difficult. Looking at Fig. 5a, many of the concentrations measured for the untreated samples were close to the spiked concentrations, except those for acetaminophen and caffeine. However, since the interest here is not the actual concentrations, but rather the removal with SMR, this is not an issue. Comparing the treated and untreated samples (before and after), some of the pharmaceuticals (carbamazepine, cloxacillin, diphenhydramine, enrofloxacin, and oxacillin) exhibited a high (>50%) degree of removal; some (caffeine, sulfadiazine, sulfamethizole, and sulfathiazole) were removed to some degree (<50%); and for a few (acetaminophen, lincomycin, and sulfanilamide), the treated concentrations were higher than the untreated concentrations. Treated concentrations that were higher than untreated concentrations were likely due to differences measuring the pharmaceuticals at very low concentrations or potential matrix effects from ions released from the SMR themselves. This should be investigated further. These preliminary results show some promise for the SMR: 5 out of the 12 pharmaceuticals were removed by more than 50%.

The same 12 pharmaceuticals were also spiked into a sample of secondary wastewater effluent collected from the Robert O. Pickard Environmental Centre in Ottawa, Ontario. However, due to difficulties anticipating the final concentrations of the pharmaceuticals after spiking, carbamazepine, sulfadiazine, sulfamethizole, sulfanilamide, and sulfathiazole could not be measured by the lab because they were outside of the lab's linear calibration range. Acetaminophen, caffeine, cloxacillin, diphenhydramine, enrofloxacin, lincomycin, and oxacillin were measured. Fig. 5b shows the spiked, untreated, and treated concentrations for these 7 pharmaceuticals. For the wastewater sample, with the exception of acetaminophen, all of the concentrations measured in the untreated samples were higher than the spiked concentrations. This was not surprising because the wastewater itself may have contained low concentrations of these pharmaceuticals.

The wastewater results were less promising than those for deionized water. The presence of competing substances in the wastewater may have decreased the removal of the pharmaceuticals and a higher concentration of SMR may be required to treat wastewater. For the wastewater, diphenhydramine and enrofloxacin exhibited high (>50%) removals, lincomycin was removed to some degree (<50%), and acetaminophen, caffeine cloxacillin, and oxacillin had higher treated than untreated concentrations. Again, difficulties measuring pharmaceuticals at very low concentrations and likely variations in results makes it difficult to draw any firm

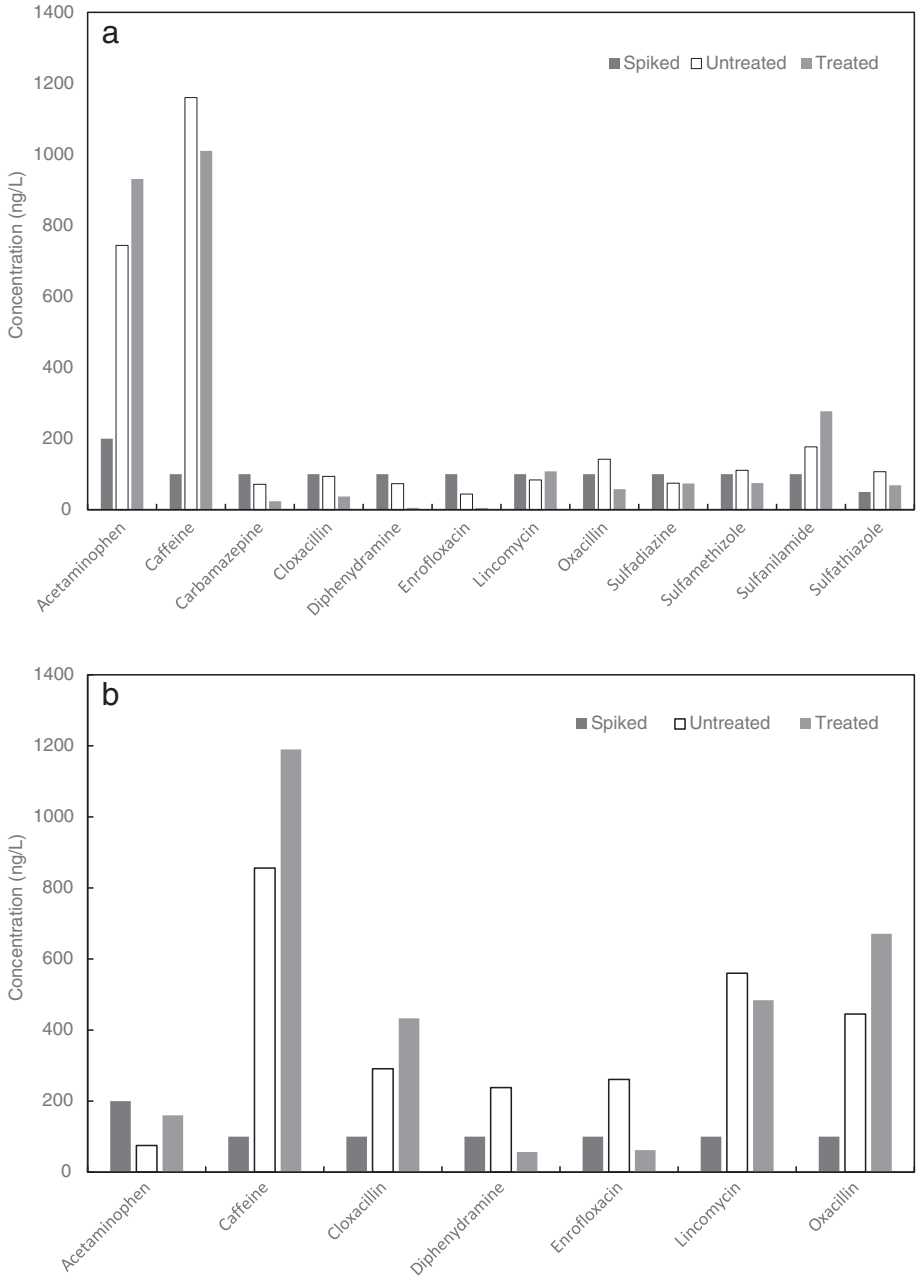

Fig. 5 – Treatment of pharmaceuticals in deionized water (a) and wastewater (b) with SMR.

conclusions, but the results do show some potential, and further investigation is merited.

3. Conclusions

SMR were highly effective for removal of EDCs from single solute solutions. SMR were able to remove 98% of spiked E2, 80% of EE2, 87% of BPA, and up to 97% of DES. SMR were also effective for treatment of water spiked with a mixture of different micropollutants. In a mixed solution with 0.5 ppm each of E2, EE2, E1, BPA, and DES, percent removals with 500 mg/L of SMR were in the range of (24 ± 13)% (E2) to (49 ± 6)% (DES), and increased with increasing SMR concentrations, suggesting the potential for more removal with higher particle concentrations. The adsorption kinetics were slow, and equilibrium was not reached within 4 days. Tests with a mixture of 12 pharmaceuticals in deionized water and wastewater were not conclusive, but did indicate that SMR merits further study as a potential treatment method for micropollutants in water and wastewater. SMR were able to remove 9 out of 12 of the pharmaceuticals to some degree from deionized water and 3 out of the 7 pharmaceuticals measured in wastewater. Further investigation is required to determine how well SMR perform in comparison to

larger resins of the same material. Further investigation should also focus on the development of isotherms for SMR for the wide variety of EDCs and pharmaceuticals studied herein.

Acknowledgments

This research was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC) (RGPIN 326978-2011) under the Discovery Grant program.

REFERENCES

Ashby, J., Houthoff, E., Kennedy, S., Stevens, J., Bars, R., Jekat, F., et al., 1997. The challenge posed by endorcrine-disrupting chemicals. Environ. Health Perspect. 105 (2), 164–169.

Ben, W., Qiang, Z., Yin, X., Qu, J., Pan, X., 2014. Adsorption behavior of sulfamethazine in an activated sludge process treating swine wastewater. J. Environ. Sci. 26, 1623–1629.

Bergman, A., Heindel, J., Jobling, S., Kidd, K.A., Zoeller, R.T., 2013. State of the Science of Endocrine Disrupting Chemicals - 2012. IOMC - Inter-Organization Programme for the Sound Management of Chemicals.

Bögi, C., Schwaiger, J., Ferling, H., Mallow, U., Steineck, C., Sinowatz, F., et al., 2003. Endocrine effects of environmental pollution on *Xenopus laevis* and *Rana temporaria*. Environ. Res. 93, 195–201.

Adsorption. In: Crittenden, J.C., Trussel, R., Hand, D.W., Howe, K., Tchobanoglous, G. (Eds.), Water Treatment: Principles and Design. John Wiley and Sons, New Jersey, pp. 1245–1358.

Ding, L., Snoeyink, V.L., Mariñas, B.J., Yue, Z., Economy, J., 2008. Effects of Powdered Activated Carbon Pore Size Distribution on the Competitive Adsorption of Aqueous Atrazine and Natural Organic Matter. Environ. Sci. Technol. 42 (4), 1227–1231.

Evgenidou, E.N., Konstantinou, I.K., Lambropoulou, D.A., 2015. Occurrence and removal of transformation products of PPCPs and illicit drugs in wastewaters: a review. Sci. Total Environ. 505, 905–926.

Helfman, G.S., 2007. Fish Conservation: a Guide to Understanding and Restoring Global Aquatic Biodiversity and Fishery Resources. Island Press, Washington DC, USA (ISBN: 9781559635950).

Jiang, M., Yang, W., Zhang, Z., Yang, Z., Wang, Y., 2015. Adsorption of three pharmaceuticals on two magnetic ion-exchange resins. J. Environ. Sci. 31, 226–234.

Kuzmanović, M., Ginebreda, A., Petrović, M., Barceló, D., 2014. Risk assessment based prioritization of 200 organic micropollutants in 4 Iberian rivers. Sci. Total Environ. 504, 289–299.

Le Noir, M., Plieva, F., Hey, T., Guieysse, B., Mattiasson, B., 2007. Macroporous molecularly imprinted polymer/cryogel composite systems for the removal of endocrine disrupting trace contaminants. J. Chromatogr. A 1154, 158–164.

Li, Q., Snoeyink, V.L., Mariñas, B.J., Campos, C., 2003. Pore blockage effect of NOM on atrazine adsorption kinetics of PAC: the roles of PAC pore size distribution and NOM molecular weight. Water Res. 37, 4863–4872.

Li, Y., Li, X., Chu, J., Dong, C., Qi, J., Yuan, Y., 2010. Synthesis of core-shell magnetic molecular imprinted polymer by the surface RAFT polymerization for the fast and selective removal of endocrine disrupting chemicals from aqueous solutions. Environ. Pollut. 158, 2317–2323.

Liao, T., Tu, X., Li, S., 2007. Selective adsorption and recognition by molecularly imprinted polymer: a study on molecular self-assembly and its effect on selectivity. Polym.-Plast. Technol. Eng. 46, 613–619.

Luo, X., Zhan, Y., Huang, Y., Yang, L., Tu, X., Luo, S., 2011. Removal of water-soluble acid dyes from water environment using a novel magnetic molecularly imprinted polymer. J. Hazard. Mater. 187, 274–282.

Ma, W., Nie, C., Chen, B., Cheng, X., Lun, X., Zeng, F., 2015. Adsorption and biodegradation of three selected endocrine disrupting chemicals in river-based artificial groundwater recharge with reclaimed municipal wastewater. J. Environ. Sci. 31, 154–163.

Matsui, Y., Aizawa, T., Kanda, F., Nigorikawa, N., Mima, S., Kawase, Y., 2007. Adsorptive removal of geosmin by ceramic membrane filtration with super-powdered activated carbon. J. Water Supply Res Technol. 56, 411–418.

Matsui, Y., Ando, N., Sasaki, H., Matsushita, T., Ohno, K., 2009. Branched pore kinetic model analysis of geosmin adsorption on super-powdered activated carbon. Water Res. 43, 3095–3103.

Matsui, Y., Nakano, Y., Hiroshi, H., Ando, N., Matsushita, T., Ohno, K., 2010. Geosmin and 2-methylisoborneol adsorption on super-powdered activated carbon in the presence of natural organic matter. Water Sci. Technol. 62, 2664–2668.

Matsui, Y., Yoshida, T., Nakao, S., Knappe, D.R.U., Matsushita, T., 2012. Characteristics of competitive adsorption between 2-methylisoborneol and natural organic matter on superfine and conventionally sized powdered activated carbons. Water Res. 46, 4741–4749.

Newcombe, G., Drikas, M., Hayer, R., 1997. Influence of Characterised Natural Organic Material on Activated Carbon Adsorption: II. Effect on Pore Volume Distribution and Adsorption of 2-Methylisoborneol. Water Res. 31 (5), 1065–1073.

Newcombe, G., Morrison, J., Hepplewhite, C., Knappe, D.R.U., 2002. Simultaneous Adsorption of MIB and NOM onto Activated Carbon II: Competitive Effects. Carbon 40, 2147–2156.

Pelekani, C., Snoeyink, V., 1999. Competitive adsorption in natural water: role of activated carbon pore size. Water Res. 33, 1209–1219.

Pelekani, C., Snoeyink, V.L., 2000. Competitive adsorption between atrazine and methylene blue on activated carbon: the importance of pore size distribution. Carbon 38, 1423–1436.

Pelekani, C., Snoeyink, V.L., 2001. Kinetic and equilibrium study of competitive adsorption between atrazine and Congo red dye on activated carbon: the importance of pore size distribution. Carbon 39, 25–37.

Pichon, V., Chapuis-Hugon, F., 2008. Role of molecularly imprinted polymers for selective determination of environmental pollutants-a review. Anal. Chim. Acta 622, 48–61.

Quinlivan, P.A., Li, L., Knappe, D.R.U., 2005. Effects of activated carbon characteristics on the simultaneous adsorption of aqueous organic micropollutants and natural organic matter. Water Res. 39, 1663–1673.

Rochester, J.R., 2013. Bisphenol A and human health: a review of the literature. Reprod. Toxicol. 42, 132–155.

Segner, H., Caroll, K., Fenske, M., Janssen, C.R., Maack, G., Pascoe, D., et al., 2003. Identification of endocrine-disrupting effects in aquatic vertebrates and invertebrates: report from the European IDEA project. Ecotoxicol. Environ. Saf. 54, 302–314.

Snyder, S.A., Adham, S., Redding, A.M., Cannon, F.S., DeCarolis, J., Oppenheimer, J., et al., 2007. Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. Desalination 202, 156–181.

Vieno, N., Tuhkanen, T., Kronberg, L., 2006. Removal of pharmaceuticals in drinking water treatment: effect of chemical coagulation. Environ. Technol. 27, 183–192.

Wei, S., Molinelli, A., Mizaikoff, B., 2006. Molecularly imprinted micro and nanospheres for the selective recognition of 17 beta-estradiol. Biosens. Bioelectron. 21 (10), 1943–1951.

Xia, X., Lai, E.P.C., Ormeci, B., 2012a. Ultrasonication assisted synthesis of molecularly imprinted polymer encapsulated magnetic nanoparticles for rapid and selective removal of 17β

estradiol from aqueous environment. Polym. Eng. Sci. 52, 1775–1783.

Xia, X., Lai, E.P.C., Ormeci, B., 2012b. Duo-molecularly imprinted polymer-coated magnetic particles for class-selective removal of endocrine-disrupting compounds from aqueous environment. Environ. Sci. Pollut. Res. Int. 20 (5), 3331–3339.

Xu, Z., Zhang, Q., Fang, H., 2003. Applications of porous resin sorbents in industrial wastewater treatment and resource recovery. Crit. Rev. Environ. Sci. Technol. 33, 363–389.