Superfine powdered activated carbon (S-PAC) coatings on microfiltration membranes: Effects of milling time on contaminant removal and flux

Pauline Amaral^a, Erin Partlan^b, Mengfei Li^b, Flavio Lapolli^a, O. Thompson Mefford^c, Tanju Karanfil^b, David A. Ladner^{b*}

^a*Department of Environmental and Sanitary Engineering, Federal University of Santa Catarina, Campus Reitor João David Ferreira Lima, s/n, Trindade, Florianópolis, SC 88040-900, Brazil.*

^b*Department of Environmental Engineering and Earth Sciences, Clemson University, 342 Computer Ct, Anderson, SC, 29625, USA.*

^c*Department of Materials Science and Engineering, 161 Sistine Hall, Clemson University, Clemson, SC 29634, USA.*

*Corresponding author: ladner@clemson.edu

1 Abstract

2 In microfiltration processes for drinking water treatment, one method of removing
3 trace contaminants is to add powdered activated carbon (PAC). Recently, a
4 version of PAC called superfine PAC (S-PAC) has been under development. S-
5 PAC has a smaller particle size and thus faster adsorption kinetics than
6 conventionally sized PAC. Membrane coating performance of various S-PAC
7 samples was evaluated by measuring adsorption of atrazine, a model
8 micropollutant. S-PACs were created in-house from PACs of three different
9 materials: coal, wood, and coconut shell. Milling time was varied to produce S-
10 PACs pulverized with different amounts of energy. These had different particles
11 sizes, but other properties (e.g. oxygen content), also differed. In pure water the
12 coal based S-PACs showed superior atrazine adsorption; all milled carbons had
13 over 90% removal while the PAC had only 45% removal. With addition of calcium
14 and/or NOM, removal rates decreased, but milled carbons still removed more
15 atrazine than PAC. Oxygen content and specific external surface area (both of
16 which increased with longer milling times) were the most significant predictors of
17 atrazine removal. S-PAC coatings resulted in loss of filtration flux compared to an
18 uncoated membrane and smaller particles caused more flux decline than larger
19 particles; however, the data suggest that NOM fouling is still more of a concern
20 than S-PAC fouling. The addition of calcium improved the flux, especially for the
21 longer-milled carbons. Overall the data show that when milling S-PAC with
22 different levels of energy there is a tradeoff: smaller particles adsorb
23 contaminants better, but cause greater flux decline. Fortunately, an acceptable
24 balance may be possible; for example, in these experiments the coal-based S-
25 PAC after 30 minutes of milling achieved a fairly high atrazine removal (overall
26 80%) with a fairly low flux reduction (under 30%) even in the presence of NOM.
27 This suggests that relatively short duration (low energy) milling is viable for
28 creating useful S-PAC materials applied in tandem with microfiltration.
29

Keywords: activated carbon, contaminant, milling time, microfiltration membranes

30 **1. Introduction**

31 Activated carbon adsorption is a common and generally effective treatment
32 method for removing small molecular weight organic compounds in water
33 treatment plants (Kemmer, 1988; Crittenden et al., 2012). Most commercial
34 carbons are produced from naturally occurring carbonaceous materials, such as
35 coal, oil, peat, coconut shell and wood, by chemical or thermal activation of
36 carbonized material. Activated carbon can be applied in powdered (PAC) or
37 granular (GAC) form (Snoeyink & Chen, 1985; Wigmans, 1989). A more recent
38 approach in carbon adsorption is the use of its superfine powdered form (S-PAC)
39 produced by grinding PAC until its particle size has been reduced to near or below
40 one micrometer (Partlan et al., 2015).

41 The motivation behind S-PAC is an improved adsorbate uptake rate, since
42 smaller carbon particles have faster adsorption kinetics than larger carbon
43 particles (Najm et al., 1990). The faster adsorption kinetics can be explained by
44 a shorter travel distance for intraparticle radial diffusion in the smaller particles
45 (Sontheimer et al., 1988; Matsui et al., 2009). Studies showed a better adsorbate
46 uptake rate by S-PAC, when compared with PAC, of compounds such as
47 geosmin, 2-methylisoborneol (MIB), atrazine, and natural organic matter (NOM)
48 (Heijman et al., 2009; Matsui et al., 2009, 2012, 2013; Ando et al., 2010; Ellerie,
49 et al., 2013).

50 We recently examined the effects of varied milling time by pulverizing PAC into
51 S-PAC with a bead mill (MiniCer, Netzsch Premier Technologies, Exton, PA,
52 USA) for different lengths of time while holding recirculation flow rate and mill
53 rotational speed constant (Partlan et al., 2015). Adjusting milling time is a
54 convenient way to vary the energy received by each carbon sample; thus, we

55 examined the effects of varying energy of pulverization; in our discussion *milling*
56 *time* is a surrogate for *energy input*. Other milling machines operated with
57 different rotational speeds and flow rates would, of course, impart different
58 energies than in this study. Our previous work treats this topic in some detail
59 (Partlan et al., 2015). In addition to particle size reduction, the milling process
60 may cause several other physicochemical changes that also impact the
61 adsorption performance, such as shifts in oxygen content and pH. An increase in
62 oxygen content can result in decreased adsorption of organic compounds by
63 activated carbons (Karanfil et al., 1999; Considine et al., 2001). The pH_{pzc} values
64 indicate the acidity/basicity characteristics of the carbon, which affect preferential
65 adsorption with respect to adsorbate charge (Dastgheib et al., 2004).

66 One of the challenges of working with S-PAC is the removal of such small
67 particles from water after the adsorption process. PAC removal is usually done
68 through coagulation/flocculation, sedimentation, and granular media filtration.
69 Membrane filtration is also effective for PAC, though the membrane module and
70 process design should be engineered to accommodate PAC presence (Chang et
71 al., 2005; Kim et al., 2005; Gai & Kim, 2007; Damayanti et al., 2011; Khan et al.,
72 2011). When using membranes to remove S-PAC, a cake layer is formed from
73 the accumulation of particles on the membrane surface. This layer can also be
74 applied intentionally to serve as a thin adsorption column (Heijman et al., 2009;
75 Ellerie et al., 2013). The pre-coat is responsible for a significant amount of
76 micropollutant removal and can also protect the membrane from fouling, since
77 the foulant is adsorbed or attached to the pre-coat before it can reach the
78 membrane. PAC particle sizes are large enough that membrane pores are not
79 blocked, but smaller particles, such as S-PAC, can block pores and/or form a

80 layer of relatively low permeability that can cause flux decline (Yiantsios &
81 Karabelas, 2001; Williams et al., 2005; Ando et al., 2010; Ellerie et al., 2013).
82 One obvious engineering goal is to use S-PAC particles that are small enough to
83 achieve good adsorption kinetics, but large enough to prevent significant flux
84 reduction. Matsui et al. (2009), found that S-PAC with a median diameter of 0.88
85 μm did not reduce membrane permeability of MF ceramic membranes with
86 nominal pore size of 0.1 μm ; in fact, it alleviated long term trans-membrane
87 pressure buildup by removing foulants that contribute to hydraulically irreversible
88 fouling. Further studies are needed to evaluate how particles of various size and
89 material properties contribute to membrane fouling, and how this can be mitigated
90 while still achieving good micropollutant removal.

91 Another consideration while using activated carbon in water treatment is
92 competition from NOM adsorption. One of the drawbacks of PAC is that
93 micropollutant adsorption capacity can be dramatically reduced in the presence
94 of NOM due to pore blockage by high molecular weight (MW) NOM and by
95 loading of low MW NOM onto the intraporous adsorption sites of PAC (Kilduff et
96 al., 1998). NOM competition can be important since the NOM concentration in
97 natural waters is typically several orders of magnitude higher than the
98 concentration of micropollutants. S-PAC typically has a higher adsorption
99 capacity for NOM than PAC due to a higher specific external surface area; NOM
100 molecules do not completely penetrate the adsorbent particle but instead
101 preferentially adsorb near the exterior particle surface (Matsui et al., 2004, 2011,
102 2012; Ando et al., 2010).

103 The objective of this paper is to understand how the performance of adsorptive
104 activated carbon membrane coatings is affected by physicochemical changes in

105 the carbon when milled to small sizes. While the primary outcome of milling is
106 physical particle size reduction, secondary effects to the carbon surface
107 chemistry can affect interactions with adsorbate chemistry and affect particle
108 stability, which impacts coating formation. Coatings are evaluated for fouling
109 propensity via decline in flux over filtration time, and for adsorption performance
110 via contaminant presence in the membrane permeate. Lastly, we varied the water
111 matrix, including the addition of hardness via calcium, to evaluate applications to
112 drinking water treatment scenarios.

113 **2. Materials and Methods**

114 **2.1 Adsorbents**

115 Three commercially available activated carbon materials were chosen for
116 comparison in this study: WaterCarb-800 (bituminous coal, Standard
117 Purification), Aqua Nuchar (wood, Mead Westvaco) and Aquacarb 1230C
118 (coconut shell, Siemens), referred to as BC, WD and CS respectively.

119 The S-PAC was produced from the corresponding PAC using a wet bead mill
120 (MiniCer, Netzch Premier Technologies, Exton, PA, USA) containing 0.3–0.5 mm
121 yttrium-stabilized zirconium oxide ceramic beads. Passing one batch of PAC
122 slurry through the mill required 45 seconds, which corresponded with
123 approximately six seconds of residence time for any given particle in the mill. The
124 total milling time (the time spent recirculating slurry through the mill) was varied,
125 ranging from one pass to six hours for BC and WD carbons and from one pass
126 to four hours for CS carbon.

127 Material characteristics and characterization methods for these PACs and S-
128 PACs were reported previously (Partlan et al., 2015). For particles smaller than
129 6 μm , size distributions were determined by dynamic light scattering (DLS) using

130 a Zetasizer NanoZS (Malvern, Worcestershire, UK). Particles larger than 6 μm
131 were measured by optical microscopy imaging using a Zeiss Axioskop 2 Plus
132 optical microscope (40x objective lens) with a Zeiss AxioCam MRc5 camera
133 attachment running AxioVision AC version 4.2 software. Surface area was
134 calculated with the Brunauer-Emmett-Teller (BET) equation, using the N_2
135 physisorption data at 77K obtained with an ASAP 2020 analyzer (Micromeritics
136 Instrument Corp. U.S). The pH at which the adsorbent surface had net zero
137 charge (pH_{pzc}) was determined using the pH drift method. In this method, for each
138 pH tested, 100 mg of dry carbon was contacted with 20 mL of pH-adjusted 0.1 M
139 NaCl. After a minimum of 48 hours on a shaker table pH was measured in the
140 sample vial and compared to a no carbon blank vial. The measurement of weight
141 percent of oxygen was performed using a Flash Elemental Analyzer 1112 series
142 (Thermo Electron Corporation). A scanning electron microscope (SEM, Hitachi
143 SU6600) was used for acquiring images of the platinum coated dried membrane
144 and S-PACs.

145 Surface area, external surface area, particle size, pH_{pzc} and oxygen content for
146 all PACs and S-PACs are shown in Table 1. We use the milling time as the
147 designation for each sample in our discussion; the reader is referred to Table 1
148 to connect these milling time designations with the sample properties.

149 **2.2 Filtration through Membrane Coatings**

150 The direct-flow MF setup consisted of an 800 mL capacity pressure vessel that
151 held the feed solution, a 10 mL membrane cell (Amicon, Millipore) containing the
152 MF membrane and mesh support material, a flask for permeate collection, and a
153 balance connected to a computer to monitor flux (Fig. 1). Pressure for filtration,
154 fixed at 10 psi, was supplied by a nitrogen tank connected to the pressure vessel.

155 The membranes were hydrophilic PVDF (Millipore VVLP) with 0.1 μm pore size
156 and 2.5 cm diameter (2.1 cm active diameter when installed in the filtration cell);
157 each membrane was soaked in distilled and deionized (DDI) water overnight
158 before use. The uncoated membrane flux was determined via DDI water filtration
159 for 20 minutes. A stock solution of 2000 mg/L S-PAC in deionized water was used
160 for carbon addition. Aliquots of 40 mL stock solution were sonicated for 4 minutes
161 with a probe sonicator at 50% power (S-4000, Qsonica, LLC), before addition to
162 ensure disaggregation. An appropriate volume of the sonicated stock solution to
163 achieve the desired carbon mass was added to water directly in the membrane
164 cell without a stirring system. The filtration process caused the particles to
165 accumulate on the membrane surface forming a non-rigid carbon layer. The
166 carbon mass added to the membrane cell was 1, 2 and 4 mg, depending on the
167 experiment.

168 In each experiment 400 mL of feed solution was filtered and the permeate was
169 collected in 20 mL glass vials. Samples for analysis were prepared by mixing two
170 consecutive 20 mL vials, then pulling 5 mL out for further analysis (described
171 below); ten such samples were measured per filtration.

172 **2.3 Feed Water Composition**

173 The herbicide atrazine was chosen as the model micropollutant for this study.
174 Atrazine is one of the most widely used herbicides in the world; due to his high
175 mobility in soil, atrazine and its metabolites are commonly found in ground water,
176 surface water and drinking water supplies (Pereira & Rostad, 1990; Koplin et al.,
177 1997; Brown et al., 2004; Graziano et al., 2006). Several studies have been
178 conducted aiming to improve the removal efficiency of this compound from water

179 (Berg et al., 1997; Li et al., 2003; Yoon et al., 2006; Jia et al., 2006; Chen et al.
180 2009), which allows a comparison with the S-PAC data presented here.

181 Atrazine is a hydrophobic compound with a moderate water solubility ($S_w = 30$
182 mg/L), low octanol/water partition ($\log K_{ow} = 2.75$) and electron rich nitrogen and
183 chlorine groups that make it polar (Colombini et al., 1998). The atrazine
184 concentration in the feed solution was 15 $\mu\text{g/L}$. ^{14}C labeled atrazine, with a
185 specific activity of 160 mCi/mmol (American Radiolabeled Chemicals, Inc), was
186 used as a tracer among non-labeled atrazine (Accustandard) in a ratio of 1:300.
187 Radioactivity was measured by liquid scintillation counting (LSC) (Tri-Carb
188 B2910TR, PerkinElmer) of samples mixed 1:1 with scintillation cocktail
189 (UltimaGold XR). The detection limit of the method was approximately 0.07 ppb.

190 Suwannee River NOM (SRNOM) (International Humic Substances Society,
191 Golden, Colorado) was used as the primary NOM source. SRNOM stock solution
192 (500 mg/L) was prepared in DDI water and filtered through a 0.15 μm microfiber
193 filter (Whatman). In all trials with SRNOM, the dissolved organic carbon (DOC)
194 concentration was adjusted to 8 mg/L. Additionally, a buffer of 1 mM NaHCO_3
195 plus NaCl for a total ionic strength of 10 mM was added. Some experiments were
196 performed with the addition of 40 mg/L Ca^{2+} (111 mg/L CaCl_2) to contribute 3 mM
197 ionic strength; NaCl was reduced in these cases to maintain a total ionic strength
198 of 10 mM. The pH of all solutions was adjusted to 7.0 ± 0.1 with HCl or NaOH as
199 required.

200 Water from the Edisto river (South Carolina, US) was used in some experiments
201 as a natural water source. The DOC concentration was approximately 6.5 mg/L,
202 and the water was filtered by microfiber filters (Whatman) to remove suspended

203 particles before use. In experiments with SRNOM and Edisto water, DOC was
204 measured with a Shimadzu TOC-VCHS analyzer.

205 **2.4 Batch Adsorption Kinetics**

206 Bottle point kinetic experiments were performed with atrazine and BC carbon. In
207 each experiment, 200 mL of the solution containing 15 µg/L of atrazine, with and
208 without SRNOM (8 mg/L), were contacted with 2.5 mg/L of carbon in 250 mL
209 glass bottles with Teflon-lined screw caps. The bottles were mixed on a benchtop
210 shaker. Samples were taken every five minutes for the first 30 minutes and every
211 30 minutes after that for a total time of four hours. Carbon was promptly removed
212 from samples via filtration through a 0.15 µm microfiber filter (Whatman), with
213 membrane retention of less than 2% of the atrazine.

214 **3. Results and discussion**

215 **3.1 Flux Decline**

216 In DDI, membrane coatings with BC S-PACs resulted in little loss of flux, only 1–
217 14%, except for BC-6 hrs, which resulted in 55% flux decline. Flux reduction was
218 higher when SRNOM was present (Fig. 2a). BC PAC had a flux reduction of 27%,
219 around the same as BC-1 Pass (27%), BC-15 min (27%), BC-30 min (29%), as
220 well as the uncoated membrane (23%). Thus, SRNOM was the main driving force
221 for flux decline, not the carbon particles. BC-2 hrs and BC-6 hrs had very
222 accentuated flux decline, 76% and 84% respectively, which was significantly
223 higher than their flux declines without SRNOM.

224 The addition of calcium improved flux in the presence of NOM (Fig. 2b). Calcium
225 improved the BC-2 hrs flux decline from around 75% to 25%, and even the most
226 heavily fouling carbon, BC-6 hrs, saw improvement from 84% to 77%. This
227 improvement would not be expected since many researchers (Hong & Elimelech,

1997; Zhu & Elimelech, 1997; Seidel & Elimelech, 2002; Li & Elimelech, 2006) pointed out that the presence of divalent ions may add to the development of fouling by NOM. Calcium has a strong potential to complex with NOM and is capable of forming bridges between the membrane surface and NOM (Li & Elimelech, 2004; Listiarini et al., 2009). With regard to membrane coatings, we speculate that the flux improvement may be due to the carbon layer acting as a protective barrier and absorbing some of the NOM, thus not allowing it to reach the membrane and cause flux decline. In addition to facilitating NOM coiling for access to internal pores, calcium can also enhance NOM adsorption by acting as a bridge between NOM and the carbon in the same way as the NOM-membrane bridge, which allows for adsorption of NOM aggregates onto carbon. These mechanisms also explain the decrease in atrazine removal and slight increase in NOM removal by the carbon in the presence of both NOM and calcium.

SEM images were taken of membranes coated with BC-1 Pass and BC-6 hrs that filtered feed solutions containing atrazine in a mild NaCl solution (Fig. 3). The carbon deposition is visible on the membrane surface, especially for images (a) and (c) which show the entire membrane thickness. The difference in the carbon layer formation between the two S-PACs is clear; the small particles of BC-6 hrs compressed to form a compact cake layer, while BC-1 pass with larger particles did not form a tight cake.

Particle size was an important parameter for the S-PAC coated membrane permeate flux decline. The data discussed above in Fig. 2 showed that the longest milling time had the greatest flux decline in the BC carbon case. When plotted with particle size explicitly on the X-axis (Fig. S1) we can observe the flux vs. particle-size relationship and make a direct comparison with the WD and CS

253 carbons. All carbon types showed a much lower average permeate flux with the
254 smallest particles (longest milling times). For the other milling times, there is a
255 general trend of higher flux with higher particle size (though WD-1 Pass is an
256 outlier). It is noteworthy that the trend is not linear; there seems to be a size
257 threshold where flux decline is suddenly intense for the smallest particles, and
258 that threshold depends on carbon type. This suggests that as long as the particle
259 size remains above a certain value, one can gain the adsorption benefits of
260 smaller particle size without paying a significant penalty in flux decline. The
261 adsorption (i.e. contaminant removal) benefits are described in the following
262 section.

263 When increased masses of carbon were used to coat the membrane, changes in
264 flux decline were relatively minimal; membranes coated with 4 mg of BC PAC,
265 BC-1 Pass and BC-6 hrs had almost the same flux decline as the corresponding
266 1 mg coating, while other carbons resulted in slight increases (Fig. S2). The
267 largest increase was from 27% with 1 mg to 55% with 4 mg using BC-2 hrs.

268 **3.2 Contaminant Removal**

269 For every condition studied and for each carbon tested, the atrazine removal by
270 S-PACs was superior to the respective parent PACs. Feed solutions containing
271 atrazine in a) DDI, b) SRNOM, and c) SRNOM with Ca^{2+} were filtered through 1
272 mg of BC coated on an MF membrane (Fig. 4). Controls revealed that uncoated
273 membranes adsorbed at most 20% of atrazine, depending on the water
274 composition. In DDI water, BC PAC had high initial atrazine adsorption, 92%;
275 however, the retention dropped to 50% after filtering 200 mL and to only 15%
276 after filtering 400 mL for an overall removal of 45% (Fig. 4a). BC S-PACs removed
277 more than 90% of atrazine on average, reaching 99% for BC-15 min, BC-30 min,

278 BC-1 hr and BC-6 hrs. These results are consistent with previous studies that
279 show faster adsorption onto S-PAC due to its smaller size (Ando et al., 2010;
280 Ellerie et al., 2013; Matsui et al., 2013).

281 In the presence of SRNOM, the atrazine retention increased with milling time,
282 except for BC-6 hrs (Fig. 4b). BC PAC, BC-1 Pass, BC-15 min and BC-30 min
283 showed high initial atrazine removal that decreased over the course of filtration.
284 BC-1 hr and BC-2 hrs had consistent atrazine removal over the course of
285 filtration, with an overall removal of 95% each. Similar results were observed in
286 experiments using Edisto River water instead of SRNOM; again, atrazine removal
287 increased with milling time except for BC-6 hrs (Fig. S3). These data are
288 consistent with a previous report where better atrazine retention was achieved by
289 S-PAC membrane coatings in water containing NOM (Heijman et al., 2009). The
290 results of this study confirm that size is the dominant factor in atrazine removal
291 performance.

292 With the addition of calcium, atrazine broke through earlier (Fig. 4c). BC PAC
293 only removed 7% of the atrazine with no atrazine removal after 200 mL filtered.
294 Again, atrazine removal increased with milling time, except for BC-6 hrs, from
295 24% (BC-1 Pass) to 81% (BC-2 hrs). The decrease of atrazine removal in this
296 case may be related to coiled NOM. Some authors (Braghetta et al., 1997;
297 Leenheer, 2007) state that NOM macromolecules may change shape, including
298 coiling and uncoiling, as a function of pH, ionic strength and interactions with
299 cations and minerals. Coiling can occur when calcium complexation causes
300 reduced electrostatic repulsion among the branches of NOM macromolecules
301 (Hong & Elimelech, 1997). The coiled NOM is smaller and can reach deeper into

302 the carbon internal pores, thus competing more readily with atrazine for
303 adsorption sites or blocking atrazine out the pores.

304 Filtration experiments performed with additional carbon types exhibited varied
305 results. WD showed no correlation between milling time and atrazine removal;
306 the highest atrazine removal was obtained with WD-10 min and WD-20 min, 58%
307 and 55%, and the lowest, 18%, was obtained with WD-5 min (Fig. 5a). CS
308 showed an increase in atrazine removal with milling time, from an overall removal
309 of 13% with the parent PAC to 93% with CS-4 hrs (Fig. 5b).

310 Atrazine concentrations were measured during the increased carbon mass trials
311 where 2 mg and 4 mg of BC carbon were used in water containing SRNOM and
312 calcium (Fig. S4). BC PAC had ten times higher atrazine removal with 4 mg than
313 with 1 mg, and BC-1 Pass had twice the removal with 2 mg as 1 mg and an
314 additional 50% removal from 2 mg to 4 mg. The other BC S-PACs achieved more
315 than 90% atrazine removal with 2 mg, which is a significant improvement
316 considering BC-15 min, BC-30 min and BC-6 hrs had an overall removal below
317 70% with the 1 mg coating, though the 4 mg coating did not result in additional
318 removal (Fig. S4a, Fig S4b). Removal of NOM did not change with increased
319 carbon mass and was generally minimal (Fig. S4c, Fig. S4d).

320 Results of removals through carbon coatings are in agreement with batch
321 adsorption kinetics that showed high atrazine adsorption onto S-PAC under very
322 short contact times (Fig. 6). In DDI water, BC PAC showed 61% atrazine removal
323 within 5 minutes, BC-1 Pass had 73%, and other S-PACs had over 97% removal
324 (Fig. 6a). Similar results were seen in the presence of NOM; within 5 minutes, BC
325 PAC had 28% atrazine removal, while BC-30 min, BC-1 hr, BC-2 hrs and BC-6
326 hrs had near or over 90% atrazine removal (Fig. 6b). These results support the

idea that faster adsorption kinetics is the mechanism behind the enhanced contaminant removal observed in membrane coatings with smaller S-PAC particles.

For all carbons, the atrazine adsorption uptake was smaller in SRNOM-containing water. The presence of SRNOM reduced the atrazine removal by BC-PAC around 35% and by BC S-PAC about 48% (1 Pass), 17% (15 min), 13% (30 min), 4% (1 hours), 3% (2 hours) and 36% (6 hours). Those results indicate that NOM competition is less intense for most of the S-PACs.

NOM adsorption, either from the SRNOM source or the Edisto River water, was not found to be significantly higher on S-PAC than PAC (Fig. S5 and Fig. S6). At equilibrium, NOM can be expected to have a larger adsorption capacity on S-PAC since NOM mainly adsorbs close to the external adsorbent particle surface and does not completely penetrate into internal pores (Ando et al., 2010, 2011; Matsui et al., 2011). However, here, under high NOM concentrations and short contact times, the unchanged NOM adsorption rate and increased atrazine adsorption rate results in reduced NOM competition with S-PAC, probably because there were more pores available than in PAC.

3.3 Adsorbent Properties Influencing Performance

In order to elucidate the key S-PAC properties that affect performance, atrazine removal was correlated against physical and chemical properties of S-PAC, including oxygen content, specific surface area, particle size, and specific external surface area. In drinking water treatment, effects of adsorbent surface chemistry are important since adsorption proceeds via displacement of the existing water-covered surface by the dissolved pollutant molecules (Pendleton et al., 1997).

352 For a 1 mg coating of BC, CS, and WD PAC and S-PACs, atrazine removal
353 correlated most strongly with specific external surface area, and less with the
354 other measurements (Fig. 7). Oxygen content increased with milling time for the
355 carbons BC, WD and CS, which was a result of external surface oxidation likely
356 originating from a highly abrasive milling environment (Partlan et al., 2015). The
357 oxygen content density, that is the oxygen content normalized to the external
358 surface area, is consistent among S-PACs. Oxygen content was the best single
359 predictor of CS atrazine adsorption (Fig. 7a). BC and WD results are consistent
360 with those presented by Yu et al. (2007); for MIB and geosmin adsorption on a
361 carbon with a broad pore volume distribution, they saw no statistically significant
362 correlation between the adsorption capacity and the carbon's oxygen content or
363 surface functional groups.

364 Though surface area typically correlates with increased adsorption capacity,
365 several studies also found that higher surface area does not always result in
366 higher removal efficiency of the carbon (Mondal et al., 2015; Liu et al., 2013;
367 Sardella et al., 2015; Hadi et al., 2015). WD had the highest surface area,
368 approximately 1500 m²/g compared to 1000 m²/g or less in BC and CS carbons,
369 as well as the largest change with milling time, losing 500 m²/g over 6 hours of
370 milling, but these changes did not correlate with WD atrazine removal (Fig. 7b).

371 Atrazine adsorption increased with the decreased particle size between PAC and
372 S-PAC, where removals increased from 20% to 99%, but correlated less so
373 among S-PACs (Fig. 7c). Specific external surface area, as calculated from
374 particle size measurements, proved to be the best predictor of atrazine removal
375 on BC S-PACs and WD S-PACs, despite a poor correlation due to one outlier
376 data point for WD, as well as a fair predictor of CS S-PACs (Fig. 7d).

Multiple linear regression analysis was used to predict atrazine removal from these four parameters. A significant regression equation was found ($F(3, 17) = 15.64$, $p < 0.0001$), with an R^2 of 0.734. Atrazine removal was predicted by $15.89 + 0.04 (\text{OXY}) + 5.98 (\text{SA}_{\text{ext}}) - 1.26 (\text{OXY} \cdot \text{SA}_{\text{ext}})$ where oxygen content (OXY) is measured in weight percent oxygen and specific external surface area is measured in m^2/g . Oxygen content and specific external surface area are correlated with each other since it is expected that the majority of new oxygen is attached to the external surfaces only (Partlan et al., 2015). With these two parameters as the most significant predictors of atrazine removal, the model suggests that interactions at the external surface may be the most crucial component of the adsorption pathway. In regards to membrane filtration with carbon coatings—a situation with very short contact times—the best way to achieve good contaminant removal is to increase the surface area that water and contaminants contact first as they travel through the adsorbent layer.

3.4 Tradeoffs between contaminant removal and energy requirements

The benefits of carbon particle size reduction to increased atrazine removal are countered by the increased energy requirements of producing the S-PACs and increased cost of application due to higher head loss. To evaluate S-PAC efficiency, atrazine removal for each S-PAC is compared with the permeate flux of coated membranes as well as production energy, given that milling time is linearly related to energy input. The best scenario would require minimal processing, result in minimal flux decline, and provide high atrazine removal. BC S-PACs milled for 15 minutes and 30 minutes showed atrazine removal over 60% and a relatively low flux decline (Fig. 8). WD also showed a good balance between atrazine removal and permeate flux at lower milling times; WD-10 min

402 was the most favorable WD S-PAC. CS S-PACs also followed this pattern, with
403 CS-20 min as the most favorable S-PAC due to flux decline, but it did not have
404 the highest atrazine removal, which was achieved with CS-4 hrs and a flux
405 decline of 70%. Additional milling times for CS may reveal an ideal milling time
406 between 20 minutes and 4 hours. Overall, BC-15 min and BC 30-min had the
407 best performance in this sample set; they showed high atrazine removal
408 combined with lower energy input.

409 **Conclusions**

410 The main conclusions from this study are as follows:

- 411 • Rapid adsorption onto S-PAC allows for the creation of useful adsorbent
412 membrane coatings. All S-PAC coatings removed atrazine better than the
413 parent PAC coatings regardless of NOM or calcium presence.
- 414 • Oxygen content and specific external surface area (both of which
415 increased with longer milling times) were the most significant predictors of
416 atrazine removal. The two are correlated, since oxygen increases
417 preferentially on the external surfaces.
- 418 • Membrane coating performance depended heavily on water quality. NOM
419 caused increased flux decline and also lowered atrazine removal. It is
420 important to note that the NOM was the main cause of fouling in most
421 cases, rather than the S-PAC. If this is true at full scale, it bodes well for
422 this hybrid process, as the fouling from S-PAC addition may be
423 inconsequential compared to the fouling already present.
- 424 • Calcium resulted in improved flux in the presence of NOM because
425 calcium aided the capture of NOM in the carbon layer, rather than allowing

426 it to reach the membrane. Calcium also resulted in less atrazine removal,
427 demonstrating a tradeoff between NOM aggregation/capture and trace
428 contaminant removal.

429 • An ideal particle size balances an increased adsorption rate with
430 acceptable loss of flux. Only the longest milled carbons (those that
431 received the highest total milling energy) caused severe flux decline, while
432 atrazine removal increased steadily with increased milling time. In this
433 study carbons milled for the relatively short time (relatively low energy) of
434 10–30 minutes were the most favorable.

435

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620

621 **Table**

622

623 Table 1: Surface area, external surface area, particle size, pH_{pzc} and oxygen content of PACs
 624 and S-PACs (Partlan et al., 2015).

Carbon	Specific Surface Area (m ² /g)	Specific External Surface Area (m ² /g)	Particle Size (nm)	pH _{pzc}	Oxygen Content (%)
BC					
PAC	644	0.24	12300	10.37	2.41
1 pass	777	4.78	628	9.31	2.79
15 min	786	6.95	431	9.09	3.51
30 min	857	7.53	398	8.92	4.19
1 hr	872	9.12	329	8.07	5.23
2 hrs	642	9.10	329	8.10	5.87
6 hrs	762	12.00	230	7.75	7.86
WD					
PAC	1676	0.26	11300	6.20	7.14
1 pass	1642	2.54	1183	6.25	7.25
5 min	1575	3.30	1287	6.03	7.80
10 min	1542	4.51	665	5.72	7.85
20 min	1521	5.08	590	5.82	8.30
1 hrs	1269	6.11	491	5.11	9.15
6 hrs	1008	6.80	440	4.95	10.50
CS					
PAC	1027	0.26	11300	10.79	3.38
1 pass	1134	3.90	770	10.73	3.71
2 pass	895	4.92	610	10.44	3.84
5 min	932	4.94	633	10.57	3.91
10 min	938	4.86	617	10.47	3.99
20 min	1047	5.18	579	10.33	4.06
4 hrs	1097	8.98	334	8.00	5.38

625

626

627 **Figure Captions**

628

629 **Fig. 1. Schematic of the direct-flow MF setup (Millipore).**

630 **Fig. 2. Flux measurements for the 1 mg BC carbon coated MF membranes with (a) SRNOM,**
631 **NaHCO₃ and NaCl and (b) SRNOM, Ca²⁺, NaHCO₃ and NaCl. In all the experiments the pH**
632 **was adjusted to 7.0.**

633 **Fig. 3. SEM images of BC 1 Pass (a) 500X magnification and (b) 5,000X magnification as**
634 **well as BC 6 hours (c) 500X magnification and (d) 5,000X magnification, deposited on the**
635 **MF membrane surface. The white scale bar is 20 μm long.**

636 **Fig. 4. Normalized atrazine concentration (measured concentration divided by the 15 μg/L**
637 **feed concentration) after filtration with 1 mg BC carbon coated MF membranes and feed**
638 **solution (a) DDI water (b) SRNOM, NaHCO₃ and NaCl and (c) SRNOM, Ca²⁺, NaHCO₃ and**
639 **NaCl. In all the experiments the pH was adjusted to 7.0.**

640 **Fig. 5. Normalized atrazine concentration (measured concentration divided by the 15 μg/L**
641 **feed concentration) after filtration with (a) WD carbon and (b) CS carbon 1 mg MF coated**
642 **membranes and feed solution with SRNOM, Ca²⁺, NaHCO₃ and NaCl. In all the experiments**
643 **the pH was adjusted to 7.0.**

644 **Fig. 6. BC carbon batch adsorption kinetics of atrazine with (a) DDI water and (b) SRNOM,**
645 **NaHCO₃ and NaCl. In all the experiments the pH was adjusted to 7.0.**

646 **Fig. 7. Comparison between characterization data as (a) oxygen content, (b) surface area,**
647 **(c) particle size and (d) external surface area with atrazine removal (%) for the carbons BC,**
648 **CS and WD 1 mg coated MF membranes. The feed water contained SRNOM, Ca²⁺, NaHCO₃**
649 **and NaCl and the pH was adjusted to 7.0.**

650 **Fig. 8. Comparison between atrazine removal and normalized permeate flux obtained with**
651 **1 mg BC, WD and CS S-PAC coated MF membranes. The feed water contained SRNOM,**
652 **Ca²⁺, NaHCO₃ and NaCl and the pH was adjusted to 7.0.**

653

Figure 1

Figure 2

● BC-PAC	■ BC-1 hr
▲ BC-1 pass	◆ BC-2 hours
▼ BC-15 min	■ BC-6 hours
◆ BC-30 min	○ No carbon

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

BC-PAC	WD-PAC	CS-PAC
BC-1 Pass	WD-1 Pass	CS-1 Pass
BC-15 min	WD-5 min	CS-2 Pass
BC-30 min	WD-10 min	CS-5 min
BC-1 hour	WD-20 min	CS-10 min
BC-2 hours	WD-1 hour	CS-20 min
BC-6 hours	WD-6 hours	CS-4 hours

Figure 8

Carbon milled briefly

Carbon milled extensively

Activated-carbon-coated membranes (dried)