

# Super-bridging Fibrous Materials for Water Treatment: Impacts on Removal of Plastic Particles, Phosphorus and Natural Organic Matter

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## Abstract

Aggregation combined with gravitational separation is the most commonly used method to treat water globally, but it carries a significant economic and environmental burden as the chemicals used in the process (e.g., coagulants) generate ~8 million tons of metal-based sludge waste annually. To simultaneously deal with the issues of process sustainability, cost, and efficiency, we developed materials reengineered from pristine or waste fibers to serve as super-bridging agents, adsorbents, and ballast media. This study shows that these sustainable fiber-based materials considerably increased the floc size (~6630  $\mu\text{m}$ ) compared to conventional physicochemical treatment using a coagulant and a flocculant (~520  $\mu\text{m}$ ). The fiber-based materials also reduced coagulant (up to 40%) and flocculant usage (up to 60%). Moreover, the unprecedented size of flocs produced using fiber-based materials (up to ~13 times larger compared to conventional treatment) enabled easy floc removal by screening, thereby eliminating the need for a settling tank, a large and costly process unit. Our results show that fiber-based materials can be effective solutions at removing classical (e.g., natural organic matter (NOM) and phosphorus) and emerging contaminants (e.g., microplastics and nanoplastics). Due to their large size (> 3000  $\mu\text{m}$ ), some Si-grafted and Fe-grafted fiber-based materials can be easily recovered from settled/screened sludge and reused multiple times for coagulation/flocculation. Our results also show that these materials could be used in synergy with coagulants and flocculants to improve settling in existing water treatment processes. Furthermore, these reusable materials combined with separation *via* screening could allow global water treatment facilities to reduce their capital and operating costs as well as their environmental footprint.

## 27    **Introduction**

28    Improving process sustainability and reducing costs are important challenges for the water treatment industry.  
29    Innovative approaches that consider more than just contaminant removal are thus needed to design water treatment  
30    systems for growing populations<sup>1,2</sup>. Gravitational separation technologies are used for the majority of solids removal  
31    globally. In North America, settling is at the core of water treatment, producing >70% of drinking water and treating  
32    >75% of municipal wastewater<sup>3-5</sup>. The performance of the aggregation/settling process is highly dependent on floc size  
33    and density and largely reliant on the use of costly and non-reusable coagulants/flocculants. These metal-based  
34    coagulants and synthetic flocculants are lost to the sludge that is subsequently sent to landfill – their accumulation can  
35    increase sludge toxicity and reduce the quality of sludge for potential use as agriculture fertilizer (Fig. 1a)<sup>6-8</sup>. Currently,  
36    water treatment relies on >25 million tons/year of coagulant and flocculant worldwide. The utilization of \$18 billion of  
37    heavy metal-based coagulant and synthetic flocculant<sup>9,10</sup> generates ~7.8 million tons of sludge yearly, representing one  
38    of the major environmental burdens of this technology. Coagulants account for up to 30–50 wt% of dried sludge<sup>11-13</sup>.  
39    Moreover, concerns about the toxicity of synthetic flocculants such as polyacrylamide have led to restrictions in some  
40    countries<sup>14,15</sup>.

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42    Advanced materials or processes that can reduce flocculant requirements represent important steps towards meeting  
43    regulations for polyacrylamide concentrations in water treatment. Reductions in coagulant and flocculant demand also  
44    directly translate into less sludge production<sup>16</sup>, lower energy and landfiling requirements<sup>6,7</sup>, and less heavy metals in  
45    sludge that can potentially be reused as agricultural fertilizer (Fig. 1a). One strategy is the use of naturally abundant  
46    fiber-based waste and recycled renewable resources, to fabricate reusable and versatile fiber-based materials to  
47    sustainably improve water treatment.

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49    In this study, cellulosic fibers were grafted with Si to generate reusable super-bridging and ballasting materials to  
50    promote particle aggregation and removal. The Si-fibers and porous Si-microspheres were generated using pristine  
51    fibers and fibers from recycled paper. These Si-grafted materials and other waste fibers such as polyester and cotton  
52    were synergistically used with coagulant, synthetic flocculant, and a bioflocculant (extracted from potato residue) to

53 increase floc size, density, and, ultimately, contaminant removal efficiency. Large flocs produced using these  
54 sustainable materials reached unprecedented sizes and settled considerably faster ( $\sim 8 - 26$  times).

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56 For decades, engineers and researchers have focused efforts on increasing floc settling velocity with the aim of reducing  
57 the settling tank size, cost, and footprint. With the large floc sizes that can be obtained using the super-bridging agents  
58 presented herein, compact screening methods for floc removal that are more sustainable and cost-effective can be  
59 implemented (Fig. 1b). A key advantage of screening versus settling is that floc removal is not controlled by the floc  
60 density and settling velocity, but rather by its size. Hence, very dense ballast media that offer a low active surface area,  
61 are no longer required. Finally, a three-in-one porous material was created by reengineering cellulosic fibers into Fe-  
62 stabilized flakes which effectively removed both particulate and soluble matter. This work shows that reusable grafted-  
63 fibers, fiber-based microspheres, and fiber-based flakes combined with screening are promising solutions to sustainably  
64 reduce the use of water treatment chemicals while reducing the size of water treatment plants.

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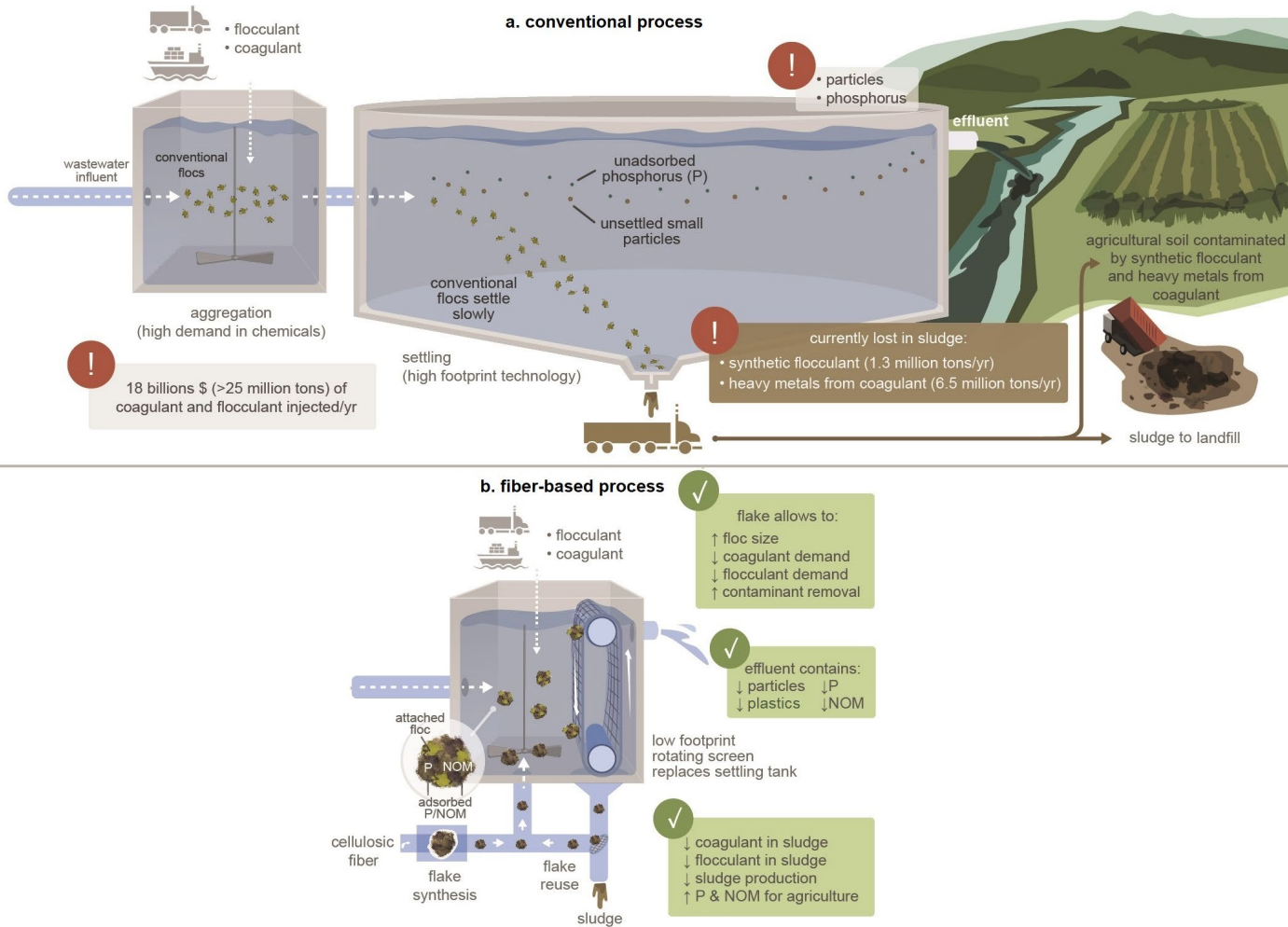
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77 **Results and discussion**

78 The objective of this work was to use fiber-based materials (Supplementary Table 1) to form flocs of unprecedented  
79 size, in an effort to improve the most commonly used separation technology (i.e., settling, Fig. 1a) or to replace it with  
80 a potentially more economical approach (i.e., screening, Fig. 1b).

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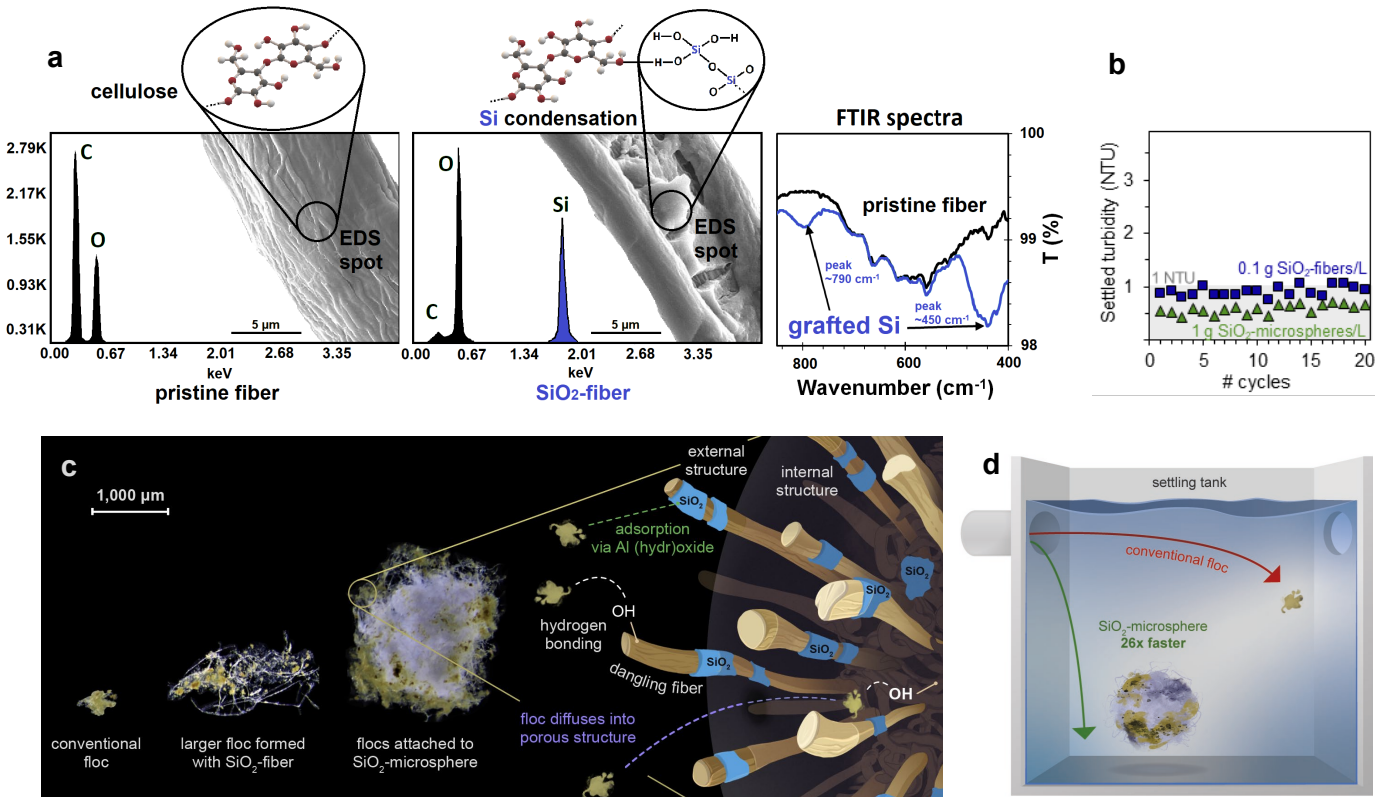
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83 **Fig. 1 | Using fiber-based materials in water treatment to improve process efficiency and sustainability. a,** The conventional  
84 water treatment process, which is responsible for more than 25 million tons of coagulant/flocculant are used globally to meet  
85 regulatory targets. The settling velocity of conventional flocs is low and large settling tanks are thus needed to compensate for their  
86 poor settleability. Single-use coagulants/flocculants are sent to landfill and agricultural soils. **b,** The fiber-based process. Fibers  
87 (cellulose, cotton, polyester, etc.) are converted into Fe-stabilized flakes that can be used as three-in-one  
88 bridging/ballasting/adsorbing material to simultaneously bridge colloids, ballast flocs, and adsorb contaminants whilst reducing  
89 coagulant and flocculant usage. Very large flocs generated with fiber-based materials are screenable, which allows to replace settling  
90 tanks with very low footprint screens.

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**Cellulose-based materials as effective bridging and ballasting agents**

We hypothesized that pristine and surface-modified fibers with lengths on the order of 1000  $\mu\text{m}$  could be used as effective bridging agents to achieve larger floc sizes, hence improving settling velocities. Silicon dioxide ( $\text{SiO}_2$ ) was grafted onto cellulosic fibers (Fig. 2a) to increase the material’s specific gravity and modify its interaction with coagulants (Al-based flocs diffuse in the porous structure and adsorb on grafted Si, Fig. 2c, far right). The presence of Si on the modified fiber surface was confirmed by Fourier-transform infrared spectroscopy (FTIR), and the amount of grafted Si was measured by thermogravimetric analysis (TGA) (Fig. 2a and Supplementary Fig. 1a). Depending on the synthesis method, the amount of grafted Si ranged from 4 to 26 wt% (Supplementary Fig. 1b). Grafting the pristine fibers with 26 wt% Si increased the relative density by  $\sim 10\%$  (from 1.40 to 1.54) (Supplementary Equation 1).  $\text{SiO}_2$  was grafted onto fibers as a thin layer estimated to be  $\sim 50\text{--}600$  nm thick (340 nm on average, Supplementary Equation 1), hence increasing the fiber cross-sectional area.



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**Fig. 2 | Characteristics and performance of fiber-based materials.** **a**, Characterization of Si-fibers by SEM-EDS and FTIR analysis confirms the presence of grafted SiO<sub>2</sub>. **b**, Turbidity removal following repeated reuse of Si-fibers and Si-microspheres (single experiment per condition) following 20 s settling time (for each cycle). Grafted materials were extracted, washed, and reused at least 20 times without loss of performance during solids removal. Shaded area (in grey) shows the industry standard after treatment (< 1 NTU). **c**, Flocs obtained with conventional treatment (left, formed with coagulant and flocculant only), Si-fiber (center) and Si-microsphere (right). Al-based flocs are expected to interact with cellulose and grafted Si via hydrogen bonding and electrostatic interactions. **d**, Schematic of floc behavior in a settling tank. When combined with a coagulant and a flocculant, flocs formed with Si-microspheres settled 26 times faster than conventional flocs. Conditions for b-d: 30 mg/L coagulant (alum), pH 6.5 ± 0.2, the 0.30 mg/L of flocculant is composed of 50% starch and 50% polyacrylamide.

Using a conventional treatment approach (i.e., adding coagulant and flocculant to a representative surface water, without fibers), a mean floc diameter of 520±50 µm was obtained. However, the addition of Si-fibers with a structure ~10000 times longer than traditional flocculants produced flocs with sizes of 4950±480 µm, ~10 times larger than those obtained through conventional treatment (Fig. 2c).

To further enhance floc size and density and treatment efficiency, fibers were rearranged into “microspheres” and reinforced through SiO<sub>2</sub> grafting. The density of the resulting porous Si-microsphere was estimated to be 1.61 ± 0.23 (Supplementary Equation 1). Simultaneously used as super-bridging agents, as ballast medium, and as adsorbents, the fibrous Si-microspheres were significantly more porous than the mineral sands (silica and magnetite)<sup>17</sup> typically used as ballast media and offered more reactive surface area for interaction with target contaminants. Surface areas of fibers and silica sands were calculated to be ~280 m<sup>2</sup>/g and 0.017 m<sup>2</sup>/g, respectively – thus, the cellulose fiber surface area was estimated to be ~16000 times higher than the non-porous silica sand used traditionally in ballasted flocculation.

The performance of conventional treatment (coagulant and flocculant) with no fibers was compared against treatment with pristine cellulosic fibers, Si-fibers, and the fibrous Si-microspheres in Fig. 3a and b (optimal concentrations of materials are shown in Supplementary Fig. 2a and b). Conventional treatment required more than 180 s to reach the target treatment value of 1 NTU, while pristine cellulosic fibers required only ~24 s (~8 times faster). Due to their

133 higher density, Si-fibers were even more efficient than pristine cellulosic fibers during settling and attained the same 1  
134 NTU turbidity after only ~14 s (~13 times faster than conventional treatment).  
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136 Increasing the floc size through particle bridging is a key element in water treatment as it determines both the floc  
137 settling velocity and contaminant removal rates. The effective chain length and hydrodynamic volume of a flocculant  
138 (a soluble organic polymer) are good indicators of that flocculant's potential in aggregation processes<sup>18-20</sup>. Traditional  
139 synthetic flocculants such as polyacrylamide that are used worldwide have an effective chain length less than ~100  
140 nm<sup>20,21</sup>. The filamentous morphology (Fig. 2c) and higher density of Si-microspheres compared to Si-fibers enabled  
141 their use as simultaneous bridging agent and ballast medium. The flocs formed using Si-microspheres were ~13 times  
142 larger (mean diameter of  $6630 \pm 540 \mu\text{m}$ ) compared to those obtained with the conventional treatment. As the target  
143 turbidity of 1 NTU was achieved after only ~7 s when using the Si-microspheres (~26 times faster than the conventional  
144 technology, Fig. 2d), in practice, a considerably smaller (*i.e.* more sustainable) settling tank could be used without  
145 affecting the turbidity removal. Thus, this new material has the potential to reduce the process cost for new or  
146 refurbished treatment plants as compact designs are more economical. Land requirements make up a significant fraction  
147 of the overall cost of water treatment plants. Moreover, in dense, urban areas, land usage represents lost economic  
148 value<sup>22,23</sup>. Due to their super-bridging/ballasting effects, Si-fibers and Si-microspheres reduced the coagulant demand  
149 by ~20% and ~40%, respectively (based on turbidity, Fig. 3c). With Si-fibers, the reduction in flocculant demand was  
150 more than 60% (Fig. 3d). To further reduce the use of synthetic flocculant, a homemade starch was extracted from  
151 potato residue and used as a partial replacement of the synthetic oil-based polyacrylamide (Supplementary Fig. 4).  
152 Finally, both Si-fibers and Si-microspheres were shown to be reusable and were extracted, washed, and reinjected 20  
153 times in the process without affecting the treatment performance (Fig. 2b).

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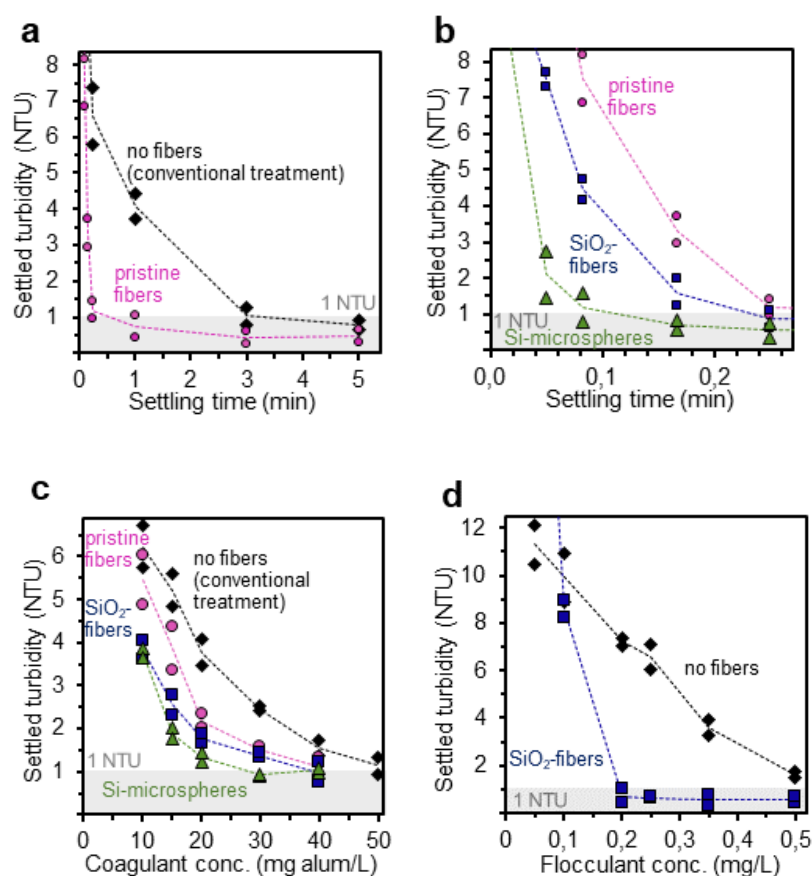
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**Fig. 3 | Fiber-based materials considerably reduced floc settling time during water treatment.** **a, b,** Impact of pristine cellulosic fibers (100 mg/L), Si-fibers (100 mg/L), and Si-microspheres (1000 mg/L) versus conventional treatment (no fibers) on turbidity removal rates. **c,** Impact of fiber-based materials on the required coagulant (alum) concentration. **d,** Impact of Si-fibers on the required flocculant (polyacrylamide) concentration. Reduction in flocculant demand was greater than ~60% after 20 s of settling, when 100 mg Si-fibers/L was used. Conditions for a-c: 30 mg/L coagulant (alum), pH  $6.5 \pm 0.2$ , the 0.30 mg/L of flocculant was composed of 50% starch and 50% polyacrylamide. Dashed lines are included as eye guides connecting average values obtained from duplicate experiments. Shaded area (in grey) shows the industry standard after treatment (< 1 NTU).

## Replacing settling with screening

Noting the unprecedented size of the flocs formed using Si-fibers and Si-microspheres, we hypothesized that these large flocs could be separated from the treated water using screens with sufficiently wide mesh sizes that reduce the risk of clogging and through which conventional flocs would readily pass (Fig. 4a). To verify whether screening could be used



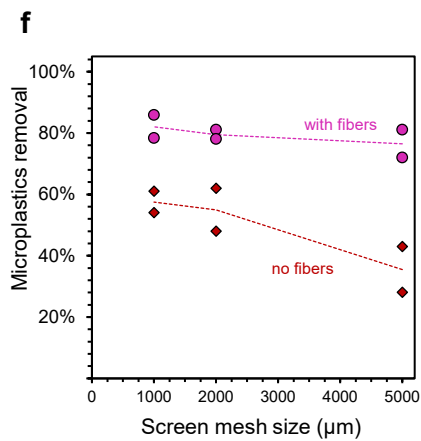
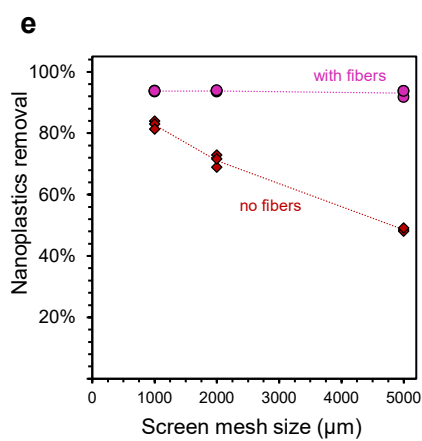
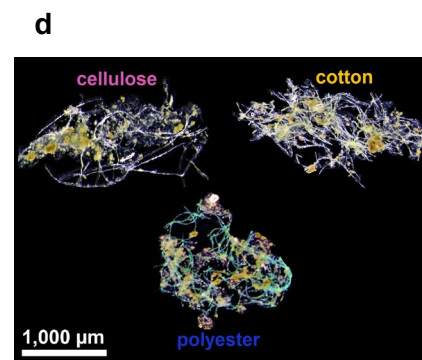
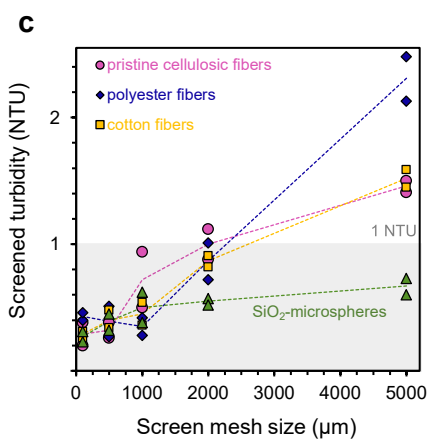
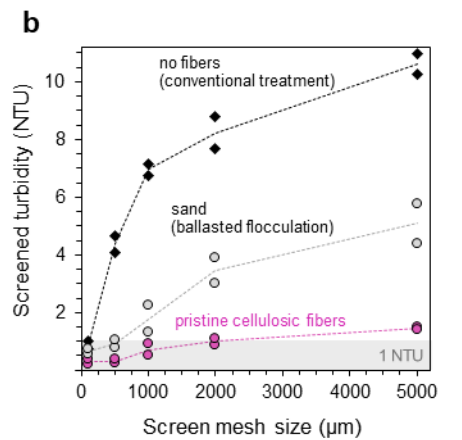
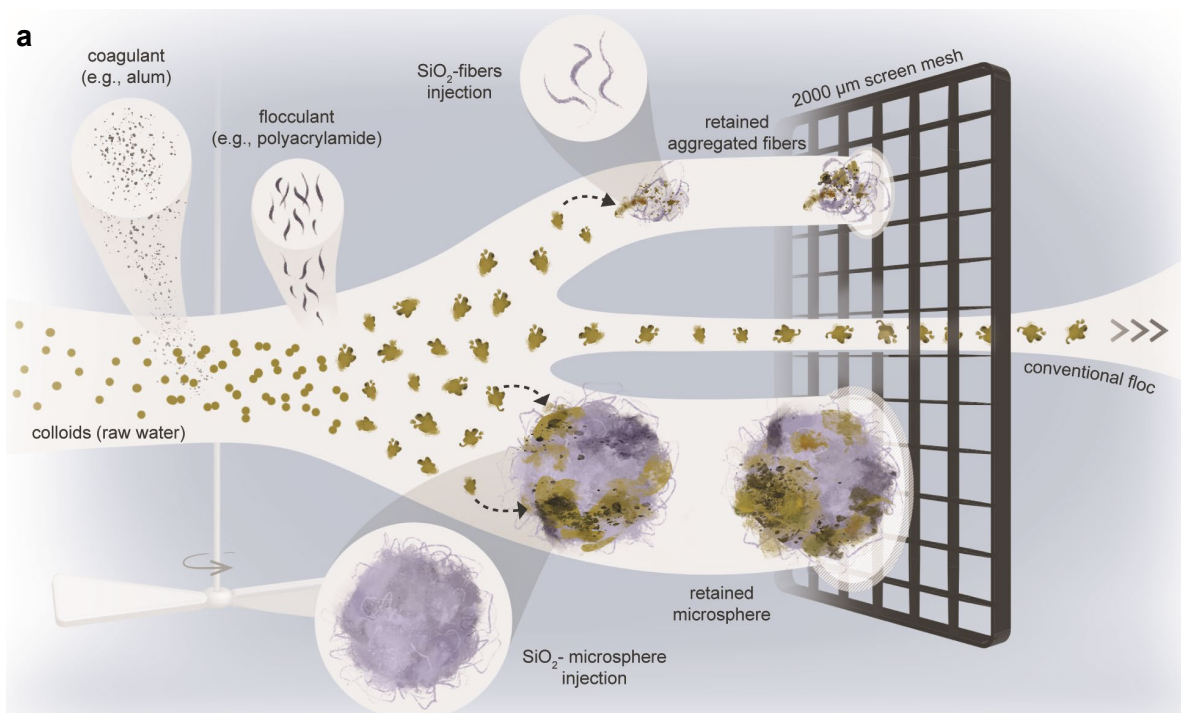
169 as a viable separation method, turbidity measurements were assessed after flocs were screened directly in the beaker  
170 during flocculation using different nylon screens.

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172 Due to their smaller size, flocs produced by conventional treatment ( $520\pm 50\text{ }\mu\text{m}$ ) and ballasted flocculation ( $960\pm 230$   
173  $\mu\text{m}$ ) required a mesh of  $100\text{ }\mu\text{m}$  and  $500\text{ }\mu\text{m}$ , respectively, to achieve the treatment target of 1 NTU. Other studies have  
174 reported the mean size of ballasted flocs to be lower than  $600\text{ }\mu\text{m}$ <sup>15,24,25</sup>. However, as the fiber-based materials developed  
175 herein enabled the formation of flocs with a mean size of  $\sim 4000\text{--}7000\text{ }\mu\text{m}$ , the 1 NTU target value was reached with  
176 much larger mesh sizes of  $2000$  and  $5000\text{ }\mu\text{m}$  during treatment with fibers and Si-microspheres, respectively (Fig. 4b  
177 and c). Si-microspheres as large as  $10000\text{ }\mu\text{m}$  were produced by modifying the grinding and mixing conditions before  
178 stabilizing the fibers via Si-grafting, which suggests that industrial screens with a larger mesh size than those tested in  
179 this study ( $5000\text{ }\mu\text{m}$ ) could also be used. After being collected, the aggregated fibers and microspheres were retrieved  
180 from the screen, cleaned, and reinjected in the aggregation tank (the measured fiber/microsphere recovery  $> 95\%$ ).  
181 Larger mesh sizes ( $>2000\text{ }\mu\text{m}$ ) would be more easily cleaned compared to smaller ones and would reduce clogging by  
182 limiting screen pore blocking. Moreover, screens with larger mesh sizes are typically cheaper and can be cleaned by a  
183 simple pressurized air/water system; thus, considerably less water is expected to be required compared to backwashes  
184 during granular filtration.

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186 Besides grafted fibers, different unmodified fibers can be used to form ultra-large flocs that can be separated by  
187 screening. Pristine and recycled cellulosic fibers, cotton fibers, and polyester fibers (waste from textile industry) were  
188 tested as bridging agents and all reached the  $\sim 1$  NTU target when screening was performed with a  $2000\text{ }\mu\text{m}$  screen (Fig.  
189 4c and d). The optimal concentrations of cellulosic fibers ( $\sim 100\text{ mg/L}$ ) are shown in Supplementary Fig. 2c. Thus, the  
190 use of the fiber-based super-bridging agents can enable the replacement of the traditional settling tank with a simple  
191 screen, thereby potentially reducing the capital expenditures of the treatment process. This approach also considerably  
192 improved the removal of microplastics and nanoplastics (Fig. 4e and f) compared to conventional treatment.



196 **Fig. 4 | Screening methods can replace large settling tanks in water treatment.** **a**, Floc formation and trapping during  
197 screening. Conventional flocs (formed with coagulant and flocculant only) were not removed, while flocs formed with different types  
198 of fibers or Si-microspheres were easily trapped. **b, c** Impact of screen mesh size and type of fibers/microspheres on screened  
199 water turbidity performed at 100 mg/L fibers and 1000 mg/L microsphere concentrations. Shaded area (in grey) shows the industry  
200 standard after treatment ( $< 1$  NTU). **d**, Flocs formed with various waste fibers (cellulose, cotton, and polyester). All fibers  
201 considerably increased the floc size and improve solids removal. **e, f**, Impact of pristine cellulosic fibers on the removal of  
202 nanoplastics and microplastics. Conditions for b – f: 30 mg alum/L, 0.30 mg flocculant/L (50% starch and 50% polyacrylamide), pH  
203  $6.5 \pm 0.2$ . Dashed lines are included as eye guides connecting average values obtained from duplicate experiments. In **e**, symbols  
204 represent triplicate measurements from a single jar test for each screen size (a dotted line is included as an eye guide).

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## 206 **An alternative material for simultaneous bridging, ballasting, and contaminant adsorption**

207 We fabricated flakes composed of cellulose fibers with grafted Fe (hydr)oxides which acted as sites for NOM and  
208 phosphorus adsorption via attractive electrostatic interactions<sup>26-29</sup>. Fig. 5a and b describe the adsorption and floc  
209 aggregation pathways on the flake and the flake collection method. Conventional flocs were also expected to interact  
210 with sections of exposed fibers *via* hydrogen bonding (*e.g.*, aluminum hydroxide-based flocs attached on cellulose  
211 hydroxyl groups). Fig. 5c shows the atomic Fe content grafted on the flakes (1–9%, obtained by X-ray photoelectron  
212 spectroscopy (XPS)) and the mass content of iron (hydr)oxides on the flakes (6–32%, obtained by TGA) as well as the  
213 ungrafted Fe (2–31% of total Fe remained in the water following flake synthesis). From XPS analysis, which  
214 characterizes the surface of a material, the atomic Fe content reached an asymptote when 26 mM Fe is used during flake  
215 synthesis. In contrast, TGA analysis showed that the mass of grafted iron (hydr)oxides on flakes continued to increase  
216 when higher Fe concentrations are used (up to 42 mM Fe). This may be attributed to the formation of thicker Fe patches  
217 on fibers.

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219 We observe a NOM residual concentration of 5.2–4.2 mg C/L (9–26% removal with 0.3–7.5 g flakes/L; Fig. 5d). This  
220 suggests that in practice, the Fe-grafted flakes could reduce the formation of disinfection by-products in drinking  
221 water<sup>30</sup>. The potential applicability of flakes in municipal wastewater treatment was also evaluated by measuring soluble  
222 phosphorus removal<sup>28</sup>. We observed a residual phosphorus concentration of 0.80–0.17 mg P/L (17–82% removal with

223 0.3–7.5 g flakes/L; Fig. 5e), which would reduce local anthropogenic pressures in lakes and rivers<sup>31</sup>. The Fe  
224 concentrations after treatment show that the flakes did not release Fe into the treated wastewater (Fig. 5e).

225

226 In contrast to conventional ballast media such as silica sand, the flake was designed to simultaneously bridge colloids,  
227 ballast flocs, and adsorb NOM and phosphorus (with capacities up to 1.7 mg NOM/g flakes and up to 0.6 mg P/g flakes).  
228 The flake tested herein with a Fe surface coverage of ~ 9% had a lower adsorption capacity than granular activated  
229 carbon (1.2–27.1 mg NOM/g GAC<sup>32</sup>). However, GAC does not promote aggregation via bridging. The adsorption  
230 capacity of the flake could also be improved by increasing the Fe surface coverage on fibers. Using 7.5 g flakes/L  
231 combined to a coagulant (30 mg alum/L) and a flocculant (0.3 mg flocculant/L) during screening, we achieved a  
232 turbidity < 1 NTU, with no settling required. If used during settling rather than screening, such large and dense flakes  
233 also eliminate the need for non-renewable and less sustainable ballast media (*e.g.* silica and magnetite sands extracted  
234 from natural geological sites). However, for future water treatment plants, the formation of very large flakes of tunable  
235 size (Fig. 5b) could allow for the substitution of large and costly settling tanks (~20% of the total plant construction  
236 cost<sup>33</sup>) with a compact and inexpensive screening process.

237

238 We were able to synthesize flakes larger than 10000  $\mu\text{m}$  and smaller than 300  $\mu\text{m}$  (the size of a few fibers). At a larger  
239 production scale, the size could be controlled by the fragmentation technique (*e.g.*, mechanical grinding), intensity, and  
240 time. Larger flakes were denser and offered less specific surface area ( $\text{m}^2/\text{g}$ ) compared with free metal-coated fibers;  
241 thus, the ideal flake size will be a compromise between NOM removal (for which smaller flakes present a greater metal  
242 (hydr)oxide surface area) and flake separation (for which larger and more dense flakes are optimal). In this study, the  
243 dried Fe-grafted pulp was fragmented into large fragments of 1000–10000  $\mu\text{m}$  to improve removal during screening.  
244 We show that flakes can also be reinforced with either a high molecular weight polyacrylamide or  $\text{SiO}_2$  to improve their  
245 mechanical resistance over time and during high-shearing conditions such as in mixing tanks (Supplementary Fig. 3d).  
246 Polyacrylamide was injected during the initial step of the flake synthesis to improve fiber binding (Supplementary Fig.  
247 3b), while  $\text{SiO}_2$  was grafted on already synthesized flakes, producing a  $\text{SiO}_2$  shell-like reinforcement (Supplementary  
248 Fig. 3c).

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250 The concept of binding fibers with (hydr)oxides was extended by using different types of waste fibers. We tested the  
251 use of dryer lint (mostly composed of polyester, cotton, and hair), as an alternative to cellulosic fibers. Flakes produced  
252 with dryer lint (Supplementary Fig. 3e) successfully removed turbidity ( $< 1$  NTU after only 20 s of settling). Hence, the  
253 synthesis of flakes does not solely rely on cellulose, as other – more sustainable and cheaper – types of fibers can be  
254 used. Fiber-based materials such as flakes and Si-microspheres could also be filled with light or dense media to increase  
255 the settling or rising velocity (e.g., flake stuffed with recycled glass, Supplementary Fig. 3f), or be functionalized/grafted  
256 with other metal (hydr)oxides (e.g., grafted with Al instead of Fe, Supplementary Fig. 3g) or polymers to increase  
257 durability.

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259 The water treatment industry currently uses three classes of additives for high-rate clarification processes (i.e.,  
260 superficial velocity  $> 40$  m/h): coagulants, flocculants, and ballast media. Technically and economically,  
261 aggregation/settling is currently the most efficient and common way to treat water globally, especially for large water  
262 treatment plants. In many cases, the coagulant concentration is determined by the turbidity, or target level of residual  
263 NOM after treatment (or by total suspended solids and residual phosphorus for wastewater treatment). By combining  
264 aspects of the different reengineered materials presented above, an ultimate material for effective bridging, ballasting,  
265 and adsorption was achieved. Cellulose flakes formed by grafting iron (hydr)oxides onto cellulose present an interesting  
266 sustainable alternative to existing practices. Flakes served as a three-in-one bridging/ballasting/adsorbing medium that  
267 can simultaneously i) reduce turbidity (or total suspended solids in wastewater) by bridging colloids to form larger  
268 flocs, ii) improve the screening/settling removal rate by increasing the floc size/density, and iii) remove NOM (or  
269 phosphorus in wastewater which can lead to eutrophication) by adsorption. The flake synthesis is both inexpensive and  
270 sustainable as it requires only recycled cellulosic fibers (10 times less expensive than pristine cellulosic fibers), soluble  
271 iron/metal ( $\text{FeCl}_3$  in this study), and a base/buffer (NaOH in this study).

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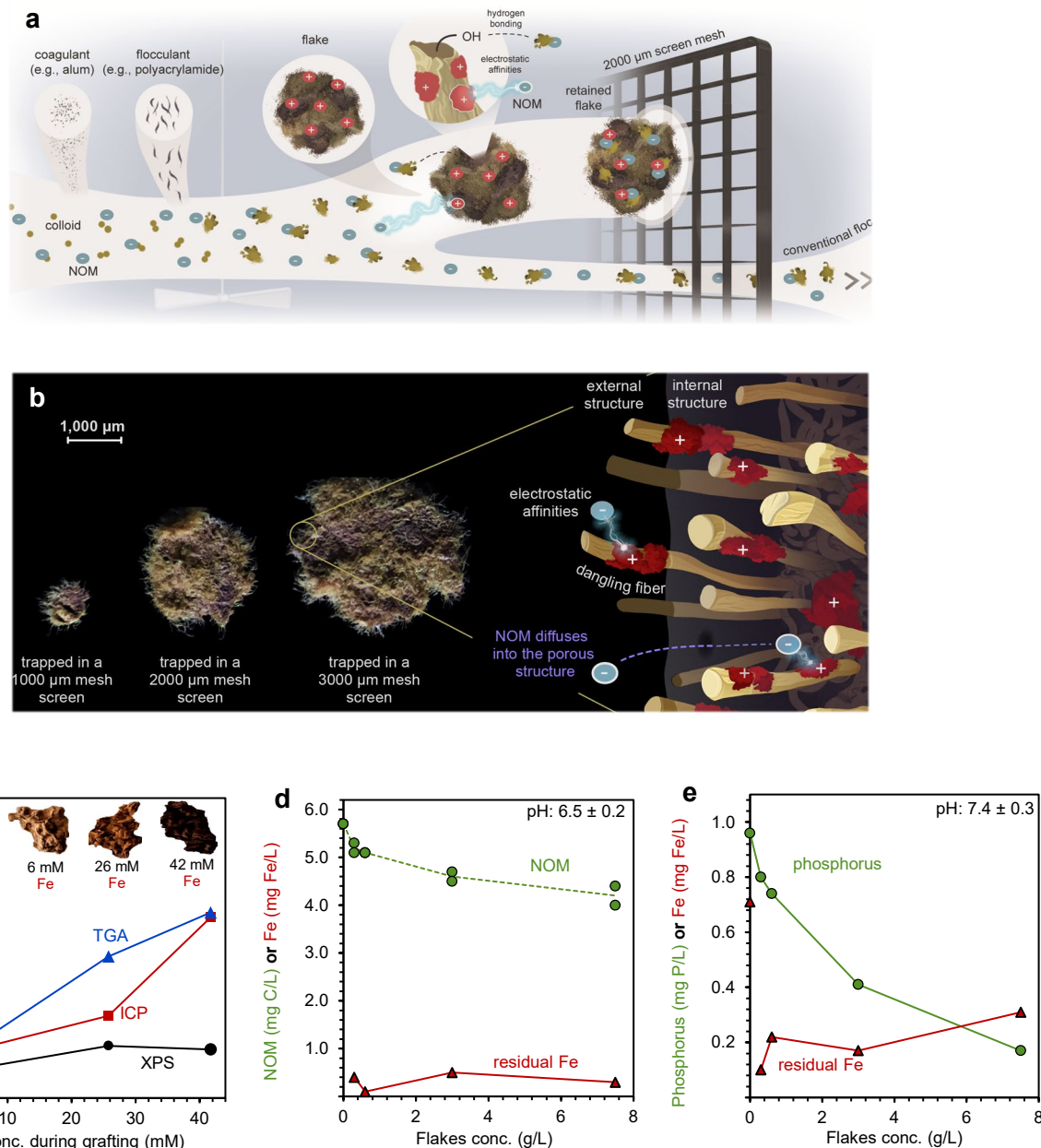
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**Fig. 5 | An alternative material for simultaneous NOM and turbidity removal.** **a**, Schematic of negatively charged NOM adsorption and colloid aggregation on positively charged flakes via electrostatic interactions. Conventional flocs aggregate with flakes via hydrogen bonding while contaminant-loaded flakes are trapped on a 2000  $\mu\text{m}$  screen. No settling tank is required. **b**, Schematic of NOM diffusion into the flake's filamentous/porous structure followed by adsorption on positively charged iron (hydr)oxides (in red). The flake size can be adjusted to prioritize adsorption or separation. **c**, Impact of Fe concentration during grafting (0.6 mM – 42 mM Fe) on atomic Fe content (via XPS, in black), on ungrafted Fe (via ICP, in red) and on mass of grafted Fe (hydr)oxide (via TGA, in blue) (single measurement per condition). **d**, NOM removal as a function of flake concentration. **e**, Preliminary measurements of phosphorus removal as a function of flake concentration (single jar test per condition). Adsorption

285 tests (d and e) were performed during 30 min and at 21 °C. In panel d, dashed lines are included as eye guides connecting  
286 average values obtained from duplicate experiments. Conditions for d, e: no coagulant or flocculant added.

287

## 288 **Conclusion**

289 The water treatment industry is facing rapid urbanization and increasing demands both on capacity and water quality.  
290 Meanwhile, global environmental concerns dictate the need for sustainable processes. In this study, we developed new  
291 fiber-based materials for use in the water treatment industry with the goal of reducing chemical usage and the footprint  
292 of treatment processes. Our results show that pristine fibers, grafted fibers, and fiber-based microspheres and flakes can  
293 be of interest to municipalities, industries, and engineers for the optimization of existing plants and for the design of  
294 future water treatment plants, notably by considerably increasing the floc size (> 10 times). The significantly larger floc  
295 size will considerably improve settling, or enable it to be replaced entirely with a more compact separation unit: rotating  
296 screens. For example, the Si-grafted microsphere increased the floc settling velocity by 26 times compared to  
297 conventional treatment; this material would consequently improve solids removal or allow the construction of a smaller  
298 settling tank. The fiber-based materials developed in this study also outperformed conventional treatment and ballasted  
299 flocculation during screening, as fibers, microspheres and flakes required larger mesh size of 2000 – 5000  $\mu\text{m}$  to reach  
300 the 1 NTU objective, while conventional treatment and ballasted flocculation needed a finer mesh size of 100 and 500  
301  $\mu\text{m}$ , respectively. The flake, used as a three-in-one porous material, was created by reengineering recycled cellulosic  
302 fibers and designed to simultaneously remove particulate and soluble matter, while improving process performance.  
303 The reusable fiber-based materials presented herein were shown to be versatile by removing several contaminants  
304 (NOM, phosphorus, microplastics, and nanoplastics), and by bridging/ballasting flocs. By enabling a reduction in  
305 chemical demand of 20-60%, these proposed low-cost fiber-based materials could lead to water treatment scalability  
306 and support an industry transition to chemicals and processes with lower environmental impacts. Many opportunities  
307 for reusing low-cost waste fibers from industrial sectors have been overlooked due to the challenges associated with the  
308 reengineering of resources. We believe that our results motivate the need for more research using this holistic approach  
309 to optimize the multiple aims of water treatment process efficiency, cost, and sustainability.

310

## 311 **Materials and Methods**

### 312 **Synthesis and characterization of Si-fibers and Si-microspheres**

313 Two types of cellulosic fibers (80–2000  $\mu\text{m}$  long) were used during jar tests and for the grafting process, either as received or acid-  
314 washed: (i) pristine cellulosic fibers (NISTRM8496, Sigma-Aldrich), or (ii) recycled and deinked fibers from the pulp and paper  
315 industry (Cascades Inc). Prior to the Si grafting procedure, all cellulosic fiber types were washed in deionized water. The wet pulp  
316 was dried using two drying procedures: one was carried out by drying at 40  $^{\circ}\text{C}$  for 24 h before the Si grafting, while in the second  
317 procedure, the dried pulp fibers were further washed with ethanol (70 %) and air-dried for 24 h to remove any excess water prior  
318 to carrying out the grafting reaction described elsewhere (Supplementary Fig. 1b). This showed that the extra ethanol  
319 washing/drying steps enhanced the amount of  $\text{SiO}_2$  grafted onto the fibers<sup>34–37</sup>. Briefly, to graft  $\text{SiO}_2$ , 7 mL water and 43 mL ethanol  
320 were mixed and used as the reaction solvent, into which 1 g of the treated fibers was dispersed. 20–30 mL of tetraethoxysilane  
321 (TEOS) (98%, 131903, Sigma-Aldrich) as the reagent, and 60 mg phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) (P4006, Sigma-Aldrich) as  
322 the catalyst were added to the pulp dispersion. The mixture was then vortexed to achieve a well-mixed dispersion before being  
323 stirred (120 rpm) for 24 h at room temperature. To reduce the process footprint and chemical consumption in full-scale applications,  
324 the ethanol-water-catalyst mixture used in the Si grafting process could be partially reused. Based on the data presented by Sequeira  
325 et al.<sup>35</sup>, we estimate that ~70% of the initial catalyst/solvent/water mixture could be reused at least once without significantly  
326 affecting the amount of grafted Si. The grafted Si-fibers were then separated from the solvent using a 160  $\mu\text{m}$  sieve and rinsed twice  
327 with deionized water to remove any unreacted residual reagent or catalyst. The final product was air-dried for 24 h prior to use in  
328 jar tests. A small sample of Si-fibers were frozen at -80  $^{\circ}\text{C}$  and then lyophilized using a benchtop Labconco freeze dryer for  
329 characterization. Other pristine fibers such as cotton and polyester (SanMar Canada, ATC, ATC3600Y) were also used to produce  
330 bridging materials.

331  
332 The same grafting technique was used to form Si-microspheres using dried pulp as a starting material. The desired aggregate shape  
333 and size was produced by manually grinding the dried pulp into fragments. Fragments were then mixed in ethanol, producing the  
334 microsphere shape that was subsequently reinforced and stabilized with grafted silica. Following grafting with TEOS as above,  
335 mixing at 120 rpm for 24 h produced a suspension of 81–92 wt% Si-microspheres; the balance consisting of Si-fibers that could be  
336 reused. Under higher shearing conditions (200 rpm), the proportion of Si-microspheres decreased to 25–30%. The relative  
337 proportion of Si-microspheres to Si-fibers obtained after synthesis can be further optimized by modifying the ethanol/water and  
338 TEOS/water ratios, or by modifying the amount of fibers present during the synthesis<sup>34,36,38</sup>. The Si-fibers were separated from the  
339 Si-microspheres by gravitational separation. The Si-grafted material was suspended in 500 mL of deionized water and allowed to



340 settle for 10 s. The Si-fibers remained in suspension while the Si-microspheres quickly settled ( $< 10$  s) to the bottom of a glass  
341 beaker. The grafted Si-microspheres were rinsed twice with deionized water to remove any residual unreacted reagent or catalyst.  
342 Both fibers and microspheres were tolerant of high shearing (velocity gradients as high as  $1000\text{ s}^{-1}$ ). The amount of grafted silica  
343 was determined by thermogravimetric analysis (TGA, Discovery TGA 5500) under nitrogen with an oven ramp from 25 to  $800\text{ }^{\circ}\text{C}$   
344 at  $10\text{ }^{\circ}\text{C}/\text{min}$ . The compositions of pristine fibers (control) and grafted materials were characterized by Fourier-transform infrared  
345 spectroscopy (FTIR, Spectrum II, PerkinElmer) with a single bounce-diamond in attenuated total reflection (ATR) mode, and by  
346 X-ray photoelectron spectroscopy (XPS, K-Alpha X-ray Photoelectron Spectrometer, Thermo Fisher Scientific). The morphologies  
347 of all materials and the Si layer thickness were obtained using scanning electron microscopy (SEM, FEI Quanta 450) coupled to  
348 energy dispersive x-ray spectroscopy (EDS).

### 349 350 **Synthesis and characterization of metal-grafted flakes**

351 A sustainable approach was used to produce flakes as a three-in-one bridging/ballasting/adsorbing material. Cellulosic fibers  
352 (pristine or recycled) or dryer lint (1 g) were rinsed twice with deionized water and air-dried for 24 h. These were then added to a  
353 100 mL  $\text{FeCl}_3$  or  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$  solution (0.6–42 mM Fe or Al) (Sigma-Aldrich). The suspension was adjusted to pH 7 using  
354 0.4–30 mL of 1 M NaOH and stirred at room temperature for 5 min. Under these conditions, the metal salts are hydrolyzed to  
355  $\text{Fe}(\text{OH})_3$  or  $\text{Al}(\text{OH})_3$  which adsorb and precipitate on the fiber surface. The grafted fibers were separated from the solution with a  
356 160  $\mu\text{m}$  sieve and subsequently heated at  $90\text{ }^{\circ}\text{C}$  for 2 h. After sieving, the residual Fe concentration in the filtrate was measured by  
357 inductively coupled plasma mass spectrometry (ICP-MS, ICAP, Thermo Fisher Scientific), following a pH adjustment  $< 2$  (using  
358 1 M  $\text{HNO}_3$ ). The iron or aluminum (hydr)oxides generated after heating simultaneously functionalized and linked fibers together  
359 to form the metal/cellulose-based flakes. Loosely bound Fe or Al were removed by mixing in deionized water at 150 rpm for 30  
360 min and then separated with a 160  $\mu\text{m}$  sieve from the flakes, which were then air-dried for 24 h. Flakes were then characterized by  
361 SEM-EDS, TGA and XPS.

362  
363 After synthesis, the dried metal-coated pulp was manually fragmented to form flakes of different sizes, which can be tuned for a  
364 specific separation application. In selected experiments, to increase the mechanical resistance of flakes (42 mM Fe), 5 mg/L of a  
365 high molecular weight polyacrylamide (191973, Sigma-Aldrich) was added to bridge iron hydroxides (during synthesis, 4 min after  
366 metal salts), providing internal reinforcement, prior to sieving/heating. Grafting  $\text{SiO}_2$  on the external surface of the already  
367 synthesized flake provided another method to improve the mechanical resistance: 1 g of dried flakes was combined with 43 mL

ethanol, 7 mL DI water, 60 mg phosphotungstic acid, and 20 mL TEOS and the suspension was stirred for 24 h at 120 rpm and room temperature. The reinforced flakes were then air dried for 24 h prior to use in jar tests.

## Tracking conventional indicators of water treatment and microplastics/nanoplastics

Jar tests were performed on surface water samples to probe the performance of the fiber-based materials. Samples were first coagulated with alum in a 500 mL beaker (250 mL of water) at 300 rpm for 2 min and then flocculated at 150 rpm for 4 min<sup>39</sup>. A mixed solution of polyacrylamide and a homemade starch polymer was used for flocculation (see below). To reduce floc breakage, the flocculant addition was divided into two equal injections<sup>8</sup>. Fibers, Si-microspheres, or flakes were injected at the onset of flocculation. Turbidity measurements were assessed after flocs were screened in the beaker during the flocculation using different nylon screens having mesh sizes of 100, 500, 1000, 2000, and 5000  $\mu\text{m}$  (Pentair). Turbidity measurements were also assessed after settling for 5–300 sec. All screened and settled samples were collected at a depth of 2 cm from the top of the water surface. After treatment, fiber-based materials were extracted from the screened/settled flocs, washed, and reused several times in the processes. Jar test experiments were conducted using surface water from the Chomedey drinking water treatment plant (mean flow rate: 180 000 m<sup>3</sup>/d; turbidity:  $8 \pm 2$  NTU (TB300-IR turbidimeter, ClearTech); pH:  $7.1 \pm 0.3$ ; dissolved organic carbon (DOC, Shimadzu TOC-VCPH analyzer, filtered on 0.45  $\mu\text{m}$  cellulose membrane) concentration:  $6.0 \pm 1.0$  mg C/L (composition: 70–75% humics, less than 5% of biopolymers, and 10–15% building blocks, and less than 10% of low molecular weight compounds)<sup>40</sup>; UV absorbance:  $0.26 \pm 0.1$  cm<sup>-1</sup> at 254 nm, which is fed by the Prairies River (Laval, Canada)<sup>41</sup>. The raw water was equilibrated to ~21 °C before each experiment. The residual turbidity objective after treatment was set to a typical industrial target of <1 NTU. Jar test experiments were also conducted using municipal wastewater influent from the city of Montréal (Jean-R. Marcotte wastewater treatment plant, Canada, mean flow rate: 2 500 000 m<sup>3</sup>/d; biological oxygen demand (BOD<sub>5</sub>):  $77 \pm 12$  mg/L (Standard Methods, 5210 B), chemical oxygen demand (COD):  $162 \pm 30$  mg/L (Standard Methods, 5220 B), total suspended solids:  $95 \pm 15$  mg/L (Standard Methods, 2540 D), pH:  $7.4 \pm 0.3$ , total phosphorus:  $1.6 \pm 0.2$  mg P/L (ICP-MS, ICAP, Thermo Fisher Scientific), soluble phosphorus:  $1.0 \pm 0.1$  mg P/L (ICP-MS, ICAP, Thermo Fisher Scientific, filtered on 0.45  $\mu\text{m}$  cellulose membrane)<sup>41</sup>. Residual iron, phosphorus and NOM analysis were performed by Environex (Eurofins, Canada). The reduction in coagulant and flocculant demand (based on turbidity) was calculated as follows:  $([\text{chemical concentration}]_{\text{no fibers}} - [\text{chemical concentration}]_{\text{with fibers}}) / ([\text{chemical concentration}]_{\text{no fibers}})$ , the turbidity targets being fixed at 1 NTU. The concentration of nanoplastics (200 nm fluorescent polystyrene carboxylated nanospheres, FluoSpheres, ex/em: 365/415 nm) was evaluated using a multimode microplate reader (Spark microplate reader, Tecan) with a calibration curve. As described by Lapointe et al.<sup>39</sup>, the microplastics (140  $\mu\text{m}$  polyethylene

microspheres, Cospheric, ex/em: 515/414 nm, initial jar test concentration of 500 microspheres/L) were extracted from samples via filtration (5  $\mu$ m polyacrylate membrane, PCT5047100, SterliTech Corporation) and were counted by stereomicroscopy (10 $\times$ ; Olympus, model SZX16, fluorescence mode). Stereomicroscopy (10 $\times$ ) was also used to measure the floc, microsphere, and flake equivalent diameters ( $D_E$ ,  $n=15$ ). DraftSight was used to evaluate the size by assuming an ellipsoidal shape, where  $D_E = \sqrt{Lx l}$  ( $L$ : ellipse longest dimension,  $l$ : ellipse shortest dimension).<sup>42</sup>

### **Extraction, cleaning, and reuse of fiber-based materials**

Screened and settled floc solutions were collected and adjusted to pH>9 to convert  $Al(OH)_{3(s)}$  precipitates (from alum used as the coagulant) into soluble aluminum species ( $Al^{3+}$  and  $Al(OH)_4^-$ , respectively) and to promote floc fragmentation. The solution was then sheared at 400 rpm during 30 s, and materials were collected using 160 and 630  $\mu$ m mesh sieves for fibers and microspheres/flakes, respectively (recovery > 95 wt% for all materials). Flakes were washed at pH >9 to exceed the isoelectric point of iron patches and to promote NOM desorption<sup>43,44</sup>. Fiber-based materials were then reused for subsequent jar tests.

### **A sustainable alternative to synthetic flocculants**

A starch-based polysaccharide flocculant was extracted from potato peels and used to partially replace the synthetic and non-biodegradable polyacrylamide. Potato peels (Dolbec, Canada) were blended (metal blade, Ninja blender) at ~1200 rpm for 5 min at room temperature. While blending, the solution was adjusted to pH 4.5 using 0.5 M HCl to disentangle, desorb, and partially extract soluble carboxylated starch chains from the pulp ( $pK_a \sim 4.5$ )<sup>21</sup>. The solution was sieved on 160  $\mu$ m sieve to separate the undesired insoluble pulp from soluble polysaccharides. As the polysaccharide chain length determines its bridging ability<sup>20,45</sup>, only molecules of high molecular weight were extracted by centrifugation at 5000g during 6 min using a Millipore 100 kDa molecular cut-off (Amicon kit from Millipore Sigma). The solution containing high molecular weight polysaccharides was adjusted to pH 7 using 1 M NaOH. Other types of potato residue or other food-based sources of polysaccharides could also be used to increase the polymer molecular weight<sup>21,46-48</sup>.

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### Competing interests declaration

N. Tufenkji and M. Lapointe have applied for U.S. provisional patents on the use of fiber-based materials for water treatment.

### Data availability statement

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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