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Sustainable granular materials improve removal of natural organic matter, turbidity and microplastics during adsorption, ballasted flocculation and granular filtration

Mathieu Lapointe [a,*], Heidi Jahandideh [b], Olubukola S. Alimi [b,c], Jeffrey M. Farner [d], Nathalie Tufenkji [b,*]

[a] École de Technologie Supérieure (ÉTS) – University of Québec, H3C 1K3 Canada
[b] McGill University, Quebec H3A 0C5, Canada
[c] University of Alberta, Alberta, T6G 2R3Canada
[d] FAMU-FSU College of Engineering, Florida A&M University, FL 32310-6046, USA

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ABSTRACT

Single-use metal-based coagulants, high molecular weight flocculants, engineered adsorbents, and porous media are key materials for several processes in water treatment. However, many of these materials are often expensive, unsustainable, and can increase the amount of sludge produced during the water treatment process. Moreover, the accumulation of toxic metals and synthetic flocculants limits sludge reusability as a fertilizer in agriculture. Herein, we propose reusable, low-cost and sustainable modified grains that can be simultaneously used as positively charged adsorbents to improve removal of soluble matter (natural organic matter), and ballast media to improve removal of particulate matter (turbidity or total suspended solids). Three different starting materials were used to synthesize these modified grains: pristine sand, recycled crushed glass, and grit extracted from a wastewater treatment plant, all of which were grafted with iron (hydr)oxides (Fe surface coverage of 13 and 81 %, synthesized with 0.02 and 2 M Fe, respectively). The modified grains were then employed as (i) adsorbents to remove natural organic matter, (ii) ballast media during flocculation to increase floc size and density, and (iii) filtration media for simultaneous removal of natural organic matter and turbidity. Compared to conventional treatment alone (coagulation and flocculation), the incorporation of modified grains simultaneously used as adsorbents and ballast media increased removal of natural organic matter (up to 16 %), microplastics (up to 92 %), and turbidity (< 1 NTU, with settling rate 18 times faster). Ultimately, modified grains could be used in existing ballasted flocculation processes – replacing conventional sand – to provide an additional NOM removal.

Synopsis

Iron-grafted sand, glass, and grit – simultaneously used as adsorbent and ballast media – reduced the settling duration by 18 times compared to conventional treatment (without iron-grafted media) and increased removal of natural organic matter (up to 23 %) and microplastics (up to 92 %).

1. Introduction

Aggregation-based treatment and gravitational separation are used and studied worldwide for drinking water production and wastewater treatment [1,2]. The design of water treatment plants typically prioritize contaminant removal performance and cost [3]. Single-use metal-based coagulants and synthetic flocculants are essential and used globally to improve floc formation and settling [4–6]. However, these chemicals increase the operational cost of water treatment plants and the concentrations of metals and synthetic flocculants in sludge [7,8]. Bio-sourced chemicals and new technologies that also consider process sustainability and footprint are henceforth needed to design water treatment systems for growing populations [9]. Reducing the consumption of single-use coagulant and flocculant, while maintaining process performance will result in more sustainable solutions in water treatment [10].

* Corresponding authors.
E-mail addresses: mathieu.lapointe@etsmtl.ca (M. Lapointe), nathalie.tufenkji@mcgill.ca (N. Tufenkji).

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Ballast media can be used, in synergy with coagulants and flocculants, to promote aggregation and increase floc size and density [11,12]. However, conventional, unmodified silica-based ballast media do not aid in the removal of natural organic matter (NOM) or other soluble contaminants. Currently, to capture soluble contaminants, water treatment plants typically rely on single-use monomeric coagulants, single-use and costly polymeric/prehydrolyzed coagulants, or costly adsorbent (activated carbon and resin) [13,14]. However, the sand surface can be modified to optimize soluble material removal via electrostatic interactions [15–17]. Thus, ballasted flocculation is not currently used to its full potential, and the opportunity to simultaneously employ ballast media as an adsorbent has been overlooked by the water industry. Furthermore, considerable amounts of non-renewable ballast media materials (e.g., 3 – 6 g sand/L) [11,18] are extracted from natural geological sites. While it's use improves floc density and settling rate and thereby reduces the size of the settling tank, the need to reduce consumption of ballast material exists to improve sustainability [12].

Silica sand is also used in granular filtration worldwide, though here again the aim is limited to the removal of colloids rather than adsorption. Iron-modified filtration materials have been demonstrated to be effective for the removal of a number of contaminants, including arsenic, lead, bacteria, and NOM [19–22], although activated carbon is typically relied upon in water treatment processes. The use and regeneration of activated carbon is expensive and energy intensive. Alternative materials may provide opportunities to reduce reliance on activated carbon.

In this study, we investigate the ability of iron-modified silica sand to improve the process of ballasted flocculation. Furthermore, we demonstrate that recovered waste grit can be used to fabricate ballast media and adsorbents that can simultaneously remove particulate and soluble materials, namely turbidity and NOM. Large flocs produced using these sustainable materials settled ~18 times faster compared to conventional flocs in the absence of ballast media. Additionally, modified media improved the removal of microplastic polyester fibers compared to conventional physicochemical treatment processes. We further show how these modified materials can be used in water filtration as functionalized granular media to simultaneously adsorb NOM and reduce turbidity. Modified ballast media were prepared by grafting iron on the following three granular materials: 1) pristine silica sand, 2) recycled crushed glass, and 3) wastewater grit extracted from the primary clarifier and destined for landfill. These modified media are designed to be reusable after being extracted from sludge and cleaned. Modified grains synthesized from waste are potential alternatives for the costly and unsustainable ballast media and adsorbents such as pristine sands (silica or magnetite-based), resins and activated carbon currently used worldwide in water treatment.

2. Materials and methods

2.1. Synthesis and characterization of modified grains

Pristine silica sand (GA39, Veolia), wastewater grit (sampled at a wastewater treatment plant in Québec, Canada), and crushed glass grains were functionalized with iron (hydr)oxides. Crushed glass was obtained by crushing glass bottles of different colors with a hammer. All media were rinsed 3 times with DI water upon reception. The grain size distributions of all media were adjusted by sieving with two sieves having a mesh size of 63 μm and 160 μm (mean diameter of ~130 μm). The iron grafting procedure was adapted from the protocols of Benjamin et al [15]. and Lin et al [23]. Briefly, 10 g media was added to 10 mL of $FeCl_3$ (2 M or 0.02 M, yielding highly and moderately modified grains, respectively). Samples were heated to 100 °C in a water bath and mixed every 15 min for 3 h to encourage nucleation and initial oxidation of iron on the surface. After heating, three post-treatments were applied to each media: 1) the media was dried at room temperature, 2) the media was heated at 225 °C for 3 h to prevent the conversion of FeOOH to Fe_2O_3 (occurring ~ 300 °C) [24], and 3) the media was heated at 550 °C for 3 h. This heating procedure at 2 different temperatures aims to compare goethite-rich media (FeOOH) to iron oxide-rich media (Fe_2O_3). Heating at 550 °C also removed organic impurities (Supplementary Fig. 1c and d) in wastewater grit. Following post-treatment, the modified grains were rinsed extensively with DI water to remove any unbound or poorly attached Fe.

Modified and unmodified (control) grains were imaged using scanning electron microscopy (SEM, FEI Quanta 450) coupled to energy dispersive x-ray spectroscopy (EDS) to confirm the presence of iron (hydr)oxide patches. The iron oxide surface area coverage was calculated by establishing the area pixel ratio of Fe-based patches/Si surface (n = 10; assuming ellipse shape for the patches). A calibrated scale in DraftSight was used to evaluate the patch equivalent diameter by assuming an ellipse shape, where equivalent diameter = $(L\times l)^{0.5}$ (L: ellipse longest dimension, l: ellipse shortest dimension) [25]. X-ray photoelectron spectroscopy (XPS, K-Alpha X-ray Photoelectron Spectrometer, Thermo Fisher Scientific) was used to evaluate the percentage of elements (Fe, Si, O, C, and other) present on the surface and to determine iron speciation.

2.2. Water characteristics

Jar test experiments were conducted using surface water from the Prairies River (Laval, Canada). The surface water characteristics are presented in Table 1. The turbidity was quantified using a TB300-IR turbidimeter (ClearTech). Typical NOM fractions for the tested water are presented in Supplementary Table 2 [26]. NOM content was quantified via dissolved organic carbon (DOC, Shimadzu TOC-VCPH analyzer, filtered on a 0.45 μm cellulose membrane). Before each experiment, the raw water was equilibrated to ~21 °C.

2.3. Jar tests

Samples of Prairies River water (250 mL) were coagulated with alum in a 500-mL beaker at ~ 300 rpm for 2 min and then flocculated at 150 rpm for 4 min using a combination of starch polymer (50 %; 0.15 mg/L) and an anionic polyacrylamide (50 %; 0.15 mg/L) [27,28]. The alum concentration was established to reach a settled turbidity below 1 NTU (industry standard for drinking water). The flocculant combination of starch and polyacrylamide was used to reduce the polyacrylamide demand and risk regarding its potential toxicity [29,30]. Briefly, a polysaccharide-based flocculant was extracted from potato peel residue and used as flocculant to initiate floc formation. As shown elsewhere [31,32], floc formation was then completed with conventional synthetic polyacrylamide (Supplementary Fig. 2) [31]. The addition of both flocculants was divided into two equal injections to limit floc breakage: 0.075 mg starch/L and 0.075 mg polyacrylamide/L were added at the beginning of the flocculation (first 50 % of the total flocculant injection), while the second 50 % was added at mid-flocculation [28]. Ballast material (*i.e.*, unmodified (control) and modified grains; 0 – 100 g/L) was added at the onset of flocculation, just after coagulation. Turbidity measurements were assessed after settling for 5–300 sec. In full-scale ballasted flocculation, the concentration of ballast media is usually between 3 – 8 g/L [11,25,33]. In this present study, higher concentrations of the coated sands were also used (up to 100 g/L) as a proof of concept (no coagulant or flocculant). The residual turbidity objective after treatment was set to a target of < 1 NTU. All

Table 1
Raw surface water characteristics.

Turbidity	8 ± 2 NTU
Natural organic matter (NOM)	6.0 ± 1.0 mg C/L
pH	7.1 ± 0.3

settled samples were collected at a depth of 2–3 cm from the top of the water surface. Floc sizes were determined with a stereomicroscope (10 × objective; Olympus, model SZX16). A pipette with a large tip (~3000 μm) was used to sample flocs during flocculation (sampling method described by Lapointe and Barbeau) [25]. After treatment, modified grains were extracted from the settled flocs, washed, and reused several times in the processes.

To reduce operational expenditure and footprint of the process, ballast media are usually extracted from sludge via hydrocyclone [34]. Here, settled flocs were collected and adjusted to pH > 9 to convert $Al(OH)_{3(s)}$ precipitates (coagulant) into soluble aluminum species ($Al(OH)_4$) and to promote floc detachment. The solution was then sheared at 400 rpm for 30 s, and the modified grains were collected using an 80 μm mesh (recovery > 95 wt%). The modified grains were washed at pH > 9 (using 1 M NaOH) to exceed the isoelectric point of iron patches and to promote NOM desorption [15,16]. The modified grains were then cleaned at 225 or 550 °C. The removal efficiency of microplastics (polyester fibers) using modified grains was investigated. As described in previous work [27,35,36], polyester fibers (mean length of 581 μm; length range: 105 −1325 μm) were injected in the raw surface water at a concentration of 500 polyester fibers/L (125 fibers/250 mL of surface water). After coagulation, flocculation and settling, 100 mL of the settled water was filtered on a 5-μm polyacrylate membrane (PCT5047100, SterliTech Corporation) and the retained fibers were counted by stereomicroscopy (10 ×; Olympus, model SZX16). For polyester fibers removal, statistical comparisons were made using paired Student's *t*-tests at 5 % significance level.

Batch adsorption tests to measure NOM removal were also performed (250 mL, ~ 300 rpm, 21 °C, for 30 min at pH 6.5 ± 0.2) with the same surface water to compare the performance of media (before and after Fe modification). For adsorption tests, 0 – 100 g of media/L was added to tested water in the absence of coagulant and flocculant. 50 mL of water was sampled in the supernatant after 3 min of settling. The sampled water was filtered on a 0.45 μm cellulose membrane before measuring NOM concentration.

2.4. Column test experiments

To examine the removal of UV absorbance (used as an indicator of NOM) via granular filtration, column experiments were performed using glass chromatography columns (16 mm inner diameter, GE Life Sciences) packed with sand grains. Pristine sand (control) and Fe-grafted sand (2 M Fe, heated at 225 ºC) were tested as filtration media. The pristine high purity quartz sand (50–70 mesh size, d_{50} = 256 μm, Sigma Aldrich) was acid-washed before usage [37]. Following procedures described in previous studies [37–39], 26 g of each sand media was soaked in filtered DI water overnight (a minimum of 12 h) before each experiment. The soaked sands were then wet packed into the glass column while ensuring uniformity in packing via gentle vibration of the column. The resulting packed filtration media length was 8.5 cm. Background solution (DI water) was pumped (using syringe pumps, KD Scientific) through the column at a flowrate of 0.9 mL/min for at least 40 min to equilibrate the column. Thereafter, the prefiltered surface water (using a 0.45-μm membrane) was injected into the column for 30 min followed by the background solution for 20 min. UV spectrophotometry (1 cm flow-through cell, Agilent HP 8453) was used to obtain the influent and effluent UV absorbance in real-time at λ = 254 nm. Column tests were conducted in duplicate.

3. Results and discussion

3.1. Characterization of granular waste converted into sustainable dual ballast-adsorbent media

Three types of granular materials (mean size of ~130 μm) were used to demonstrate the iron-grafting concept. Silica sand was employed as a standard material, and the Fe concentration during grafting significantly impacted the surface area coverage by iron (hydr)oxides. The measured iron surface coverage on the sand surface was characterized by scanning electron microscopy coupled to energy dispersive X-ray spectroscopy, SEM-EDS. Moderately coated (~13 ± 4 % surface area coverage) and highly coated (~81 ± 7 % surface area coverage) silica sand grains were obtained with 0.02 M Fe and 2 M Fe, respectively (Fig. 4c) [15,23]. To increase process sustainability, recycled crushed glass and wastewater grit extracted from primary clarifier sediments (otherwise destined for landfill) were also modified using the same procedure. X-ray photoelectron spectroscopy (XPS) analysis confirmed the presence of grafted iron (hydr)oxides on the three different media. The atomic percentage of Fe present on the surface of moderately coated grains was between 4.7–7.4 % for all media (Fig. 1b). Analysis of XPS spectra for sand grains subjected to post treatments of 225 °C and 550 °C suggest iron is present as Fe^{3+} (FeOOH at 225 °C and Fe_2O_3 at 550 °C, Supplementary Fig. 1b). When expressed as Fe_2O_3 instead of Fe, the calculated surface coverage is between 6.7–10.6 %, which is slightly lower than the value obtained via SEM image analysis for moderately coated silica sand (13 %).

3.2. Impact of modified grains on turbidity reduction and microplastics removal

If incorporated into the floc structure, dense ballast media such as silica sand are known to simultaneously increase the floc size and density [40]. In jar tests performed with highly modified grains, the settling duration required to reach 1 NTU was reduced by 18x compared to conventional treatment (without ballast media). Results for highly modified silica sand are presented in Fig. 2a. All settled turbidities were < 1 NTU for highly Fe-grafted media after 10 s of settling: 0.78, 0.82, and 0.94 NTU for sand, glass, and grit, respectively (average values obtained from duplicates). Jar tests using pristine sand yielded similar results (0.70 NTU after 10 s of settling), which is unsurprising given that the densities of the modified media were expected to not be significantly altered. These results agree with a previous study by Desjardins, Koudjonou and Desjardins [11] which observed settled turbidity < 1 NTU within 10 s using pristine silica sand as ballast medium. Conventional treatment (alum and PAM, no ballast media) was demonstrated to generate flocs of 520 ± 50 μm (data from Lapointe et al. (2022)) [31] – which required roughly 3 min to reach the 1 NTU objective (Fig. 2a), while floc size increased to 960 ± 230 μm though the use of sand ballast media [31].

The use of modified grains as ballast media is also effective for microplastic fiber removal. Polyester fiber removal was ~76 %, ~95 %, and ~92 % for conventional treatment, ballast treatment with pristine silica sand, and ballast treatment with modified sand, respectively (Fig. 2b). Similar removal for polyester fibers were reported elsewhere [27]. The difference between the conventional treatment (no ballast) versus the modified grains treatment was statistically significant (p-value < 0.05, paired *t*-test), while the difference between the unmodified sand treatment vs. the modified grains treatment was not statistically significant (p-value = 0.30). However, any difference in the performance of pristine sand vs. modified sand could be explained by the interaction of the tested flocculant (anionic polyacrylamide) with both media. It is hypothesized that the tested anionic PAM (having COO-) might interact more strongly with the positively charged Fe oxides grafted on the media. This could reduce PAM availability for other colloids, which could decrease removal efficiency. The improved removal of plastic-based fibers during ballasted flocculation versus conventional treatment is likely due to improved incorporation of plastic fibers into the larger flocs formed with ballast media [25,41]. As shown for turbidity in previous studies, these results suggest that ballast media could improve the removal of plastic fibers and turbidity in full-scale WWTPs despite fluctuations in superficial velocity (expressed as $m^3/h/m^2$) [11,42].

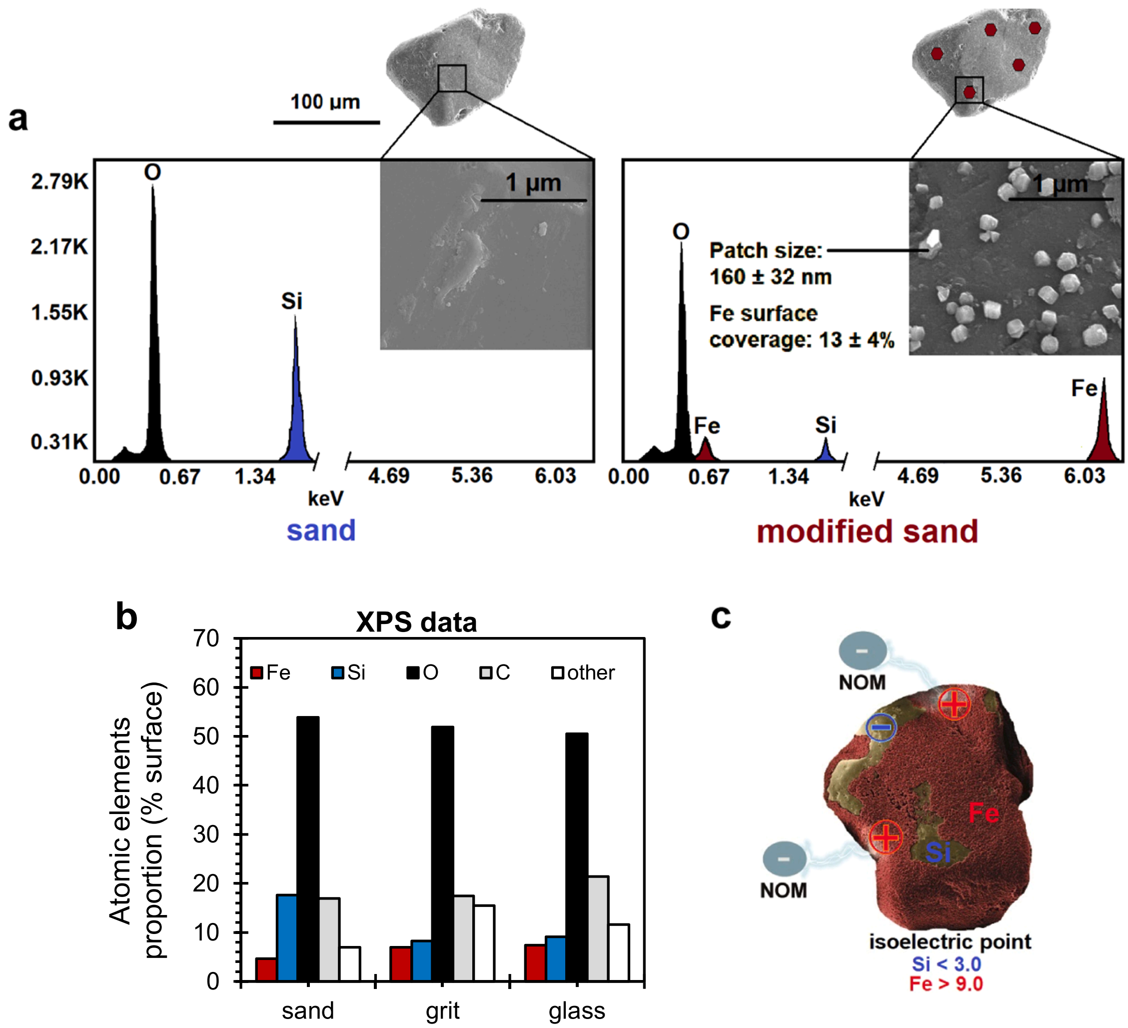

Fig. 1. Characterization of modified grains (Fe-grafted). Fe surface coverage and patch size of moderately modified sand versus unmodified (control). Coverage was measured from images taken using scanning electron microscopy (SEM) coupled to energy dispersive x-ray spectroscopy (EDS) (a). XPS analysis was used to determine the atomic elements proportion (in % surface; moderately coated grains). Starting media: silica sand, grit, and recycled glass (b). Schematic of NOM adsorption on cationic Fe (hydr)oxide patches on a highly modified sand grain (c).

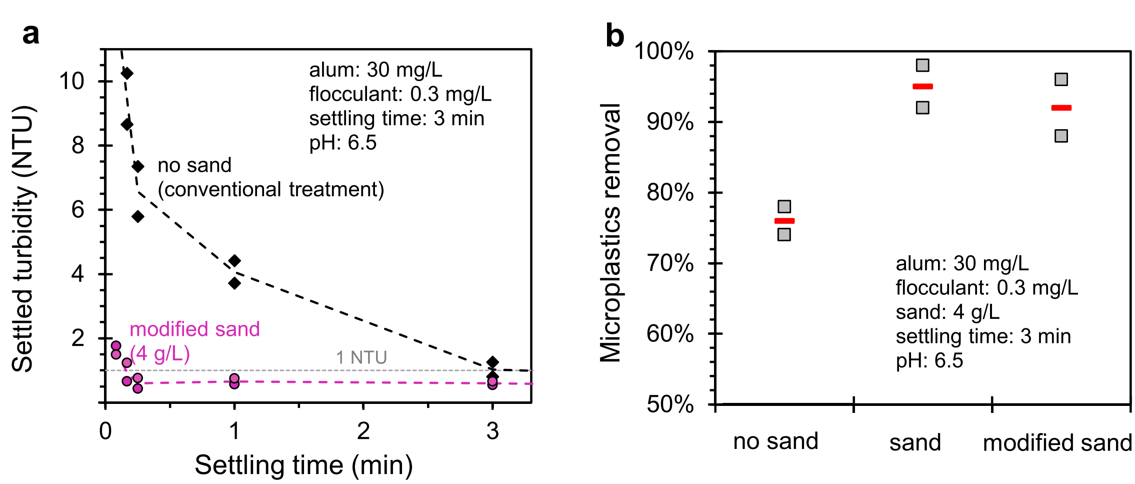

Fig. 2. Modified sand grains used as ballast media during settling. Turbidity removal when highly modified grains (Fe-grafted sand) are used as ballast media during flocculation. Dashed lines are included as eye guides connecting turbidity average values obtained from duplicate experiments. Dashed line in grey shows the industry target after treatment (<1 NTU) (a). Microplastics (polyester fibers) removal during ballasted flocculation (Fe-grafted modified sand) versus conventional treatment (no sand, control). The red symbols indicate the average value obtained from duplicates (grey symbols) (b). Modified grain synthesis: silica sand was grafted in a 2 M Fe solution and heated at 225 °C (a and b).

3.3. Impact of granular ballast media on NOM adsorption

Existing ballasted flocculation using conventional silica sand is unable to effectively reduce soluble contaminant concentrations, however negatively charged soluble contaminants such as NOM are known to interact with positively charged Fe (hydr)oxides [22]. Tests of NOM removal were performed in the absence of coagulant and flocculant using 100 g/L of either unmodified or highly modified granular media. The residual NOM measured when using conventional ballast media (silica sand) was 5.8 ± 0.1 mg C/L, representing a removal of < 3 % from the original 6.0 ± 1.0 mg C/L (Fig. 3). As reported by previous studies, when used alone without coagulant and flocculant, silica sand is not efficient for NOM removal [11,43]. The use of Fe-modified sand resulted in enhanced NOM removal, which increased both with increasing concentration of modified sand grains and with increasing Fe surface coverage (Fig. 4a). For all highly modified granular materials (coated with 2 M Fe) heated at 225 °C, an average NOM residual of 5.0 ± 0.2 mg C/L was measured, representing a 17 % reduction in NOM concentration. No appreciable differences were observed in NOM removal between the 3 highly modified granular materials, further suggesting that the Fe patches, rather than the base grain, were driving the interaction with NOM.

Despite the 100 times lower Fe concentration during synthesis, surface area coverage of iron (hydr)oxides was only reduced by ~6 times (13 ± 4 % for moderately modified sand compared to the 81 ± 7 % for highly modified sand). Moreover, the difference in NOM removal efficiency between both media was even lower: 10.3 % NOM removal and 15.5 % NOM removal for moderately modified and highly modified grains, respectively (only a 34 % decrease from highly to moderately modified sand; 100 g of grains/L). Thus, the highly modified grains may have an excess of coverage.

As described above, the inert ballast media such as silica sand can be functionalized to provide an additional NOM removal via adsorption. Thus, Fe-grafted media could be used in synergy with coagulant to improve NOM removal, helping to reduce the formation of disinfection by-products [44,45]. This adsorption could occur in the existing flocculation tank initially designed for floc maturation (contact time usually > 8 min) [11,25]. Moreover, this additional NOM removal obtained via adsorption on Fe-based ballast could potentially be translated into a reduction in coagulant demand. Doing so would also result in the reduction of single-use metal-based coagulant ending up in sludge. For some drinking water applications, single-use and/or expensive adsorbents such as powdered/granular activated carbon and resin could potentially be replaced by Fe-grafted reusable media. Furthermore, a more sustainable granular medium (e.g., crushed glass and grit) could replace pristine silica sand as a hybrid adsorbent and ballast material. This would also result in a better reuse of grit extracted from WWTP and currently buried in landfills.

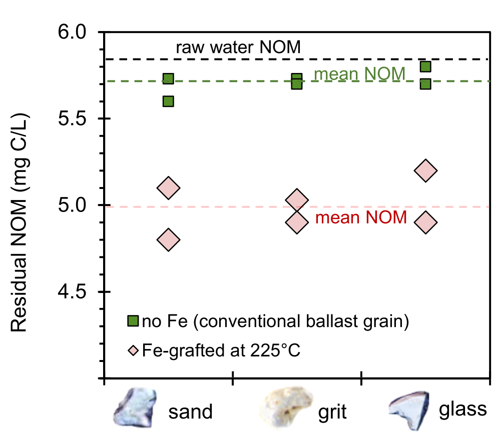

Fig. 3. NOM removal via adsorption on modified granular materials. Grains were grafted with 2 M Fe and heated at 225 °C. Impact of granular material type (100 g/L) on residual NOM was tested. Three types of media were tested as is (control) and Fe-grafted: silica sand, wastewater grit and crushed glass. Dashed lines show the raw water NOM concentration (before treatment) and the mean NOM concentrations after adsorption across all 3 material types. Adsorption conditions: initial NOM = 5.8 mg C/L, temperature = 21 °C, adsorption conditions = 30 min, 150 rpm, at pH 6.5 ± 0.2.

3.4. Potential for modified ballast media reuse

Heating at 550 °C removed organic contaminants from the media feedstock, indicated by the loss of C detected using XPS (Supplementary Fig. 1c). These contaminants include apparent spherical microplastics observed in wastewater influents that were not degraded by heating at 225 °C (Supplementary Fig. 1d). Contrary to coagulants and flocculants, which are both unrecoverable from the settled sludge, modified grains can be extracted via hydrocycloning or screening/sieving, cleaned, and potentially reused several times. The measured recovery was > 95 wt% after one cycle of treatment using an 80 µm sieve. A partial recovery in adsorption capacity is expected when the modified grains are washed at pH higher than the metal oxide isoelectric point to allow NOM desorption, while a higher surface recovery would be possible by regenerating the grains at 500–650 °C [46,47]. Unlike the industry standard adsorbent (activated carbon), the fabricated dense modified grains presented herein (i) are expected to be more temperature and mechanically resistant, (ii) are expected to be easily regenerated by heating without affecting their adsorption properties, (iii) can simultaneously act as ballast media to improve the floc settling velocity, and (iv) can be synthesized at low cost by recovering locally extracted wastewater grit and/or glass. Based on the performance of similar materials, it is expected that such modified grains would also remove negatively charged phosphorus (e.g., orthophosphate) for municipal wastewater applications via electrostatic affinities [31,48].

3.5. Impact of modified grains on granular filtration

Fe-grafted grains could also be used as porous media during granular filtration to simultaneously adsorb NOM and retain unsettled colloids. NOM removal in sand filtration is primarily due to degradation as a result of biofilm formation in the sand bed, with little removal observed due to adsorption in clean beds. Here, settled waters were collected after 3 min settling during conventional treatment (no ballast medium; 1.03 NTU) and were treated by granular filtration by using either highly modified sand or pristine silica sand. The ungrafted media (pristine silica sand) was ineffective at removing soluble NOM, with the effluent absorbance immediately reaching the influent absorbance, as denoted by the column bypass data (Fig. 5). Meanwhile, the Fe-grafted medium was effective for NOM adsorption. After 25 min of filtration with modified sand, the measured UV absorbance remained below 0.019 cm^{-1} (Fig. 5). Similar improvements in NOM removal have been observed in slow sand filtration test columns and pilot studies using iron oxide coated olivine, with removal attributed to the carboxylic acid groups in NOM undergoing organic ligand exchange with the oxides on the iron surface [22,49]. The filtered turbidity for both pristine and Fe-grafted sands was below 0.3 NTU during the entire 25 min filtration cycle, demonstrating the removal of unsettled colloids and suggesting that Fe patches are not appreciably detaching from the modified grains.

3.6. Improving water treatment sustainability

NOM removal was considerably impacted by the iron surface coverage, with the highly modified grains resulting in greater NOM removal compared to the moderately modified grains (Fig. 4a and b). However, despite being synthesized using 100 times lower Fe concentration, surface area coverage of iron (hydr)oxides was only reduced by ~6 times, while maintaining improved NOM removal compared to

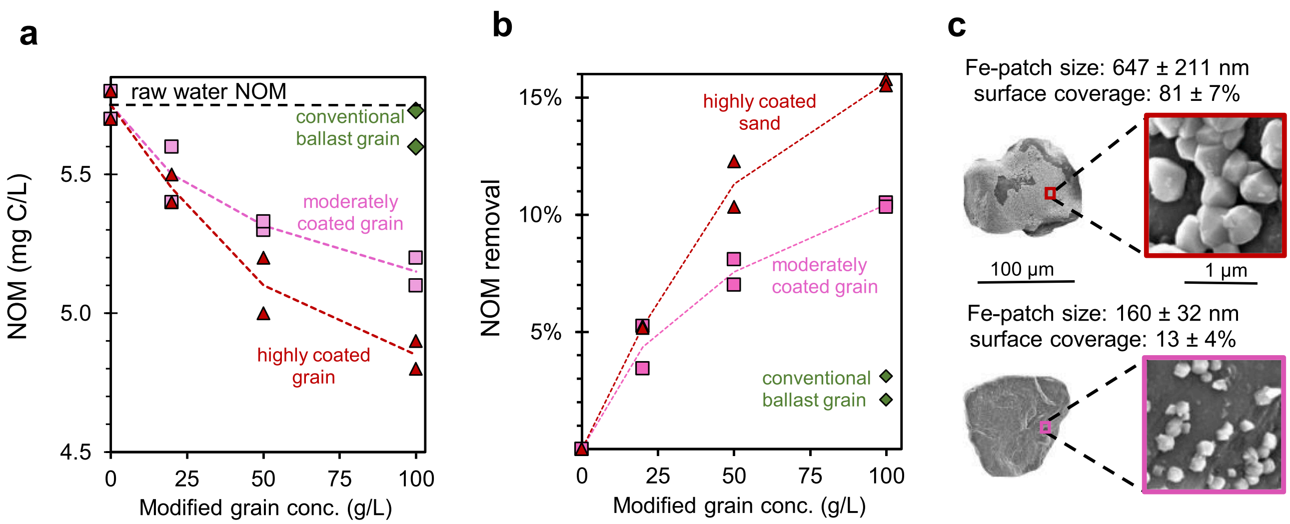

Fig. 4. NOM removal for drinking water applications. Impact of Fe surface coverage and grain concentration on residual NOM (a) and NOM removal (b). Values in b) were calculated from values in a). Adsorption conditions for a) and b): initial NOM = 5.8 mg C/L, temperature = 21 °C, adsorption time = 30 min at pH 6.5 ± 0.2. Dashed lines are included as eye guides. Average values are obtained from duplicate experiments (a and b; 0 – 100 g grain/L). Impact of Fe concentration during grafting on the surface coverage and patch size of iron (hydr)oxides. Surface area coverages of 13 ± 4 % and 81 ± 7 % were obtained when sands were coated with 0.02 (moderately coated) and 2 M Fe (highly coated), respectively. The iron patch size was also influenced by the Fe concentration: 160 ± 32 nm and 647 ± 211 nm, for 0.02 and 2 M Fe, respectively (c). Conventional grains (no grafted Fe) were also tested as a control (a and b).

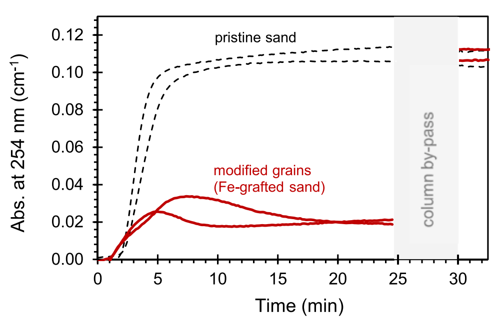

Fig. 5. Modified sand grains used as adsorbent during granular filtration. NOM removal (determined via UV absorbance) *via* adsorption on pristine sand (control) and modified grains (Fe-grafted sand) during granular filtration. Surface water was prefiltered on a 0.45-µm membrane. Modified grain synthesis: silica sand was grafted in a 2 M Fe solution and heated at 225 °C.

conventional ballast media. This could translate into considerable cost reduction during synthesis as Fe represents more than 60 % of the chemical cost. Consequently, it is expected that moderately coated grains could be used in existing ballasted flocculation processes at reasonable cost while providing an additional NOM removal. Synergistically combining coagulation (alum) and adsorption (modified grains) could help municipalities to meet regulations related to disinfection by-products [50,51].

We show that pristine silica sand could be replaced by more sustainable materials such as recycled crushed glass or wastewater-extracted grit (Fig. 6a). Grit collected from wastewater offers the potential advantage of synthesizing modified grains *in situ*, at a water treatment plant, hence limiting product transport, avoiding long-term storage of materials in large tanks, and reducing operational expenditures. Implementation of this strategy would require capital expenditures (e.g., injector, hydrocyclone, pump), but would convert conventional flocculation into ballasted flocculation and would increase the plant capacity due to the formation of denser and larger flocs [52,53]. A few promising opportunities for re-engineering waste materials extracted from wastewater treatment plants are described in Fig. 6. For example, dense Si-based media (referred to herein as grit) or other dense particles could be collected in the primary clarifier, with the media size adjusted *via* hydrocycloning. Smaller grit particles are preferable as they offer more surface area per gram of material and limit pump abrasion. Grit could be grafted with Fe (Fig. 6b) and synergistically injected in aggregation tanks with coagulant and flocculant to improve NOM removal (Fig. 6c) – and potentially phosphorus removal [48,54]. After settling (Fig. 6d), modified grains could be extracted by hydrocycloning and reused in the aggregation tank (Fig. 6e). For drinking water applications, starting materials extracted from wastewater would be avoided due to the obvious potential contamination issues. However, for drinking water applications, cleaner starting media (e.g., silica sand or washed recycled glass) could be used for the synthesis of modified grains. Finally, wastes from many other industrial sectors unexplored in this study could be employed for the synthesis of sustainable, low-cost, and advanced materials for environmental applications. Residual media from the steel and the mining industries present viable options.

The modified grains synthesised in this study by reusing municipal wastes such as recycled glass and grit outperformed conventional physicochemical treatment (alum and polyacrylamide) and conventional ballasted flocculation (alum, polyacrylamide, and silica sand) by removing more NOM and turbidity during settling and granular filtration. Microplastic removal was also improved when modified grains are used in combination with conventional physicochemical treatment. Moreover, the modified grains considerably increased the flocs' settling velocity (18 times).

4. Conclusion

With their high density (~ 2.6) and functionalized Fe patches (Fig. 1a), modified granular materials (e.g., sand, crushed glass, and grit) can be simultaneously used as adsorbent and ballast media to improve soluble contaminant removal and floc settling velocities, respectively. Iron coated grains are readily incorporated into the floc structure, leading to increased floc density (Supplementary Fig. 1a) [11,52,55]. The modified grains can also remove NOM (source of disinfection by-products in drinking water) [56] from water via the positively charged iron patches [16] (Fig. 1c). However, more work is needed to validate the stability of the modified grains over time.

The water treatment industry is facing rapid urbanization and increasing demands both on capacity and water quality. Meanwhile, global environmental concerns dictate the need for sustainable

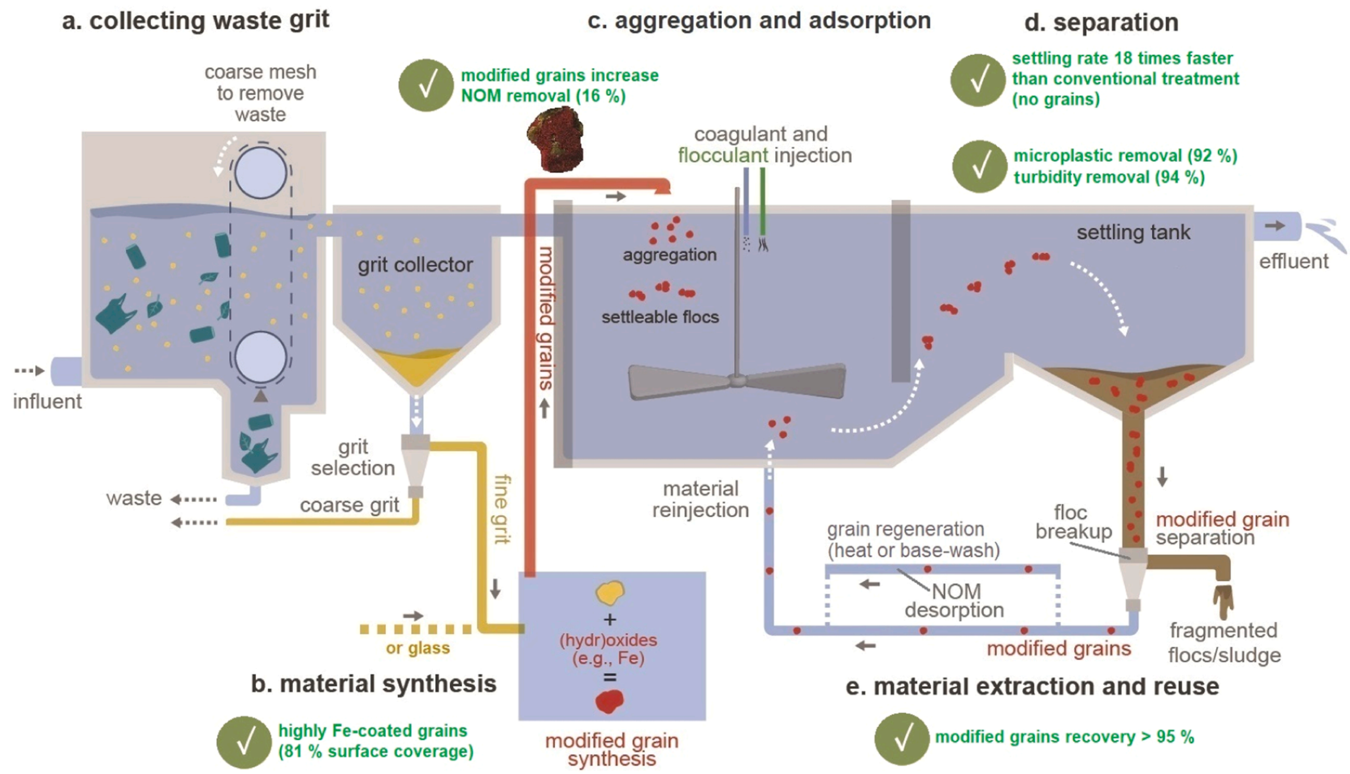

Fig. 6. Representative schematic of *in situ* grit/glass conversion into functionalized and sustainable adsorbents and ballast media for water treatment. Grit collection or recycled crushed glass addition. Large debris are removed via coarse screening, grit is collected by gravitational separation in the primary clarifier, and the grain size distribution is adjusted via hydrocycloning (labeled grit selection) (a). Material synthesis. Grit or crushed glass is Fe-grafted *in situ* to produce modified grains (b). Aggregation. Reengineered grains and (bio)flocculants (e.g., starch from potato residue) are injected in the coagulation/flocculation tank to adsorb NOM, bridge colloids and/or ballast flocs (c). Separation. Large and dense ballasted flocs produced with the grafted grains are highly settleable (d). Material extraction and reuse. Flocs are fragmented by solubilizing the coagulant ($Al(OH)_3$) into soluble metal species ($Al(OH)_4^-$) and NOM is partially desorbed from Fe-grafted grit at pH > 9.0. Modified grains are separated from the sludge via hydrocycloning (e). Modified grains are reinjected in the aggregation tank after cleaning and extraction. Fragmented flocs, desorbed NOM, and sludge are sent for sludge dewatering and drying.

processes [57,58]. Here, we have shown that modified sustainable materials can be adopted by municipalities for the optimization of existing plants and for the design of future water treatment plants. We expect and hope that these proposed low-cost and functionalized materials will lead to water treatment scalability and support an industry transition to chemicals and processes with lower environmental impacts. Many opportunities for reusing waste materials from water treatment plants and from other industrial sectors have been overlooked due to the challenges associated with the extraction and re-engineering of resources.

CRediT authorship contribution statement

Alimi Olubukola S.: Methodology, Formal analysis, Data curation. **Jahandideh Heidi:** Methodology, Formal analysis, Data curation. **Tufenkji Nathalie:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Farner Jeffrey M.:** Writing – review & editing, Visualization, Formal analysis. **Lapointe Mathieu:** Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare no conflicts of interest.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2025.116012.

Data availability

Data will be made available on request.

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