Evaluation of activated starch as an alternative to polyacrylamide polymers for drinking water flocculation

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ABSTRACT

Polyacrylamide polymers (PAM) are one of the most common water treatment chemicals used in clarification processes. Concerns have been raised with regards to the aquatic and human toxicity of acrylamide monomer. Greener polymers, produced using potato starch, were investigated at lab-scale as a potential non-toxic alternative to the use of PAM within a ballasted flocculation process (Actiflo®). Even under extreme temperature (1 °C), starch and PAM showed comparable turbidity removal performances, although higher starch dosages (four to five times) were needed to achieve such results. Compared to PAM, activated starch polymers also benefited from the use of lower mixing energy and smaller microsand. A slight biodegradable dissolved organic carbon (BDOC) release (≈0.15 mg C/L) was also measured while using starch polymer, but this did not impact trihalomethane and haloacetic acid formation. These results indicate that activated starch polymers represent a promising alternative to the use of PAM polymers in a ballasted flocculation process.

Key words | ballasted flocculation, microsand, polyacrylamide, starch, turbidity

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INTRODUCTION

Among alternative coagulation–flocculation–settling processes, ballasted flocculation is an economical technology for surface water clarification due to the possibility to operate at high superficial velocity (40–85 m/h). The process involves the injection of microsand during flocculation in order to increase settling velocity (Plum *et al.* 1998). Polymers, once attached to microsand, provide high flocs settling velocity and turbidity removal. Typically, polyacrylamide-based polymers (PAM) are used for ballasted flocculation as they improve flocs strength and compactness (Jin *et al.* 2013). However, recent studies have highlighted concerns related to the toxicity for humans and aquatic organisms of residual acrylamide monomer, which may escape in finished water or be discharged in the aquatic ecosystem (Rice 2005; Bolto & Gregory 2007). Other studies have also linked the use of synthetic polyelectrolytes to the formation of disinfection by-products (Fielding 1999; Bolto 2005). As a result, some countries have restricted (France, Germany) or abolished (Spain, Japan, Switzerland) the use of PAM in water treatment for drinking water production.

The maximum value recommended by NSF/ANSI-60 certification is typically 1–3.5 mg/L, depending on the residual acrylamide monomer content. Commercially available PAM typically contains a maximum of 0.05% acrylamide monomer. For a dosage of 1 mg/L, the maximum possible concentration in treated water is therefore 0.5 µg/L. However, a typical conventional treatment process does not remove the residual acrylamide monomer (WHO 2004). Consequently, limiting acrylamide monomer in finished water implies either (1) a reduction of the applied dosage, (2) the use of a high purity PAM (lower acrylamide content), or (3) the use of an alternative polymer to PAM.

Greener polymers manufactured from starch potatoes, recognized to be biodegradable and non-toxic, offer an economical potential alternative to replace PAM in conventional treatment processes. The general aim of this paper is to evaluate the performances of starch-based polymers for ballasted flocculation. Polymers are used within this process, commercialized as the Actiflo® process, in order to attach the flocs to the microsand. The performance of PAM and

starch polymers were compared using a modified jar test procedure and under a challenging temperature condition (1 °C). This work provides strong evidence that specific starch-based polymers can be used as an alternative to PAM within a ballasted flocculation process; for example, five plants are running in France/Spain with such product and the drinking water produced is in accordance with industrial standards.

MATERIALS AND METHODS

Ballasted flocculation: jar test simulation methodology

All assays were conducted using surface waters from the St Lambert water treatment plant, which is fed by the St Lawrence River (Quebec, Canada). This source water exhibits a moderate alkalinity (80 mg $CaCO_3$/L), a relatively high pH ($\approx$8.0), a low TOC (<3 mg C/L), and a fairly low turbidity (2.5–3.5 NTU). Ballasted flocculation using alum and the Superfloc A-100 PAM (from Kemira) is in operation at this facility.

Source waters were sampled and characterized upon reception at the laboratory. Two-liter square beakers (B-Kers™, Phipps & Bird) were used to conduct the jar tests. Alum (($Al_2SO_4)_3.14H_2O$) and ferric chloride ($FeCl_3.6H_2O$) were used as coagulants. Assays with alum were conducted at 1 and 21 °C while assays with ferric chloride were only conducted at 21 °C. Cold water assays were conducted in a thermostated cold room. Following coagulant injection, the flocculant and microsand were injected according to the sequence described in Figure 1. Either the Superfloc A-100 (a low anionic and high molecular weight (MW) PAM) or the Hydrex 3841 (a low anionic and low MW starch polymer) were injected as flocculant. The Superfloc A-100 was selected as it was the optimal polymer found by the St Lambert water facility operators. The
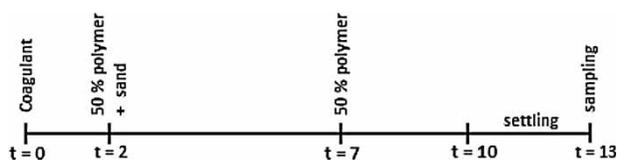
Hydrex 3841 (H3841) was selected following pre-tests that identified it as optimal among a group of three candidate starch-based polymers from Hydrex.

Figure 1 summarizes the sequential procedure used to simulate a ballasted flocculation in jar test. Briefly, raw waters are flash-mixed during 2 min at 400 s^{-1}. After flash-mix, 50% of the polymer dosage and the entire dosage of micro-sand are injected and mixed at 165 s^{-1}. The remaining polymer dosage is introduced after 5 min of flocculation to allow flocs growth. After flocculation, the process requires 3 min of settling (equivalent to an overflow velocity of 40 m/h) to ensure turbidity removal. Samples were collected 10 cm under the water surface. This simulation was established to replicate a full-scale ballasted treatment (Desjardins et al. 2001).

Modifications to the conventional ballasted flocculation procedure

The jar test procedure described previously was originally developed for PAM. Compared to PAM, starch-based polymers differ significantly in terms of their chemical properties. Therefore, a four-step experimental design was developed to evaluate whether ballasted flocculation conditions should be revisited while using starch polymers. First, triplicate assays were conducted in order to evaluate the reproducibility of the jar test procedure. Second, optimal polymer dosages were identified using the conventional procedure for both polymers. Third, the impact of microsand diameter (63–80 μm vs. 100–160 μm) was tested. Finally, variable flocculation velocity gradients (G values from 60 to 540 s^{-1}) were also tested. In all cases, settled water (SW) turbidities were used as an indicator of process performance. For the study on the impact of G, particle concentrations in SW were first evaluated by turbidity measurements and second evaluated by micro-flow imaging using a particle analyzer (Brightwell Technologies, DPA-4100).

Impacts of using a starch polymer on filtered water quality

SW, produced under optimal conditions using both types of polymers, was microfiltered (0.45 μm, Pall Supor-450, CA28147-640) to remove residual microflocs. Filtered waters were then characterized for dissolved organic

Figure 1 | Conventional ballasted flocculation procedure.

Table 1 │ Analytical methods summary

Parameters	Methods (equipment)
Turbidity	Standard method, 2130B (Hach 2100N turbidimeter)
DOC	Standard method, 5310C (Sievers 5310c total organic carbon analyzer, GE Water)
BDOC	Suspended growth method from Servais et al. (1989) (Sievers 5310c total organic carbon analyzer, GE Water)
THM–UFC, HAA–UFC	Method: Summers et al. (1996). Incubation for 24 h at pH 8.0 and 20 °C with Cl_2 dosage sufficient to maintain 1.0 mg Cl_2/L after 24 h (uniform formation conditions)

Figure 2 │ Reproducibility of SW turbidity following a jar test conducted in triplicate. Conditions: alum dosage = 0.13 meq./L, temperature = 1 °C, microsand = 4 g/L, G during flocculation = 165 s^{-1}, 3 min of settling.

carbon (DOC), biodegradable dissolved organic carbon (BDOC), trihalomethanes (THM), and haloacetic acids (HAA) using uniform formation conditions (UFC) (according to the analytical methods summarized in Table 1).

Statistical comparisons were made using paired Student's t-tests at the usual 5% significance level.

RESULTS

Reproducibility of the jar test procedure

Measurements of turbidity were performed as one of the main criteria to establish comparative differences between PAM and starch-based polymers. The reproducibility of the procedure was first evaluated by comparing SW turbidities from triplicate jar tests. Figure 2 indicates the precision obtained at 1 °C with alum and a starch polymer. The 95th centile confidence intervals indicate that the procedure was highly reproducible as turbidities varied less than ±0.05 NTU for adequate polymer dosage (>0.2 mg/L).

Optimized jar test procedure

Polymer dosage selection

The starch polymers and PAM used in this study have different MW, spatial conformation, and charge density (CD), which led to differences in optimal flocculation conditions. To assess the performance of each polymer, their optimal dosages were first evaluated with the conventional jar test
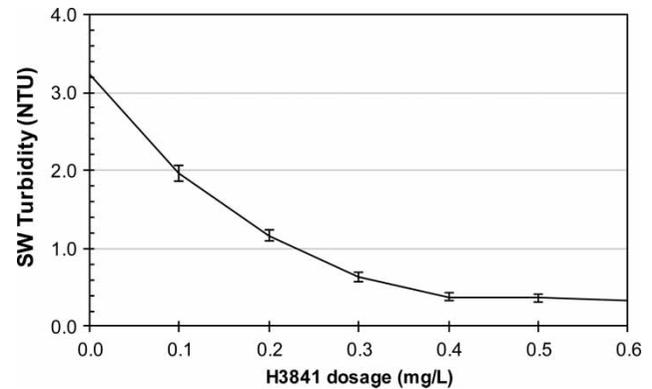
procedure detailed in Figure 1. Alum or ferric chloride (0.13 meq./L) was used as coagulant while PAM and H3841 were used as flocculants. Figure 3 indicates the optimal dosage of each polymer used in conjunction with 4 g/L of microsand while Table 2 summarizes the optimal conditions identified. Optimal dosages were selected in order to minimize SW turbidities (i.e., under 0.8 NTU) while minimizing polymer dosages. The performance of PAM was found to be independent of coagulant type and water temperature. An optimal dosage of 0.075 mg/L was identified. In the case of H3841, slight differences were observed with alum at 21 °C performing the best while ferric chloride at 21 °C had the lowest performance. However, for all three conditions, an H3841 dosage of 0.3 mg/L was found to reduce turbidity in a narrow range (0.39–0.72 NTU). Therefore, the starch polymer dosage was found to be roughly equivalent to four to five times the PAM dosage needed. The return of experience on Actiflo® drinking water plants already operated by Veolia using starch-based polymer in France reported a ratio of three to four times compared to the PAM dosage (Gaid & Sauvignet 2011).

Microsand dosage selection

To allow the formation of a denser floc, microsand is added during flocculation. The optimal concentrations of microsand (expressed in g/L) were determined while using the optimal polymer dosages identified in Figure 3(a) (with alum at 21 °C). The microsand selected for this test had an average diameter of 137 μm as shown in Figure 4(a). Figure 4(b)
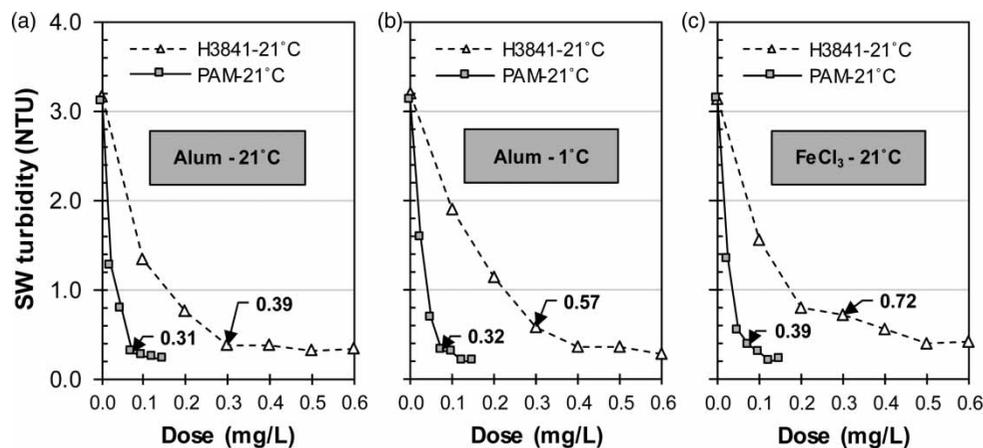
Figure 3 │ SW turbidity in relation to polymer dosage during conventional ballasted jar test procedure. Conditions: coagulant dosage = 0.13 meq./L, microsand = 4 g/L, G during flocculation = 165 s^{-1}, settling: 3 min.

Table 2 │ Optimal dosage of polymers and associated SW turbidity obtained from Figure 3 (after 3 min of settling)

	PAM		H3841		
	Dose (mg/L)	SW turbidity (NTU)	Dose (mg/L)	SW turbidity (NTU)	Dose ratio from Figure 3(a) (H3841/PAM)
Alum – 21 °C	0.075	0.31	0.3	0.39	4.0
Alum – 1 °C		0.32		0.57	
FeCl$_3$ – 21 °C		0.39		0.72	

Alum and FeCl$_3$ dosages = 0.13 meq./L.

suggests that a microsand concentration of 2 g/L was sufficient to remove turbidity for both polymers. Again, PAM provided slightly lower SW turbidity (0.19 NTU) than H3841 (0.26 NTU).

Selection of an optimal velocity gradient for flocculation (G)

Jar tests were conducted under increased velocity gradients in order to identify the optimal flocculation conditions. To achieve Camp numbers (i.e., G values) higher than 300 s^{-1}, volumes were reduced down to 1,000 mL. The concentrations of non-settleable particles (Figure 5(a)) and SW turbidities (Figure 5(b)) both indicate that the adequate velocity gradient for H3841 is lower than for the PAM polymer. Achieving a turbidity lower than 0.5 NTU in SW required using G values below 400 s^{-1} for PAM as opposed to less than 250 s^{-1} for H3841. Consequently, a higher shear

stress was more deleterious to H3841 than PAM. However, for a G close to 140 s^{-1}, both flocculants had similar performances considering non-settleable particles and SW turbidities. Figure 5(a) also showed that PAM needed a minimal energy gradient during flocculation (>60 s^{-1}) in order to reduce particles after settling.

Effect of microsand size distribution on turbidity removal

The original microsand was sieved in order to produce two microsand size fractions and compare their effects on flocculation performance. The smaller fraction included microsand with size ranging from 60 to 83 μm while the larger fraction included particle size ranging from 100 to 160 μm. These fractions represented, respectively, 7% and 50% (by weight) of the original microsand distribution. Figure 6(a) demonstrates that a sand diameter between 63 and 80 μm produced comparable SW turbidities, independently of the polymer selected. Using this size fraction, it was also possible to largely reduce the dosage of microsand required and previously obtained in Figure 4(b). For example, a 0.2 g/L dosage of microsand, PAM and H3841, respectively, yielded SW turbidities of 0.28 and 0.43 NTU. However, Figure 6(b) illustrates that using the larger microsand (100–160 μm) negatively impacted both polymers. As opposed to the optimal microsand dosage (2 g/L) found in Figure 4(b), Figure 6(a) reveals that an optimal microsand dosage approximately 10 times smaller (0.2 g/L) is found when a 63–80 μm microsand is employed during
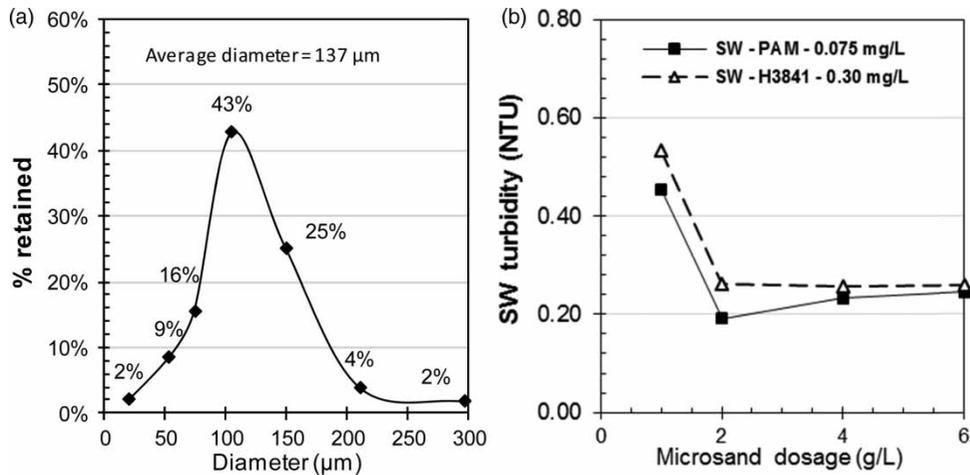
Figure 4 │ (a) Microsand grain size distribution and (b) SW turbidity for increased microsand dosage for jar testing under optimal PAM or H3841 polymer dosages. Conditions: alum dose = 0.13 meq./L, temperature = 21 °C, G during flocculation = 165 s^{-1}, 3 min of settling.
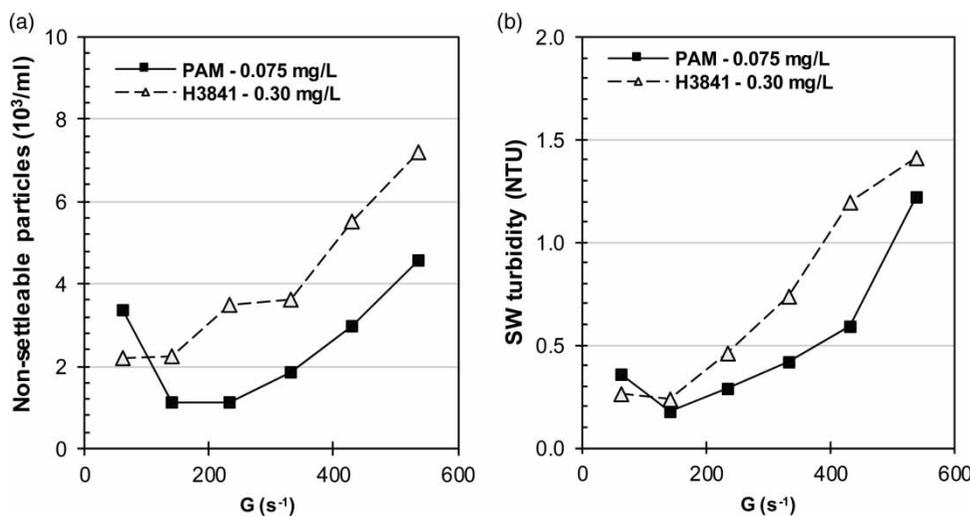

Figure 5 │ Non-settleable particles concentration and SW turbidity obtained with different velocity gradient during flocculation. Conditions: alum dose = 0.13 meq./L, temperature = 21 °C, microsand = 4 g/L, 3 min of settling.

flocculation. In addition, Figure 6(b) shows that H3841 did not bridge stable particles with the microsand larger than 100 µm. The SW turbidity achieved with this larger microsand (1.25 NTU) is equivalent to the results obtained without sand (data not shown). Similar results were also observed with waters from the Mille-Îles River (Quebec, Canada). A favorable effect of using smaller microsand for turbidity removal was also noted for this very turbid raw water (75 NTU). With 0.3 mg/L of PAM, SW turbidities produced from microsand, respectively, having diameters in the

range of 63–80, 80–100, and 100–160 µm were 0.28, 0.37, and 0.45 NTU. This impact was more significant when starch polymers were used.

Temperature effect on turbidity removal

Both polymers were tested at 1 and 21 °C to observe the global impact of temperature on the clarification process. PAM was not impacted by cold temperature ($p = 0.43$) and the previous optimal dosage (0.075 mg/L) was identical for
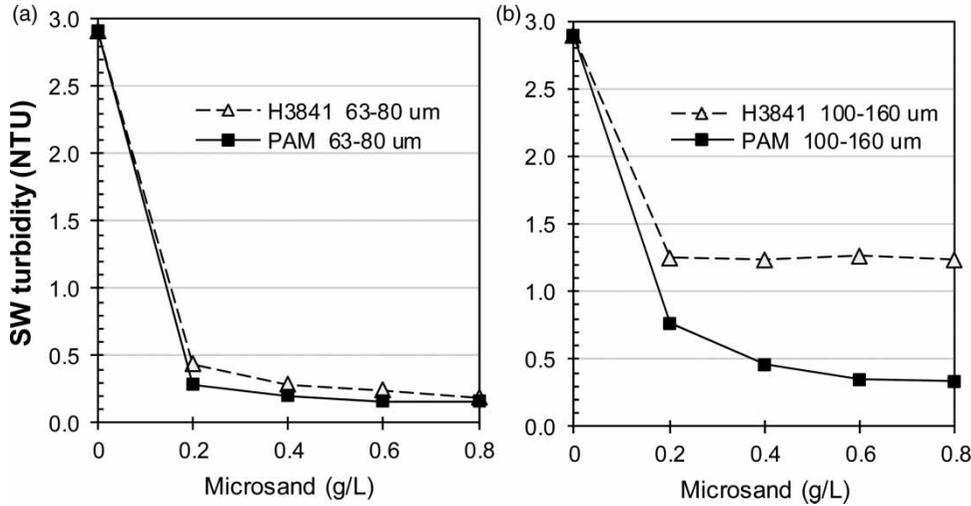
Figure 6 │ Grain size effect on turbidity removal. Conditions: alum dose $= 0.13$ meq./L, temperature $= 21\ ^{\circ}$C, G during flocculation $= 165$ s^{-1}, 3 min of settling.

both temperatures (Figure 7(a)). On the other hand, H3841 was shown to be impacted by lower water temperature ($p = 0.04$). Nevertheless, under optimal polymer dosages (0.4–0.6 mg/L) presented in Figure 7(b), the differences were not statistically significant ($p = 0.61$).

Impact of polymer dosage on filtered water quality

DOC and BDOC removal

DOC and BDOC removals from raw to coagulated/settled/microfiltered waters were measured in order to assess if the

treated waters were impacted by the polymer type. Several assays were performed using alum or ferric chloride (as coagulants) in conjunction with PAM or H3841 (as flocculants). The experiments using alum coagulant were realized at 1 and 21 °C while ferric chloride was solely tested at 21 °C. For all coagulation conditions, Figure 8(a) revealed a slightly better DOC removal with PAM than H3841. Differences in DOC removal between both polymers were statistically significant ($p = 0.02$). Alum performance was not significantly altered by cold water temperature and exhibited a similar residual DOC after filtration ($p = 0.11$). In Figure 8(b), ferric chloride (21–23%)
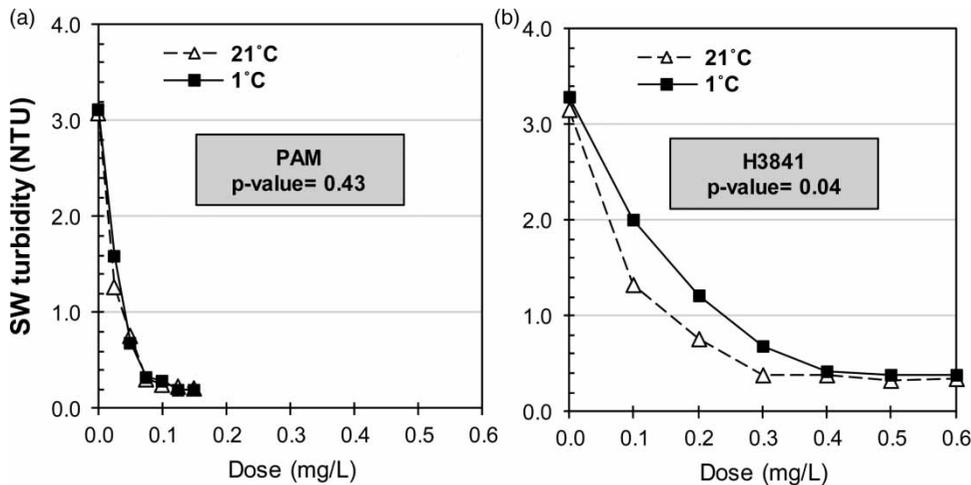

Figure 7 │ Temperature effect on turbidity removal with (a) PAM and (b) H3841 polymers. Conditions: alum dose $= 0.13$ meq./L, microsand $= 4$ g/L, G during flocculation $= 165$ s^{-1}, 3 min of settling.
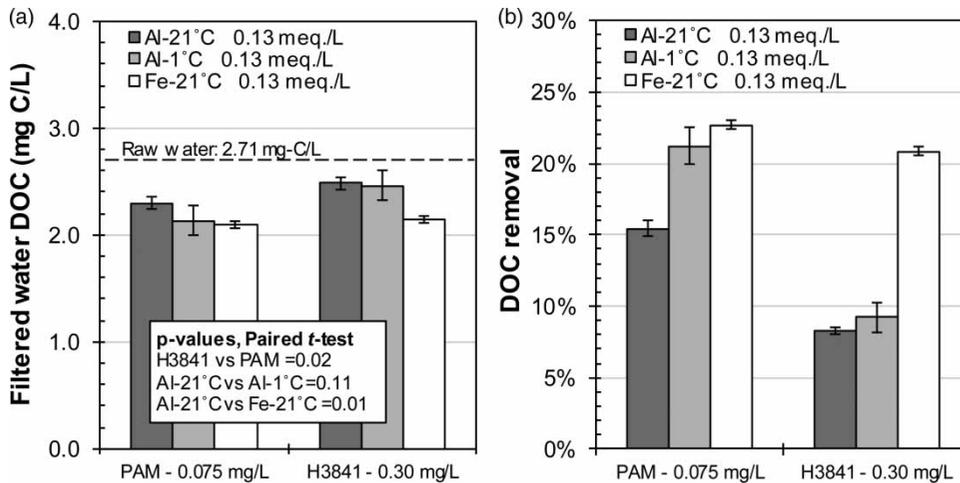
Figure 8 | (a) Residual DOC and (b) DOC removal in filtered waters according to different coagulant–polymer combinations. Conditions: microsand = 4 g/L, G during flocculation = 165 s^{-1}, filtered on 0.45 μm membrane. Error bars indicate the 95th centile confidence intervals.

provided better DOC removal than alum (8–21%), mainly when H3841 was used as flocculant ($p = 0.01$).

In the case of BDOC, Figure 9 reveals that the starch-based polymer was responsible for a small BDOC release compared to what should be expected from biodegradable molecules ($\approx$0.15 mg C/L, detection limit: 0.11 mg C/L) in filtered water. However, as shown in Figure 9(a), the release was more pronounced for alum in cold water while ferric chloride provided equivalent final BDOC (H3841 = 0.37 mg C/L vs. PAM = 0.33 mg C/L).

Removal of THM–UFC and HAA–UFC precursors

Filtered waters were chlorinated under UFC to evaluate the removal of THM and HAA precursors (Figure 10). THM–UFC and HAA formations were shown to be statistically independent of the polymer selection ($p = 0.42$ and 0.35, respectively). No significant impacts of water temperature ($p = 0.96$) and coagulant type ($p = 0.14$) on THM–CFU removals were noted while it was the opposite for HAA–UFC, which were observed to be better removed under
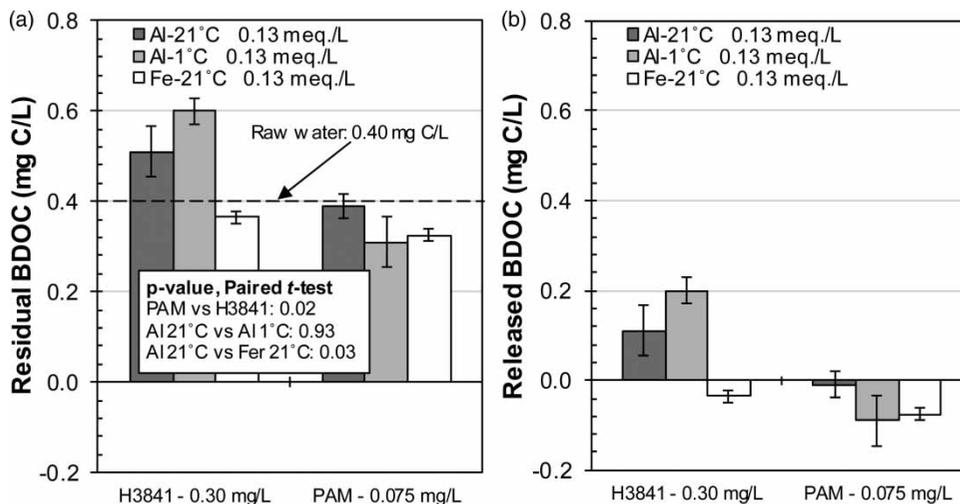

Figure 9 | (a) Residual BDOC in filtered waters according to different coagulant–polymer combinations and (b) BDOC release considering initial BDOC in raw water. Conditions: microsand = 4 g/L, G during flocculation = 165 s^{-1}, filtered on 0.45 μm membrane. Error bars indicate the 95th centile confidence intervals.
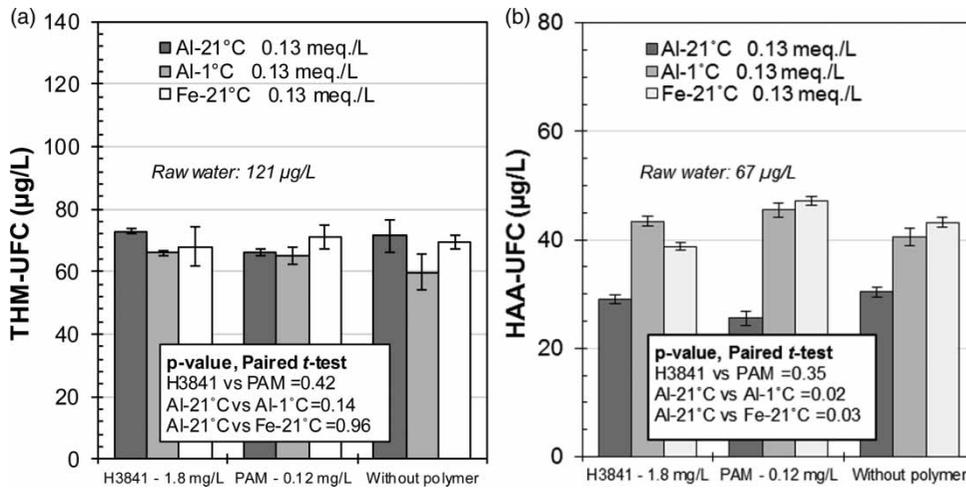
Figure 10 | (a) THM–UFC and (b) HAA-UFC formation in filtered waters using different coagulant–polymer combinations. Conditions: microsand = 4 g/L, G during flocculation = 165 s^{-1}, filtered on 0.45 µm membrane. Error bars indicate the 95th centile confidence intervals.

warm than cold water temperatures ($p = 0.02$) and using alum as opposed to ferric chloride ($p = 0.03$).

DISCUSSION

Optimal polymer dosage and properties

During coagulation–flocculation, particles are generally removed by two main mechanisms: charge neutralization and inter-particle bridging. With anionic high MW polymers, bridging is potentially the principal mechanism for particle trapping (Mpofu et al. 2003). Bolto & Gregory (2007) demonstrated the importance of selecting the appropriate MW and CD polymer to optimize flocculation kinetics and particle trapping. As coagulant aids or flocculants, polymers with high MW and low CD offer better performance. A low negative CD assures the expansion of polymer chains and gives an opened structure considered ideal for flocculation using the bridging mechanism (Somasundaran & Moudgill 1988). Contrary to a high negative CD, using a low CD does not create significant electrostatic repulsion between polymer chain and negative particles. This theory suggests that there is an optimal CD for each type of water, depending on the specific charge of residual particles after coagulation and the ionic strength.

PAM, having a tendency to be polymerized in a more linear structure than starch, leads to longer polymer chains and higher MW, up to several million (Caskey & Primus 1986). For flocculation using principally a bridging mechanism, the length of chain is an important factor (Bolto & Gregory 2007) and could explain the need for using higher dosages of starch polymer. However, replacing PAM with H3841 will probably have no significant impact on the global costs since the costs of polymer applied during flocculation are less than 1% of the total chemical costs typically observed in conventional plants (i.e., including coagulation, flocculation, settling, filtration, and chlorine disinfection). Despite the differences in dosage, H3841 and PAM showed similar and adequate SW turbidities. Performances were better with alum than ferric chloride. This outcome may have resulted from the lower amount of microflocs formed with alum compared to ferric salts. Lower performances of FeCl$_3$ concerning turbidity removal were also detailed by Matilainen et al. (2010).

Optimal microsand dosage, ballast media size, and velocity gradient

Young & Edwards (2000) showed that microsand is not part of a chemical reaction and is rather included in the floc by contact and differential momentum during flocculation. Therefore, the optimal sand dosage is strongly related to raw water turbidity, coagulant dose, and polymer dose, which will all influence the final amount of flocs formed.

This study highlighted the importance of microsand concentration and notably the importance of microsand size distribution. Young & Edwards (2000) have also noted that an over-dosage of microsand may lead to a slightly increased SW turbidity. Starch polymers' performance was improved by the use of a microsand smaller than 100 μm; otherwise, incorporation of microsand in the floc structure was problematic. This conclusion is similar to the work published by Sibony (1981) who recommended the use of microsand with a diameter between 20 and 100 μm. For low turbidity waters such as the one tested in this study, this author recommends using a range of 40–80 μm for particles' removal. Others authors have also suggested a grain diameter smaller than 160 μm to optimize the supernatant quality (De Dianous & Dernaucourt 1991). In the review of Thomas *et al.* (1999) on flocculation, these authors highlighted that hydrodynamic repulsion between large and small particles reduces collision efficiencies. Over a certain particle diameter, more specifically expressed as the ratio of $R/\sqrt{k}$ (*R*: aggregate radius and *k*: aggregate permeability), the collision efficiency is close to zero (Kusters *et al.* 1997). Furthermore, large microsand may generate substantial shear leading to flocs breakage. Consequently, the present study indicates that reduced microsand dosages up to 75% (i.e., entirely eliminating the microsand bigger than 100 μm) might be achieved by using a smaller microsand, a benefit that would especially advantage the starch-based polymer.

Another advantage related to the use of a smaller microsand relates to the reduced power needed during flocculation. The ballasting agent, in this case the microsand, is heavier than flocs and is enmeshed into the floc by inertial forces (Ghanem *et al.* 2007). The power induced during ballasted flocculation must be greater than for conventional flocculation in order to maintain the sand in suspension. Therefore, the resistance of polymers to shear is important to prevent aggregates' rupture. Starch polymers were shown to be less resistant to shearing than PAM, probably due to the higher MW of PAM, which favors interparticle bridging. Reducing the microsand diameter improved the performance of the starch-based polymer and also allowed operating at a lower mixing energy. It is therefore advisable to revisit ballasted flocculation conditions while operating with activated starch polymers.

Temperature effect

It is well known that alum hydrolysis can be significantly slowed down at low water temperatures (Duan & Gregory 2003). They also give rise to an irregular floc structure (Xiao *et al.* 2009) potentially reducing its shear strength. However, it was shown that PAM compensated the poor turbidity removal from alum at 1 °C, and the global clarification process was not impacted by these extreme conditions. It was also the case when starch polymer was employed as flocculant. However, H3841 needed a slightly higher dosage (0.4 instead of 0.3 mg/L) in cold water to compensate for non-settleable particles left from alum and to achieve a good SW turbidity (0.4 NTU).

Alum performance for DOC removal was improved under low temperature. The minimal point of solubility for Al species is increased by 1 pH unit when temperature drops from 25 to 5 °C (Driscoll & Letterman 1988; Duan & Gregory 2003). For the coagulation conditions in this study (initial pH of 8.0), an increased presence of positive alum hydrolysis products would be expected at low temperature, a benefit that favored the higher DOC removal observed.

Impacts on filtered water quality

Activated starch polymers were responsible for a slight release of BDOC in filtered waters. This carbon release explained the small gap in performance between PAM and starch polymer regarding the overall DOC removals. The current assays did not include the use of biological filters. BDOC from starch polymers could potentially have a beneficial side effect for plants using biological filtration. Yavich *et al.* (2004) described the benefits of bio-stimulants like acetate or other simple carbon chain for biomass fixed on a media. This may have a significant impact for carbon removal, specifically for raw water having initially low content of easily assimilable carbon. More studies are needed to evaluate the removal of residual starch by heterotrophic biomass present in a granular biofiltration.

Although slight differences in DOC removals were observed between both polymer types, this result did not translate into differences in THM or HAA formation. Chlorinated disinfection by-product formation was only dependent on the coagulation conditions (especially for

HAA precursor removals). Some authors have already indicated that starch is not considered to be a significant THM (Crane *et al.* 1980; Hong *et al.* 2008) or HAA precursor (Hong *et al.* 2008).

CONCLUSION

The general aim of this paper was to evaluate the potential of starch-based polymers to replace PAM in the flocculation process. This study revealed that these specific activated starch polymers offer a good alternative to polyacrylamide. However, their integration in a ballasted flocculation is subjected to new design considerations and previous typical procedures should be revised to enhance the process performance and account for the specific properties of these polymers. Lower velocity gradient (<250 s^{-1}) and smaller microsand (<100 μm) are considered to be the key elements to consider in the design of improved ballasted flocculation involving starch polymers. Future work should evaluate the fate of residual starch-based polymers in granular media and membrane filtration.

ACKNOWLEDGEMENTS

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