

Removal of trace organic contaminants from wastewater by superfine powdered activated carbon (SPAC) is neither affected by SPAC dispersal nor coagulation

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ABSTRACT

Powdered activated carbon (PAC) is increasingly used as tertiary treatment for the removal of trace organic contaminants (TrOCs) from wastewater (WW). To enhance the sorption kinetics and capacity, the PAC particles can be milled down to superfine powdered activated carbon (SPAC). However, the small-grained SPAC particles are prone to aggregation, which may impact their treatment performance. In this study we examined the effect of SPAC dispersion and aggregation on TrOC removal kinetics and sorption capacity. Specifically, we assessed how two interventions that modulate the apparent size of SPAC - ultrasonication and coagulation - affect the uptake of TrOCs in secondary WW effluent. We quantified the removal of fourteen TrOCs, of which twelve are indicator substances for micropollutant removal in WWTPs as designated by the Swiss Water Protection Ordinance. We determined that at high SPAC doses (> 1.6 mgSPAC/mg Dissolved Organic Carbon [DOC]), the TrOC removal kinetics were fast even for aggregated SPAC, such that SPAC dispersal by ultrasonication yielded no benefit. At low SPAC doses (< 1.6 mgSPAC/mgDOC) and contact times (< 2 minutes) ultrasonication was beneficial, in particular if the SPAC particles reached complete dispersion prior to exposure to TrOCs. However, the energy consumption of such an ultrasonication step should be carefully weighed against the additional energy requirement associated with using a higher SPAC dose. Finally, a coagulant to mitigate membrane fouling can be added simultaneously with the SPAC without compromising the TrOC removal efficiency. We conclude that under realistic SPAC application scenarios in WWTPs, interventions that disperse SPAC during TrOC sorption are not necessary, and processes that aggregate SPAC are acceptable.

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1. Introduction

Humans produce and consume thousands of organic compounds that are partly introduced as trace organic contaminants (TrOC) into freshwater environments via municipal and industrial wastewater treatment plant (WWTP) effluents. Even at concentrations below the microgram per liter range, these TrOCs present a risk to freshwater ecosystems (Schwarzenbach et al., 2006). WWTPs only partially remove TrOCs from the wastewater (WW) stream (Luo et al., 2014; Margot et al., 2015; Oulton et al., 2010), and discharge the remainder into the receiving waters (Bonvin et al., 2011; Gälli et al., 2009). In an effort to reduce the contamination of rivers and lakes, the Swiss Water Protec-

tion Act and Ordinance (The Swiss Federal Council, 2017, 2018) requires large WWTPs to upgrade their treatment train, such that they achieve an 80% removal of the incoming load of TrOCs. Compliance with this Ordinance is verified by monitoring the average removal of at least six and up to 12 TrOCs indicator compounds.

Currently recommended treatment processes for TrOC removal in WWTPs consist of oxidation by ozone, followed by sand filtration, or adsorption onto granular or powdered activated carbon followed by sedimentation/sand filtration (GAC/PAC-SF) (Wunderlin et al., 2017). Both approaches are effective in achieving the required 80% TrOC reduction (Margot et al., 2013), but they each have limitations. Most importantly, not all effluents are suitable for treatment by ozone, which can generate hazardous disinfection by-products (DBPs) (von Sonntag and von Gunten, 2015). While GAC/PAC-SF does not generate DBPs, this treatment method has substantial economic and environmental costs

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associated with the production of the activated carbon material (Jekel et al., 2016; Margot et al., 2013).

The costs of activated carbon-based treatments could be optimized by using a material with a more effective TrOC uptake than currently available PAC/GAC, such that an 80% TrOC removal can be achieved with a lower carbon dose. A possible method to enhance TrOC uptake is to use superfine powdered activated carbon (SPAC), which is produced by wet-milling of PAC. Based on laboratory experiments, Bonvin et al. (2016) showed that the use of SPAC would allow for a shorter contact time compared to PAC to achieve a similar TrOC removal from WW effluents. SPAC has also demonstrated greater removal capacities of taste and odor compounds compared to PAC in drinking water (DW) treatment (Matsui et al., 2013a; Pan et al., 2016, 2017), as well as an enhanced overall dissolved organic material removal (Ando et al., 2010; Matsui et al., 2012, 2013b). Traditional coagulation/flocculation, sedimentation and sand filtration steps, as well as advanced filtration membranes can be implemented downstream to remove the SPAC particles from the water or WW stream (Kweon et al., 2009; Löwenberg et al., 2014; Nakazawa et al., 2018a, 2018b).

One possible factor underlying the improved performance of SPAC compared to PAC for TrOC removal is its higher sorption capacity. An increase in the equilibrium sorption capacity was previously observed when the median particle diameter (D_{50}) of PAC was reduced down to the micron range (1–3 μm). Alternatively, the enhanced performance of SPAC may stem from faster sorption kinetics. Matsui et al. (2009, 2013a), who modeled the sorption of geosmin and 2-methylisoborneol (MIB) in drinking water onto PAC and SPAC, observed that sorption rates increased with decreasing D_{50} . More rapid sorption kinetics for SPAC compared to PAC were also observed by Bonvin et al. (2016) in WW effluents, with SPAC particles with a D_{50} of 1 μm requiring a contact time of 10 min to reach adsorption equilibrium while PAC particles took more than 2 hrs.

A potential limitation of the use of SPAC is the tendency of small particles to aggregate in solution, depending on particle concentration and solution conditions (temperature, pH, ionic strength and chemical composition) (Baalousha, 2009; Dempsey, 2006). In drinking water, Pan et al. (2016) reported a slower sorption of MIB onto dry-milled compared to wet-milled SPAC, which they attributed to a combination of lower sorption capacity and aggregation state. These authors suggest that aggregated SPAC particles have interparticle spaces that act as pseudopores, which increase the total diffusive path length, resulting in a lower sorption rate is lowered for aggregated SPAC compared to single particles (Pan et al., 2016). Based on their findings, they recommended to disperse SPAC particles by ultrasonication if the aggregated particle size is more than twice the dispersed particle size. It is not known, however, if these findings also apply to wastewater, where the higher content of organic matter may lead to competition with TrOCs for the sorption sites on SPAC.

The goal of this work was to investigate the impact of particle aggregation on the removal of TrOCs from WW effluent. In particular, we assessed the effect of two interventions that modify the apparent size of SPAC, namely ultrasonication and coagulation. Ultrasonication can be used to disperse particles prior to and during TrOC sorption. Coagulation is applied in treatment trains with a SPAC/ultrafiltration process, to facilitate suspended solids removal and mitigate membrane fouling. We monitored the removal of 14 TrOC by SPAC, including the 12 compounds designated as indicators in the Swiss Water Protection Ordinance for removal of TrOCs (DETEC, 2016), and determined the average removal under different treatment scenarios. Ultimately, this work provides operational recommendations for the application of SPAC to treat WW effluents.

2. Materials & methods

2.1. SPAC

Commercially available coal-based PAC (Pulsorb FG4; Chemviron Carbon, Belgium) was used in this study to produce SPAC by wet-milling with a DYNOMILL ECM-AP 05 (WAB AG, Switzerland). Compared to dry-milling, onsite wet-milling of SPAC in a wastewater treatment plant is a safer procedure, because the dry SPAC powder constitutes an explosion risk. SPAC of three different sizes was produced, namely with a D_{50} around 1, 3 and 5 μm (SPAC 1, SPAC 3 and SPAC 5, respectively) in disperse suspensions. SPAC suspensions with a concentration of 20–30 g/L were produced in deionised water. These suspensions were diluted with deionized water to produce SPAC stock solutions (200 mL) with a targeted concentration range of 1.5–3 g/L, and were stored at 4°C. The SPAC stock concentration was determined by extracting four aliquots of 5 mL from a stirred SPAC stock solution, oven-drying them at 200°C for > 48 hr, and weighing them on a microbalance (AT261; Mettler Toledo). The resulting SPAC concentrations were estimated at 2.3 ± 0.2 (mean \pm stdev) (SPAC 1), 1.6 ± 0.2 (SPAC 3) and 2.5 ± 0.1 g/L (SPAC 5). Throughout our work, we use the terms volume-based [mg/L] and specific [mgSPAC/mg dissolved organic carbon (DOC)] dose of SPAC to distinguish between the dose per volume of WW and the dose normalized to the DOC content of the WW.

2.2. Water matrices

Two batches (~30 L) of secondary WW effluent (after primary clarification, activated sludge treatment and secondary clarification; see supplementary information (SI)) were collected from the WWTP of Châteauneuf (Sion, Switzerland). The two batches (WW1 and WW2) were collected six months apart. The WW was collected over 24 hours in a flow proportional manner, and was mixed and stored in individual 1 L glass bottles at 4°C. Upon arrival in the lab, ammonium, nitrate, nitrite and phosphate concentrations, as well as the total suspended solids (TSS) concentration, were determined. The ammonium concentration was quantified by ion chromatography (ICS-3000, IonPacCS16 column) with electrical conductivity detection (Dionex, Switzerland). Nitrate, nitrite and phosphate concentrations were measured by ion chromatography (ICS-3000, IonPac AS11-HC column). TSS was determined according to the standard protocol (APHA, 2012). The pH, electrical conductivity (EC), and the DOC concentration of the WW changed during storage and were therefore determined prior to each experiment. The pH and EC were measured with Multi 3430 pH and conductivity meter (WTW). The DOC concentration was determined as non-purgeable organic carbon by TOC analyzer (TOC-L CPN; Shimadzu; Japan). Drinking water (DW) was collected from the tap (Lausanne, Switzerland) and was characterized analogously to WW. Detailed water matrix characteristics are given in the SI (Table S1).

2.3. TrOCs

Fourteen TrOCs were quantified during the course of our different experiments. TrOCs and their deuterated standards were purchased in high purity from Sigma-Aldrich, LGC, Dr. Ehrenstorfer and TRC (Toronto Research Chemicals). Twelve compounds are the indicators TrOC described in the Swiss Water Protection Ordinance for monitoring the removal of trace organic compounds (DETEC, 2016) and are known to be efficiently removed by AC: amisulpride, benzotriazole, candesartan, carbamazepine, citalopram, clarithromycin, diclofenac, hydrochlorothiazide, irbesartan, methylbenzotriazole, metoprolol, venlafaxine. Two more TrOCs that

are weakly adsorbed by AC were added to our list: mecoprop and sulfamethoxazole. TrOC concentrations were determined in each water matrix prior to each experiment as described below. If the concentration of a given TrOC was too low to detect an 80% removal, this TrOC was spiked into the matrix (SI, Table S1) to raise its concentration. To this end, a methanol (MeOH) solution was prepared containing the TrOCs of interest. This solution was left open for > 12 hours under a fume hood to evaporate the MeOH. Acidified Evian water was added and the solution was shaken for 1 min. The resulting aqueous TrOC solution was then stored for no more than 2 days at 4°C before being used as a spiking solution.

TrOC concentrations were quantified by online solid phase extraction, followed by ultra-performance liquid chromatography and tandem mass spectrometry (UPLC-MS/MS; Acquity Xevo, Waters). Samples were diluted 1:1 with acidified Evian water (pH ~2.5, HCl 25%) and a deuterated analogue of each target TrOC was spiked into every sample as an internal standard. The analytical method was adapted from previous work (Bonvin, 2013; Margot, 2015; Morasch et al., 2010) and details can be found in the supplementary information. TrOC concentrations were calculated based on calibration curves using all 8 calibration points for high concentrations and only the 5 lowest standards for low concentrations. Correlation coefficients for the calibration curves were typically >0.990. The analytical limit of quantification (LOQ) was defined as the concentration of the lowest standard with a signal-to-noise ratio > 10 (SI, Table S2). The uncertainty associated with the sample concentrations, calculated as the relative standard deviation, was <30% for the large majority of the compounds (Bonvin, 2013).

2.4. Sorption kinetics

Three types of kinetic experiments were conducted to investigate the impact of SPAC characteristics without and with external interventions on TrOC removal kinetics. First, we characterized the influence of SPAC dose and particle size on TrOC uptake from WW effluent. Second, we investigated the effect of ultrasonication (to break up SPAC aggregates) on TrOC uptake. And third, we tested if the impact of Fe coagulant on SPAC size and TrOC removal.

2.4.1. Influence of SPAC dose and particle size on TrOC uptake without interventions

Samples (500 mL) of WW were stirred by a magnetic stir bar at 300 rpm in glass a beaker. Then, the SPAC stock solution of interest was spiked into the WW using a pipettor with a 5 mL tip, which had a mouth wider than 1 mm to avoid particle retention during the spiking process. Samples (20 mL) were periodically taken and were filtered through a 0.02 µm homemade filter to ensure the complete removal of the SPAC. The filters consist of a single PES hollow fiber from a drinking water filtration membrane, with a syringe glued onto one side and a plug on the other side (SI, Figure S1). The filtration process took between 15–20 seconds. Filtered samples were analyzed for TrOCs within hours of the experiment.

2.4.2. Effect of ultrasonication

TrOC uptake experiments were conducted as described above, except that they were conducted in a temperature-controlled water bath (recirculating cooler F240; Julabo) kept at 18°C. The temperature of the water matrix was checked at the end of each experiment to ensure that it did not rise above 25°C. An ultrasonication power of 13 W (100 % power; Telsonics with ultrasonication probe; 50/60 Hz) was applied. The power was confirmed according to a calorimetric method proposed by Taurozzi et al. (2011) (see SI for detailed procedure). For each experiment, the ultrasonication probe tip was placed in the center of the beaker, around 2 cm above the bottom. Ultrasonication was accomplished either simultaneously to sorption (i.e., sonication was started while spiking

the SPAC; sim.) or prior to and simultaneously to sorption (i.e., the sonication started 10 min prior to SPAC spiking and was maintained throughout the experiment; prior + sim.). For the latter set of experiments, DW was used instead of WW, to allow for prior sonication in the absence of TrOCs. After 10 min of sonication, the DW was then amended with the TrOCs of interest and sorption was monitored. Sample workup and analysis were conducted as described above.

2.4.3. Impact of Fe coagulant

Experiments with coagulants were conducted as described above. However, in addition to TrOC and SPAC, the WW was amended with FeCl₃. Specifically, a coagulant stock solution of 100 ppm Fe (96.8 mg FeCl₃ · 6 H₂O in 200 mL; Acros) was spiked into the reactor to achieve a concentration of 2 ppm Fe in WW. The coagulant was spiked shortly before the SPAC, and the solution was mixed at 300 rpm throughout the experiment to ensure SPAC suspension. Sample workup and analysis were conducted as described above.

For each set of experiments, SPAC-free control experiments were conducted. The different sorption kinetics experiments performed are summarized in the SI (Table S3).

2.5. Particle size distribution (PSD)

Besides TrOC removal, the particle size distribution of SPAC without intervention, and while sonicating or adding a coagulant was determined. The measurements were performed with a Mastersizer S (Malvern; UK), with the stirring chamber running at 1400 rpm for all measurements. The D₅₀ was calculated from the cumulative distribution, which was derived from the volume distribution corrected post-measurement for artifact peaks (peaks in the > 100 µm range likely due to air bubbles).

2.5.1. Dispersed (D-PSD) and aggregated particle size distribution (A-PSD)

Two droplets of the 20–30 g/LSPAC suspension (collected after wet-milling) were spiked into 100 mL of deionized water (DI water) or WW effluent with a plastic Pasteur pipette with an approximately 2 mm wide tip, to achieve a final concentration 20–40 mg/L SPAC. The WW effluent was filtered (mixed cellulose esters membrane, hydrophilic, 0.45 µm pore size; Millipore) and pasteurized for 1 hr at 55°C to avoid contamination of the measuring device, while simultaneously conserving the ionic composition and pH of the WW. To determine the D-PSD, the SPAC-spiked samples were stirred for 10 min at ~ 300 rpm while sonicating at 13 W in a beaker with water to avoid heating the sample. The A-PSD was determined with the same procedure, except that the mixture was not sonicated. Each D-PSD and A-PSD measurement was performed in triplicate or quadruplicate from the same solution.

2.5.2. Dispersal and aggregation kinetics

Dispersal or aggregation kinetics were determined under conditions similar to those used in the TrOC sorption experiments. Specifically, 500 mL of filtered and pasteurized WW effluent were amended with SPAC to a concentration around 8 mg/L. Samples were either ultrasonicated at 13 W, or were amended with 2 ppm Fe coagulant. A control sample with a SPAC concentration of ~8 mg/L but without ultrasonication or coagulant was also included. The PSD in each experiment was measured after increasing time intervals up to 60 min, in sacrificial samples. Results show the average of triplicate samples spiked and treated separately.

2.6. Data analysis

The distribution of the removal values of the different TrOCs were reported as boxplots, where each box represents data from

Table 1

D₅₀ comparison between D-PSD and A-PSD for SPAC/PAC in DI water and WW used in our experiments. Numbers in parentheses indicate the 10th (D₁₀) and 90th (D₉₀) percentile of the PSD. Detailed PSD curves are shown in SI, Figure S2).

	D-PSD DI water D ₅₀ (D ₁₀ , D ₉₀) [μm]	A-PSD DI water D ₅₀ (D ₁₀ , D ₉₀) [μm]	WW D ₅₀ (D ₁₀ , D ₉₀) [μm]
PAC	18.5 (2.2, 61.7)	24.0 (3.6, 78.2)	
SPAC 1	1.1 (0.4, 3.4)	4.6 (2.2, 8.4)	5.8 (2.9, 10.4)
SPAC 3	2.8 (0.7, 17.6)	4.5 (1.9, 41.9)	6.5 (2.8, 18.1)
SPAC 5	5.5 (1.2, 29.5)	8.2 (2.6, 47.2)	7.9 (3.0, 41.1)

one experiment. For every time step, all experimental conditions were compared by means of a Kruskal-Wallis test, with the null hypothesis being that the median removal for all tested conditions are equal, considering a distribution similar in shape and spread. If the Kruskal-Wallis test yielded a p-value <0.05, a post-hoc pairwise Mann-Whitney U-test with Benjamini & Hochberg correction was further performed. Statistical analyses were conducted in R (R Core Team, 2018), using the functions `kruskal.test` and `pairwise.wilcox.test` with `p.adjust.method` equal to "BH" (R package {stats}). Data acquired for the PSD determination were treated in R with the `cumsum` and `approx` functions (R package {stats}).

3. Results and discussion

3.1. Characterization of SPAC size

Wet-milling of PAC produced three SPAC stock solutions, in which disperse particles (measured under ultrasonication) had a D_{50,D-PSD} of roughly 1, 3 and 5 μm (Table and SI, Figure S2). This corresponded to an up to 17-fold decrease from the original PAC (D_{50,D-PSD} of 18.5 μm). In the absence of sonication, the SPAC particles were present in solutions as aggregates, with D_{50,A-PSD} values of 5.8, 6.5 and 7.9 μm in WW. Similar D_{50,A-PSD} values were measured in DI water (Table 1 and SI, Figure S2), indicating that the matrix had only a minimal effect on the aggregation of SPAC particles. Interestingly, the smaller the disperse particle size, the larger was the relative increase in D₅₀ between disperse and aggregated particles. In DI, PAC, SPAC 5, SPAC 3 and SPAC 1 exhibited D_{50,A-PSD}:D_{50,D-PSD} ratios of 1.3, 1.5, 1.6 and 4.2, respectively. A similar trend was reported by Pan et al. (2016), who observed a higher D_{50,A-PSD}:D_{50,D-PSD} ratio for PAC particles compared to the smaller SPAC.

3.2. TrOC uptake by SPAC without interventions

To characterize the uptake of TrOCs by SPAC in the absence of any external intervention, we tested the sorption performance for different SPAC doses and sizes.

3.2.1. Influence of dose

The influence of SPAC dose on the TrOC removal kinetics was assessed using volume-based SPAC 1 doses of 6, 12 and 15 mg SPAC/L, corresponding to specific SPAC doses of 0.8, 1.6 and 2.7 mg SPAC/mg DOC. These doses approximate the PAC doses typically applied in WW treatment in Switzerland (Horisberger et al., 2019; Margot et al., 2013; Zöllig et al., 2017), which extend from 10 to 20 mg/L.

More than 80% TrOC removal was observed after 2 min of SPAC exposure at specific doses of 1.6 and 2.7 mg SPAC/mgDOC (Fig. 1). For these two doses, sorption equilibrium of most compounds was reached within 2–10 minutes (SI, Figure S2). The lower dose of 0.8 mg SPAC/mgDOC also achieved an 80% removal but required

a longer contact time of up to 60 min to reach sorption equilibrium (Fig. 1 and SI, Figure S3). Discrepancies in the effect of dose on removal kinetics were observed at the level of individual compounds (SI, Figure S3). Increasing the dose exhibited no effect on citalopram, clarythromycin and irbesartan, whereas the impact was pronounced for candesartan, mecoprop and sulfamethoxazole (SI, Figure S3). These latter compounds are hydrophilic (low D_{ow}; see SI, Table S4) and negatively charged at the pH of WW. Compounds with these properties tend to be poorly removed from WW effluent by activated carbon, as was previously shown for GAC and PAC (De Ridder et al., 2011; Margot et al., 2013).

The rapid average removal kinetics by SPAC observed herein confirm earlier findings by Bonvin et al. (2016), who demonstrated that for 15 mg/L dose, PAC usually required 1 to 2 hours contact time to reach equilibrium sorption capacity whereas for SPAC less than 10 min were sufficient. However, our results also highlight the importance of the SPAC dose on the sorption kinetics, in particular for poorly sorbing TrOCs.

Finally, a substantial TrOC removal can likely be achieved at even shorter time intervals than tested herein. Specifically, an average removal of around 30% with up to 50% for amisulpride, methylbenzotriazole and metoprolol was observed by simply filtering 20 mL of WW through a filter pre-treated with 20 mL of a DI solution containing 8 mg/L SPAC 1 (SI, Figure S4). The filtration step yields a contact time around 10–20 sec. This finding thus demonstrates that even at a low SPAC dose a significant amount of TrOCs is sorbed almost instantaneously.

3.2.2. Influence of particle size

To determine the effect of SPAC particle size, TrOC removal kinetics were compared for SPAC 1, 3 and 5 (Table 1). Because no ultrasonication was applied, the SPAC materials in these experiments had D_{50, A-PSD} values of 5.8, 6.5 and 7.9 μm, respectively (Table 1). As shown in Fig. 2, SPAC 1 and 3 exhibited similar (p>0.05) average removal kinetics for the totality of TrOCs studied, while SPAC 5 μm was significantly slower (p<0.05). At the individual compound level, some differences in removal kinetics were observed, with carbamazepine, citalopram, clarithromycin and irbesartan exhibiting significantly slower removal by SPAC 3 compared to SPAC 1 (SI, Figure S5). These compounds have the highest D_{ow} among the TrOCs studied (SI, Table S4), indicating that hydrophobic compounds respond most readily to changes in SPAC particle size. TrOC removal by SPAC 5 was slower than SPAC 1 and 3 for all compounds except candesartan, which was poorly removed by SPAC of all sizes (SI, Figure S5). These findings are consistent with those by Matsui et al. (2013a), who observed slower removal of geosmin and MIB from diluted lake water (~1.5 mgDOC/L) by wet-milled, wood-based SPAC particles with D_{50, D-PSD} of 4.9 μm compared to 0.9 μm.

From these results we can infer that the size of SPAC influences the TrOC removal kinetics. However, in these experiments, both the dispersed particle size, as well as the aggregated particle size increased from SPAC 1 to SPAC 3 to SPAC 5 (Table 1). It thus remains to be determined whether it is the dispersed, or the aggregated particle size that determines the uptake kinetics. Therefore, in the following, we applied two interventions, ultrasonication and coagulation, to modify the aggregation state of the SPAC particles, and to disentangle the effects of basic particle size and SPAC aggregation on the TrOC removal.

3.3. Effect of ultrasonication on TrOC uptake

The application of ultrasonication during the sorption phase was tested in WW for SPAC 1, using an ultrasonication power of 13 Watts. As shown in Section 3.2, variations in TrOC removal under different conditions were mostly evident during the first 10

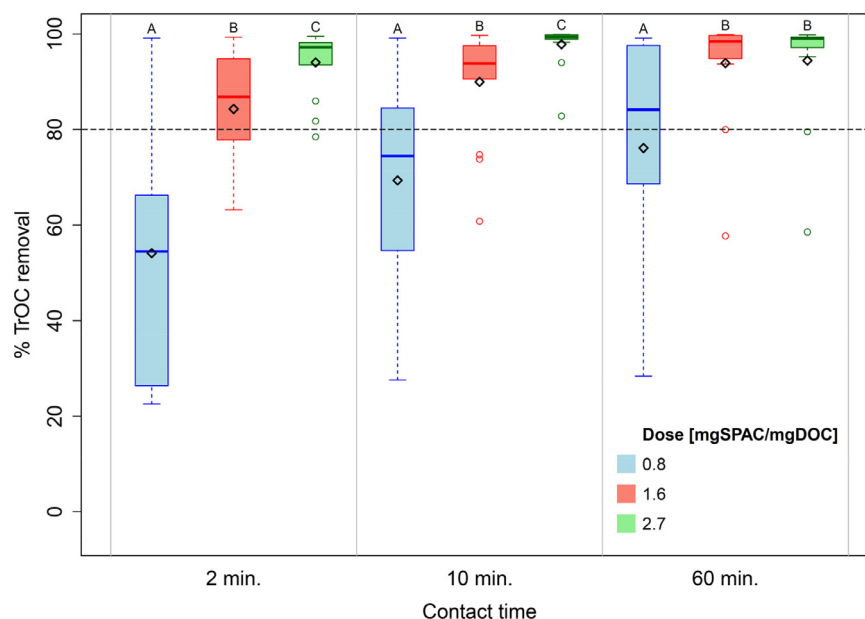


Fig. 1. TrOC removal kinetics by SPAC as a function of the specific SPAC dose [mg SPAC/mgDOC]. SPAC 1 ($D_{50,D-PSD} \approx 1 \mu\text{m}$) was applied in volume-based doses of 6, 12 and 15 mg SPAC/L (blue, red and green respectively), corresponding to specific doses of 0.8, 1.6 and 2.7 mg SPAC/mgDOC. Data are shown in boxplot format, where the thick line indicates the median removal of the 14 TrOCs studied. The box is bounded by the first and third quartiles (50% of the data), the whiskers indicate the minimum and maximum removal measured and the dots are the outliers. Open black diamonds show the average removal of the 14 TrOC, and the horizontal dashed line indicates the removal objective set by the Swiss Water Protection Ordinance (80% average removal). Boxplots with different letters have significantly different ($p < 0.05$) median removal values. Removal kinetics of each individual TrOC are shown in the SI (Figure S3). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

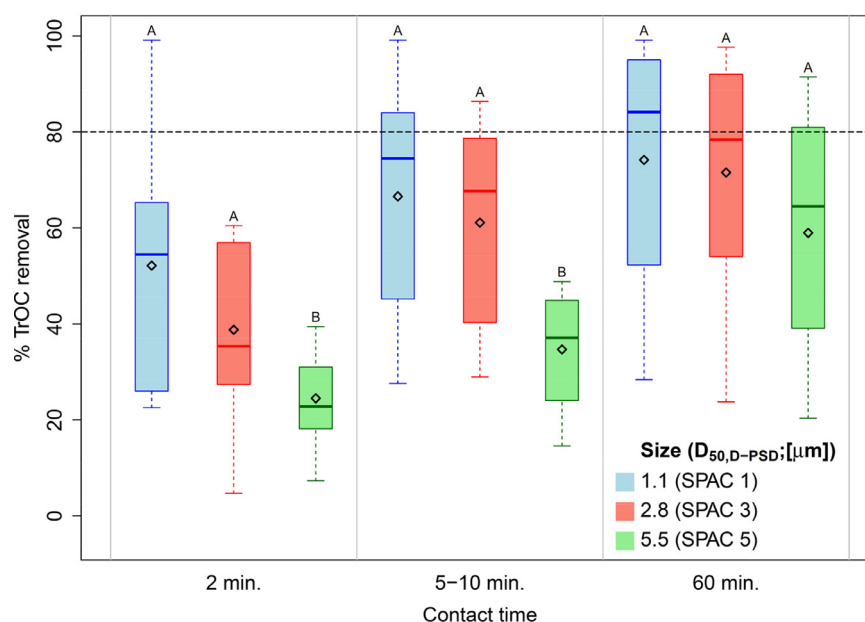


Fig. 2. TrOC removal kinetics as a function of SPAC size. SPAC particles tested had a $D_{50,D-PSD}$ of 1.1, 2.8 and 5.5 μm , but because no ultrasonication was applied, the SPAC particles had actual ($D_{50,A-PSD}$) sizes of 5.8, 6.5 and 7.9 μm (Table 1). The volume-based dose SPAC dose was 6 mg/L (specific dose: 0.8 mg SPAC/mgDOC for SPAC 1 and SPAC 3, and 1.3 mg SPAC/mgDOC for SPAC 5, respectively). Data are shown in boxplot format, where the thick line indicates the median removal of 12 TrOCs studied (citalopram and hydrochlorothiazide were omitted for all conditions, because they were not quantifiable in the experiment with SPAC 5). The box is bounded by the first and third quartiles (50% of the data), the whiskers indicate the minimum and maximum removal measured and the dots are the outliers. Open black diamonds show the average removal of the 14 TrOC, and the horizontal dashed line indicates the removal objective set by the Swiss Water Protection Ordinance (80% average removal). Boxplots with different letters have significantly different ($p < 0.05$) median removal values. The removal of each individual compound is shown in the SI (Figure S5). SPAC 1 and 3 were tested in WW1, and SPAC 5 was tested in WW2.

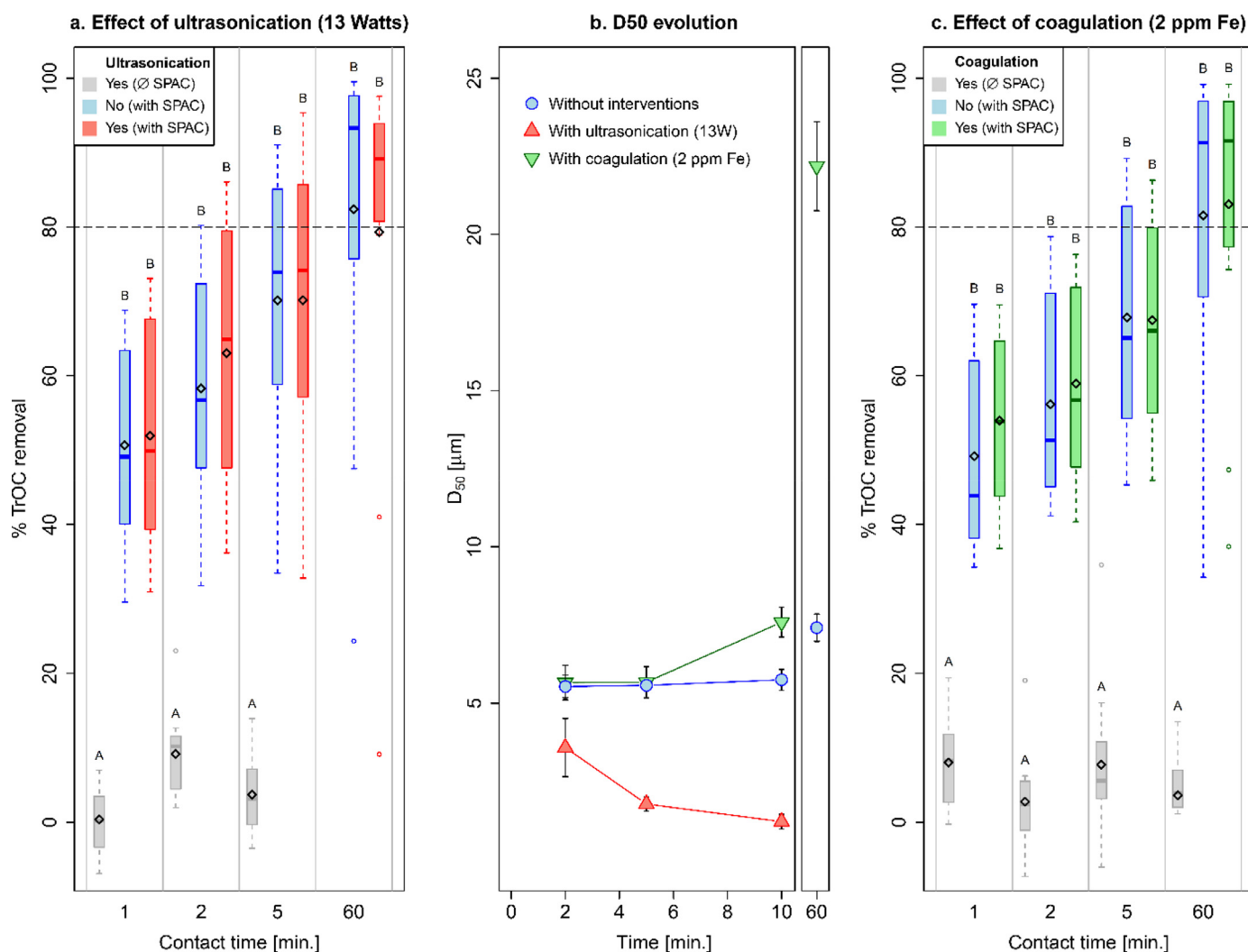


Fig. 3. Effect of interventions (ultrasonication or coagulation) on TrOC removal by SPAC. (a) TrOC removal by SPAC 1 (6 mg/L or 1.3 mg SPAC/mgDOC) without ultrasonication (blue), under simultaneous ultrasonication (red), and with ultrasonication in the absence of SPAC (grey). Data are shown as boxplots, where the thick line indicates the median removal of 12 TrOCs studied (citalopram and hydrochlorothiazide were omitted because they were not quantifiable). The box is bounded by the first and third quartiles (50% of the data), the whiskers indicate the minimum and maximum removal measured and the dots are the outliers. Open black diamonds indicate the average removal of all quantifiable TrOCs. The black dashed line indicates the removal objective set by the Swiss Water Protection Ordinance (80% average removal). Boxplots with different letters have significantly different ($p < 0.05$) median removal values. The removal of each individual compound is shown in the SI (Figure S6). (b) SPAC dispersion or aggregation over time for 8 mg/L of SPAC 1 in filtered/pasteurized WW. Data indicate the $D_{50,A-PSD}$ values measured without external interventions (only stirring; blue circles), under ultrasonication (13W; red triangles), and in presence of a coagulant (2 ppm $FeCl_3$; green inverted triangles). The error bars depict the 95% confidence intervals ($n = 3$). Detailed PSD data are given in the SI (Figure S7). (c) TrOC removal by SPAC 1 (6 mg/L or 1.5 mg SPAC/mgDOC) without coagulant (blue), by SPAC 1 with 2 ppm $FeCl_3$ coagulant (green) and with 2 ppm $FeCl_3$ coagulant in the absence of SPAC (grey). Data are shown as boxplots as in panel a, except that the open black diamonds indicate the average removal of 13 TrOCs (only citalopram was not quantifiable). Individual compound removal is shown in the SI (Figure S8).

min of the experiment. The effect of ultrasonication was therefore investigated at low contact times (1, 2, and 5 min), along with the removal well after equilibrium was reached (60 min; Figure S6). Furthermore, the tested SPAC doses ranged from 1.0–1.6 mg SPAC/mgDOC, because in this dose range Section 3.2 the removal kinetics were sufficiently slow to identify a potential sorption enhancement.

Ultrasonication applied during the sorption experiment did not significantly enhance TrOC removal by SPAC 1, neither in the early sorption phase nor after 60 min. Both the average TrOC removal and the removal of individual compounds was comparable to the removal in the absence of ultrasonication (Fig. 3.a and SI, Figure S6). The same results were observed for SPAC 5 (SI, Figures S9 and S10). These data contradict results of Pan et al. (2016), who observed a greater removal of MIB with dispersed dry-milled SPAC particles when ultrasonication (150 W/50 mL = 3 W/mL for 1 min) was applied prior the sorption experiment ($D_{50,D-PSD} = 1.2$

μm ; $D_{50,A-PSD} = 14.2 \mu\text{m}$). This effect was smaller for wet-milled SPAC mainly because of its smaller $D_{50,A-PSD}$ (3.8 μm) for the same $D_{50,D-PSD}$. Similarly, Li et al. (2018) reported faster sorption kinetics of Rhodamine B to SPAC particles (<1 μm) if the particles were sonicated during the sorption experiment (100 W/100 mL = 1 W/mL for 30 min). The discrepancies in the findings of these two studies and the data shown herein may stem from the differences in experimental design. Both Pan et al. (2016) and Li et al. (2018) used ultrapure water spiked with the compounds of interest as their experimental matrices, and the SPAC was added as a dry powder. In this study, we used wet-milled SPAC, which has a higher equilibrium sorption capacity than dry-milled SPAC (Pan et al., 2016). Furthermore, the experimental matrix used herein (WW) had a higher DOC content than ultrapure water, and rapid sorption of effluent organic matter onto newly available sorption sites produced during ultrasonication may mitigate the effect of SPAC dispersion on TrOC removal. And finally, the ultrasonica-

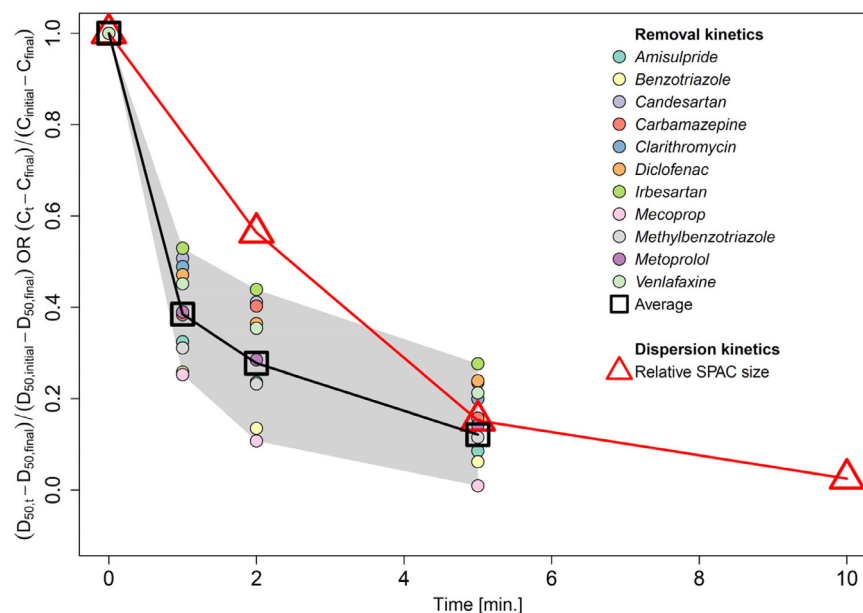


Fig. 4. Comparison of TrOC sorption and SPAC dispersion kinetics. Kinetics of TrOC by SPAC 1 without ultrasonication (black squares) was compared to the kinetics of size change of SPAC 1 during ultrasonication (red triangles). The removal values of individual compounds are shown in colored dots, except for citalopram and hydrochlorothiazide and sulfamethoxazole (removal not quantifiable). The grey area represents the domain between the minimum and maximum removal of any individual compound. TrOC removal data correspond to those shown in Fig. 3a and SI, Figure S6. SPAC PSD data correspond to those in Fig. 3b and SI, Figure S7.

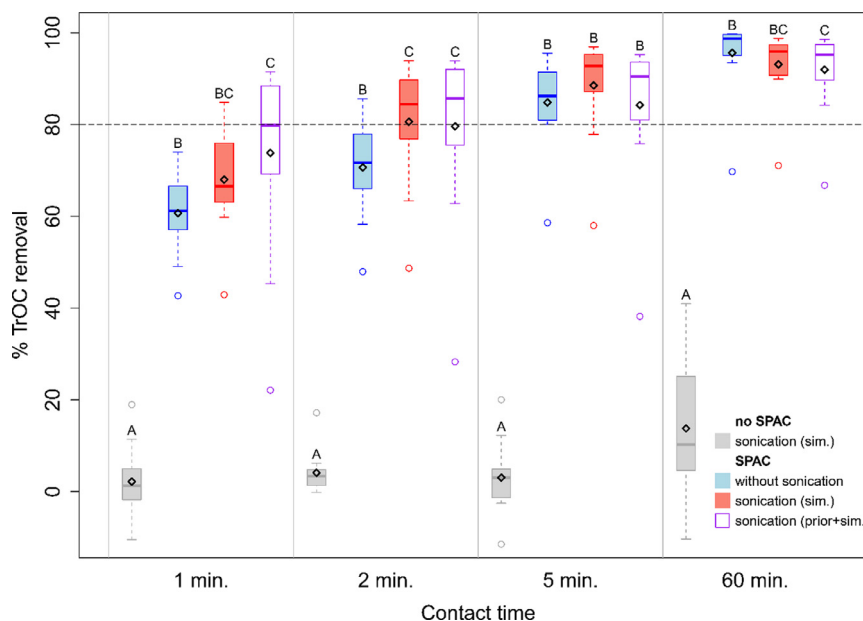


Fig. 5. TrOC removal from DW by SPAC. TrOC removal was monitored with ultrasonication applied simultaneously to TrOC exposure (red), and with ultrasonication applied both prior to and simultaneous with TrOC exposure (empty purple). Controls without SPAC (grey) or without ultrasonication (blue) were also included. SPAC 1 ($D_{50,D-PSD} \approx 1 \mu\text{m}$) was used at a dose of 4 mg/L or 5 mgSPAC/mgDOC. Data are shown as boxplots, where the thick line indicates the median removal of 12 TrOCs studied (Citalopram and diclofenac were not quantifiable). The box is bounded by the first and third quartiles (50% of the data), the whiskers indicate the minimum and maximum removal measured and the dots are the outliers. Open black diamonds indicate the average removal of the 12 TrOC. The black dashed line indicates the removal objective set by the Swiss Water Protection Ordinance (80% average removal). Boxplots with different letters have significantly different ($p < 0.05$) median removal values. The removal of each individual compound is shown in the SI (Figure S11).

tion energy to disperse the SPAC used herein ($13 \text{ W}/500 \text{ mL} = 0.03 \text{ W/mL}$ for 0–60 min) was lower compared to earlier studies. Those higher energy inputs may alter the sorption capacity by modifying or producing sorption sites.

To further rationalize the absence of an effect of ultrasonication, we compared the rate of SPAC dispersion to the rate of TrOC sorption. In the absence of ultrasonication, SPAC 1 exhibited a

$D_{50,A-PSD}$ around $6 \mu\text{m}$ that was stable over 60 min (Fig. 3.b and SI, Figure S7). If ultrasonication was applied, complete particle dispersion was achieved after 10 min, resulting in a decrease in D_{50} of 35 % (from 5.5 to $3.6 \mu\text{m}$), 68% (from 5.5 to $1.8 \mu\text{m}$) and 78% (from 5.5 to $1.2 \mu\text{m}$) after 2, 5 and 10 min respectively. The rates of SPAC dispersal and TrOC removal could be directly compared once they were each normalized to their respective values reached at

equilibrium (see SI for details). This comparison revealed that the average TrOC removal, as well as the removal of individual compounds, exhibited faster kinetics within the first 5 minutes compared to SPAC particle dispersion (Fig. 4). This implies that all the compounds studied herein were more rapidly adsorbed than the SPAC was dispersed from its aggregated state. Thus, the dispersion kinetics under our experimental conditions may not be fast enough to enhance TrOC sorption kinetics.

Faster dispersion kinetics may be achieved by applying ultrasonication with a higher power during SPAC exposure to TrOCs. However, even with the low power 13 W device used in this work, ultrasonication of SPAC would require substantial energy beyond that required for SPAC grinding. An estimation based on the conditions used in this study (continuous sonication of 13 W/0.5 L WW) indicates that milling requires around 0.055 kWh/m³ treated WW, whereas ultrasonication consumes approximately 500-fold more energy (see SI for the detailed calculation). Increasing the wattage of the ultrasonication device would further increase the energy consumption of the whole SPAC treatment process and render it more complex in terms of design and operation.

Alternatively, the SPAC could be periodically dispersed in the concentrated stock solution, prior to its dilution into WW. Pan et al. (2016) have reported stable D_{50} values for up to 10 days in a SPAC stock solution of 10–50 g/L after dispersion by ultrasonication at 150 W for 1 min. We attempted to replicate this result in SPAC stock solutions with different concentrations (2–3 g/L and 20–30 g/L), and with the highest ultrasonication power at our disposition (~60 W; SI, Table S5). Even after 10 min of sonication, however, the SPAC remained aggregated (SI, Table S5). For the SPAC material used in this study, SPAC sonication prior to the addition to WW thus is not feasible.

To nevertheless evaluate if there are benefits of using completely dispersed SPAC particles for TrOC removal, ultrasonication was applied to a dilute SPAC solution in (largely TrOC-free) DW. Once the particles were dispersed, TrOCs were then added to the DW from a spiking solution. This approach allowed us to temporarily separate SPAC dispersion and TrOC uptake, and avoid TrOC sorption during dispersal. A lower SPAC dose was used (4 mg/L) compared to experiments in WW (6–8 mg/L) to decelerate the sorption process in DW, which has a low DOC (0.8 mg/L) (SI, Table S1). Dispersion of the particles prior to TrOC exposure yielded a small benefit over ultrasonication applied simultaneously with TrOC exposure, though this benefit lasted for only the first minute of the experiment (Fig. 5 and Figure S11). This implies that the slow SPAC dispersal kinetics are not limiting the average TrOC uptake. Interestingly, sulfamethoxazole, and to a lesser extent mecoprop, even showed slower removal kinetics in the case where SPAC was sonicated prior to TrOC exposure (SI, Figure S11).

Furthermore, unlike in WW (Fig. 3 and SI, Figure S6), simultaneous ultrasonication of SPAC in DW enhanced the removal kinetics of TrOCs compared to experiments without sonication (Fig. 5 and SI, Figure S11). This allows us to draw some conclusions regarding the role of organic matter in TrOC uptake kinetics by SPAC. Specifically, the lower content of organic matter in DW may less efficiently consume new sorption sites created during particle dispersion, such that these sites are more readily available to adsorb TrOCs. A gain in removal kinetics can thus mainly be expected in low DOC matrices. However, even this gain diminishes after 5 min of contact time, such that no further benefit of dispersion could be observed (Fig. 5).

In summary, particle dispersion benefits TrOC removal only in processes that require a very short contact time and take place in low DOC matrices. In contrast, using a small basic SPAC particle size is also beneficial for TrOC sorption in high DOC waters and over long contact times (Fig. 2).

3.4. Effect of coagulant on TrOC uptake

Lastly, we analyzed the effect of coagulant on TrOC removal in WW to examine if TrOC removal is affected by particle aggregation, or by the coagulant itself. Ferric chloride was chosen as it was previously used in other studies and is commonly used in wastewater treatment (Altmann et al., 2015; Mailler et al., 2016; Margot et al., 2013).

Coagulant without SPAC did not show any relevant effect on the average TrOC removal (Fig. 3.c), though it reduced the concentration of clarithromycin and hydrochlorothiazide by 30–40% after 5 min (SI, Figure S8). The addition of 2 ppm coagulant to WW did not alter the average nor the individual TrOC removal kinetics by SPAC (Fig. 3.c & SI, Figure S8). This finding could be rationalized by monitoring the SPAC size change in presence of the coagulant. During the 10 min of SPAC exposure to TrOCs required to reach sorption equilibrium, the presence of coagulant had only a slight effect on the SPAC size. Specifically, the $D_{50,A-PSD}$ increased by a factor of 1.3 during 10 min (from 5.5 to 7.6 μm), though ultimately the D_{50} was > 4 times larger after 60 min (22.2 μm) (Fig. 3.b).

When adding a coagulant in WW at pH 7–8, the negatively charged SPAC particles are neutralized and the repulsion between particles is therefore decreased (Nakazawa et al., 2018b; Pan et al., 2016). The SPAC particles can aggregate, though the aggregation rate depends on their concentration. The slow aggregation rate in our experimental system is consistent with the low SPAC concentration used (Fig. 3.b). In addition, the high stir rate (300 rpm) employed to ensure SPAC suspension during WW treatment may cause SPAC aggregates to redisperse and may slow down particle growth and prevent the formation of large aggregates.

Finally, a coagulant can also neutralize or remove a fraction of the DOC, and hence may reduce competition with the TrOCs for the sorption sites (Mailler et al., 2016). Under our experimental conditions, DOC removal by the coagulant was not sufficiently pronounced to result in a change in SPAC sorption capacity. We can thus conclude that the Fe coagulant did not interfere in the sorption of the TrOCs and therefore this coagulant can be added in a process with SPAC without implications for the SPAC performance, and without constraints to the sequence at which the SPAC and coagulant are added.

Similar to our findings, Mailler et al. (2016) reported no or a small positive effect of adding 2.5 mg/L Fe coagulant for the removal of 13 pharmaceuticals in a fluidized bed reactor with 10 mg/L PAC ($D_{50,A-PSD} = 16 \mu\text{m}$). Altmann et al. (2015) also observed little influence of Fe coagulant at concentrations up to 10 mg/L on the removal of carbamazepine, diclofenac and sulfamethoxazole from WW effluent by PAC ($D_{70} < 40 \mu\text{m}$; 5 to 50 PAC mg/L). They further concluded that the incorporation of PAC particles in coagulated flocs did not limit the adsorption of TrOC for Fe concentration < 10 mg/L. However at higher coagulant concentrations (> 10–20 mg/L of an aluminum coagulant), Ho et al. (2005) reported a decrease of MIB removal with a coconut-based steam-activated PAC.

4. Conclusions

We investigated the influence of SPAC aggregation state on TrOC removal. Specifically, we tested the effects of dispersion by ultrasonication and coagulation by addition of FeCl_3 on the removal of up to 14 TrOCs from WW effluent. Based on our observations, we can draw the following conclusions and make recommendations for using wet-milled SPAC in the micron size range for TrOC removal from wastewater):

- If the SPAC dose applied is high (> 1.6 mgSPAC/mgDOC), the removal kinetics are very fast even in an aggregated state, such that ultrasonication yields no relevant benefit.

- If the SPAC dose applied is limited ($< 1.6 \text{ mgSPAC/mgDOC}$):
 - For a contact time > 2 minutes: there are no significant effect of ultrasonication. The removal kinetics increases with decreasing basic particle size, but not with decreasing aggregate size. To limit energy consumption, it is more efficient to spend energy on milling the SPAC to small sizes than on ultrasonication. Furthermore, the downstream separation step (membrane ultrafiltration, sand filter) may benefit from particle aggregation to remove SPAC from the final treated effluent.
 - For a contact time < 2 minutes: an ultrasonication step can be beneficial. However, one should carefully consider the energy requirement for ultrasonication, which could be prohibitive for processes that aim at treating large volumes of water. Further investigations on low-energy consuming methods to keep concentrated SPAC stock in a dispersed state need be conducted.
- Coagulant can be added simultaneously with the SPAC without compromising the TrOC removal efficiency.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.watres.2020.116302](#).

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