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Article in *Journal of Membrane Science* · April 2017

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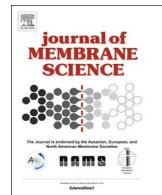
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Effect of intermittent ultrasound on controlling membrane fouling with coagulation pre-treatment: Significance of the nature of adsorbed organic matter



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ARTICLE INFO

Keywords:
Ultrafiltration
Membrane fouling
Ultrasound
Coagulation
Hydrophilic organic matter

ABSTRACT

This study considers the potential advantages of applying intermittent ultrasound to the ultrafiltration (UF) process to control long term membrane fouling in the context of water treatment. By means of parallel, bench-scale tests using traditional coagulation pre-treatment prior to UF, and intermittent ultrasound during the operation (3 min/10 min every 3 days), the development of fouling material, and its nature (e.g. hydrophilic and hydrophobic), within the cake layer and membrane pores, have been evaluated in detail. In particular, the impact of intermittent ultrasound on bacteria growth and the production of extracellular polymeric substances (EPS) have been investigated. The results have shown that, compared to a control UF process, intermittent ultrasound reduces both reversible and irreversible fouling, with a 50% reduction in transmembrane pressure development over 60 days of operation. The intermittent ultrasound led to a much thinner cake layer which contained less EPS/biopolymers in the form of polysaccharides (g/g) and protein, as well as DNA concentrations. Material removed from the UF membrane by ultrasound was predominantly of high molecular weight (~100 kDa) and hydrophilic in nature. Compared to the control membrane, pore deposits in the membrane receiving intermittent ultrasound contained much less high molecular weight, biopolymer-type substances, which was consistent with the reduced extent of irreversible fouling observed.

1. Introduction

The application of ultrafiltration (UF) membrane technology is increasing rapidly for the treatment of surface waters and ground waters as it can produce high quality water economically, especially for the removal of bacteria and viruses. However, membrane fouling is the main obstacle to its widespread application, as fouling leads to more frequent chemical washing and higher energy consumption. Therefore, in recent years there has been considerable research interest in methods of controlling membrane fouling, and in particular the removal of organic and bio-organic contaminants from the membrane feed water.

Chemical coagulation is a common unit process in water treatment plants worldwide and many studies have shown that its application as a pre-treatment to UF separation can mitigate membrane fouling [1]. However, coagulation pre-treatment alone is unable to control membrane fouling with long-term operation [2] and therefore additional or alternative methods are needed. Frequent backwashing and chemical cleaning after a certain period of time can be effective, but have inherent disadvantages, such as the generation of secondary pollution (waste flows) that requires further treatment. As an alternative,

membrane fouling has been shown to be effectively mitigated by pre-ozonation [3,4], with beneficial effects to both external and internal fouling [5], and recently we reported that the combination of coagulation and ozone was highly effective [6]. Studies of other types of pre-treatment have included adding cationic polymeric material [7] and flocculants [8–10], integrated magnetic ion exchange (MIEX) and coagulation [11], flocculation and adsorption [12], and mechanical methods, such as adding suspended carriers [13] and moving media [14], and microbubble aeration [15].

The potential application of ultrasound for mitigating membrane fouling has been considered in a number of previous studies [16,17], and has been found to be beneficial. Thus, in one study it was shown to effectively clean a polytetrafluoroethylene microfiltration membrane fouled by humic acid and bentonite [18]. When associated with forward flushing, ultrasound was reported to be an effective method for the recovery of permeate flux [19], while in other studies it was found that particles on the fouled membrane surface could be fully removed after the application of high, and then low, frequency of ultrasound [17,20]. Turbulence associated with ultrasound causes the transport of particles away from the surface following detachment [21]. The most vigorous

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particle disruption/disintegration was achieved in the initial period of sonication or low sonication times, and subsided subsequently [22,23]. However, the characteristics of foulant particles are important: as indicated when silica particles were modified to be hydrophobic, this could result in less effective control of fouling by ultrasound [24]. In addition, particle concentration and size affected the ability of ultrasound to control ceramic membrane fouling, and higher particle concentrations and smaller particle size caused less effective control of fouling [24].

In terms of the applied conditions, a higher power intensity and lower frequency of ultrasound has been reported to increase particle removal from a fouled membrane [21]. Similarly, low frequency ultrasound can significantly enhance the flux of UF and the membrane cleaning process by effectively decreasing the concentration polarization and the cake layer resistance [25]. In wastewater treatment it was observed that ultrasound primarily controlled the cake layer fouling, but did not modify the digested broth properties [26,27]. Depending on the applied conditions, sonochemical reactions may lead to the degradation of organic matter [28], such as that present on membrane surfaces and within pores, and reduce fouling; in a recent study the fouling of ceramic membranes caused by hydrophilic natural organic matter (NOM) was effectively controlled by ultrasound [29].

Whilst it is reasonable to assume that ceramic membranes are resistant to any adverse, physical effects caused by ultrasound, this may not be the case for the range of polymer membranes used for ultrafiltration. Previously, the potential effects of ultrasound on three membrane materials were investigated and it was found that significant changes were only found with polyethersulfone (PES), in contrast to the absence of effects with polyvinylidene fluoride (PVDF) and polyacrylonitrile (PAN) [30]. The absence of any damage to PVDF by ultrasound is consistent with the use of ultrasound during PVDF membrane preparation to improve its performance [31]. Therefore, in this study PVDF membranes were chosen as the UF material because of its resistance to ultrasound and general suitability for the treatment of contaminated waters.

Previous studies of the role of ultrasound have involved only short period tests, which have not revealed the impact of ultrasound on possible longer term effects of fouling, such as for a continuous period of UF operation of up to 60 days. In this study, we have considered the potential advantages of applying intermittent ultrasound to control long term UF fouling in the context of water treatment. By means of parallel, bench-scale tests for studying membrane fouling, this work has compared traditional coagulation pre-treatment prior to UF, and the application of intermittent ultrasound during the operation. The development of foulant material, and its nature (e.g. hydrophilic and hydrophobic), within the cake layer and membrane pores, has been evaluated in detail. In particular, the impact of intermittent ultrasound on bacteria growth and the production of extracellular polymeric substances (EPS), and their effect on membrane fouling, has been investigated.

2. Materials and methods

2.1. Model raw water

The model raw water used in the experiments has been described fully in a previous paper [32], and is briefly referred here; the use of a representative model water ensured that the influent water quality to the membrane systems was unchanging throughout the 60 days of the experimental study. A small quantity of domestic sewage effluent was added to the local tap water (London, United Kingdom) in a volumetric ratio of 1:50, together with 5 mg/L Suwannee River Humic Acid (2S101H, International Humic Acid Substance Society, USA). The presence of background levels of microorganisms is expected in surface waters impacted by urban runoff and effluent discharges. Table 1 shows the characteristics of the model raw water.

2.2. The UF treatment systems

A schematic illustration of the experimental set-up involving the coagulation-UF processes with and without ultrasonic treatment (CUF and CUF-ultrasound, respectively), operated in parallel, is given in Fig. S1 (Supporting information). The process was similar to that described in a previous paper [6], except that ultrasound was used here. Model raw water from the high level tank was fed into a constant-level tank to maintain the water head for both systems. $\text{Al}_2(\text{SO}_4)_3$ coagulant (0.15 mM, calculated as Al, was based on achieving a near 0 mV zeta potential of flocs), was continuously added to the rapid mixing units (200 rpm mixing speed, and corresponding velocity gradient of 184 s^{-1}) with a hydraulic retention time (HRT) of 1 min. Then the water passed to the three flocculation tanks with a stirring speed of 50 rpm (23 s^{-1}), and each tank having a HRT of 5 min. Then the flow passed to the two membrane tanks, each containing a submerged polyvinylidene fluoride (PVDF) hollow-fiber UF membrane module (Tianjin Motimo Membrane Technology Co. Ltd, China) with a total surface area of 0.025 m^2 ; the hollow fibers had a nominal pore size of $0.03 \mu\text{m}$, an inner diameter of 0.7 mm and an outer diameter of 1.1 mm. The membrane module was briefly removed every three days from the CUF-ultrasound system and immersed in 200 mL DI water within an ultrasonic bath (Kerry Pulsatron KC3 Ultrasonic Cleaning Bath, Guyson, United Kingdom; 38 kHz, 85 W) for either 3 or 10 min. Organic matter detached from the membrane by the ultrasound was subsequently characterized. The temperature of the model water was maintained at $20 \pm 2^\circ\text{C}$ during the whole experimental period.

A suction pump was used to continuously collected the UF permeate at a constant flux of $20 \text{ L}/(\text{m}^2 \text{ h})$, operated in a cycle of 30 min filtration and 1 min backwash ($40 \text{ L}/(\text{m}^2 \text{ h})$). During each 1 min backwash, air was supplied from a position below the membrane modules in each reactor at 100 L/h. The HRT of the membrane tanks was maintained at 0.5 h and accumulated sludge was released every 3 days. During the 60 days of operation, the (reference) CUF membrane was removed and washed by high pressure tap water (10 min) and sponge wiping (10 times) at day 25 and day 50.

2.3. Extraction and measurements of EPS from cake layer and sludge

At the end of the 60 days' UF operation, the foulant materials on samples of the membrane surface (cake layer) were carefully scraped off with a plastic sheet, and analysed. A heating and extraction method [33] was used to extract the bound EPS from the cake layer and sludge [6], while internal foulants from the membrane pores were extracted by 0.01 mol/L NaOH after the membrane surface was wiped with a sponge, according to the method described and used by other researchers [5,34].

The absolute polysaccharide content in the bound EPS was measured by the phenol–sulfuric acid method with glucose as the standard [35,36]. Size exclusion chromatography (SEC) was used to determine the apparent molecular weight (MW) distribution of UV-active organic substances from the two systems [6].

2.4. Characteristics of membranes

Fouled membrane fibers were observed under high resolution field emission gun scanning electron microscope (FEGSEM, LEO Gemini 1525, Germany) as described previously [6]. Other samples of the new and fouled (with/without cake layer) membrane samples were attached to a metal sample tray using double-sided tape, and then analysed by atomic force microscopy (AFM) (Cypher ES™ Environmental AFM, Oxford instruments, United Kingdom) directly in taping mode at 250 MHz. The roughness was estimated from at least three images of the same membrane scanned over an area of $10 \mu\text{m} \times 10 \mu\text{m}$ for each sample. In addition, the membrane samples were analysed by Fourier Transform infrared spectroscopy (FTIR, Spectrum 400, PerkinElmer,

Table 1^a Water quality of raw water and UF filtrates.

Parameter	Raw water	CUF tank	CUF-ultrasound tank	CUF filtrate	CUF-ultrasound filtrate
UV ₂₅₄ (cm ⁻¹)	0.134 ± 0.017	0.045 ± 0.004	0.044 ± 0.003	0.039 ± 0.004	0.038 ± 0.002
DOC(mg/L)	3.63 ± 0.23	2.35 ± 0.24	2.28 ± 0.21	2.24 ± 0.26	2.11 ± 0.16
Turbidity(NTU)	0.86 ± 0.29	4.54 ± 0.33	6.03 ± 0.28	0.08 ± 0.01	0.09 ± 0.01
SS(mg/L)	5.2 ± 1.2	90.4 ± 12.1	110.5 ± 9.8	/ ^b	/
Zeta potential(mV)	-13.8 ± 0.6	-6.85 ± 0.32	-7.43 ± 0.39	/	/
pH	8.12 ± 0.06	7.67 ± 0.05	7.64 ± 0.04	7.68 ± 0.06	7.66 ± 0.04

^a Values are averages (± standard deviation) for all the measurements taken every 7 days^b "/" means "negligible" or "could not be measured"

USA) with Quest ATR Accessory (SPECAC Ltd, UK).

2.5. Other analytical methods

Resins of Superlite DAX-8 (Supelco, USA) and Amberlite XAD-4 (Rohm and Hass, Germany) were used for the analysis of hydrophilic and hydrophobic organic components of water samples, as fully described elsewhere [37]. The UV absorbance at 254 nm (UV₂₅₄) for water samples after filtration (0.45 µm) was determined by an ultra-violet/visible spectrophotometer (U-3010, Hitachi High Technologies Co., Japan), and dissolved organic carbon (DOC) was determined using a total organic carbon (TOC) analyzer (TOC-V_{CPH}, Shimadzu, Japan). Water samples and sludges, after freeze drying, were analysed by thermogravimetric differential thermal analysis (TG-DTA) (TA Instruments, NETZSCH STA 449 C), and Fourier Transform infrared spectroscopy (FTIR, Spectrum 400, PerkinElmer, USA). A commercial turbidimeter (Hach 2100, USA) was used to measure the turbidity of water samples and suspended solids (SS) concentrations were also quantified by standard methods. The concentration of bacteria (as colony forming units, CFU) was determined as the Heterotrophic Plate Count (HPC) by the recommended method involving the use of yeast extract agar [38]. The zeta potential of particles and their size distributions were measured by a Zeta Sizer instrument (Nano-ZS90, Malvern Instruments Ltd, UK).

3. Results and discussion

3.1. TMP development in the two systems

The operation of coagulation and subsequent membrane filtration with, and without, ultrasound was continuous for a period of 61 days for the two systems and the development of trans-membrane pressure (TMP) for both UF processes is shown in Fig. 1. Membrane fouling was represented by the TMP increase as the membrane flux of both systems was set at the same constant value. It can be seen that the TMP of the CUF membrane started to increase after 3 days of operation, from an initial value of 1.0 kPa, while no increase was evident for the CUF-ultrasound system over the first 25 days. While it is well-established that pre-coagulation can mitigate membrane fouling to a certain degree, it is often insufficient to maintain a low level of fouling over a long period of operation. After day 12, the increase rate of TMP reduced in the CUF system and the TMP increased to 5.6 kPa by day 25. At day 25, and subsequently at day 50, the membrane module in the CUF unit was removed from the tank and cleaned by high pressure tap water and sponge, as described in the materials and methods section. With the return to operation, the TMP of the CUF membrane continued to increase, but more rapidly, from 3.5 kPa to 10.4 kPa from day 25 to day 50 (0.276 kPa/day), which may be related to the accumulation of material within pores; since a new cake layer would take some time to develop after the previous layer was removed at day 25, the membrane would be unprotected from influent material penetrating the membrane surface, thereby causing an increase of membrane fouling. It can be seen in Fig. 1 that the TMP decreased by approximately 40% (2.2 kPa)

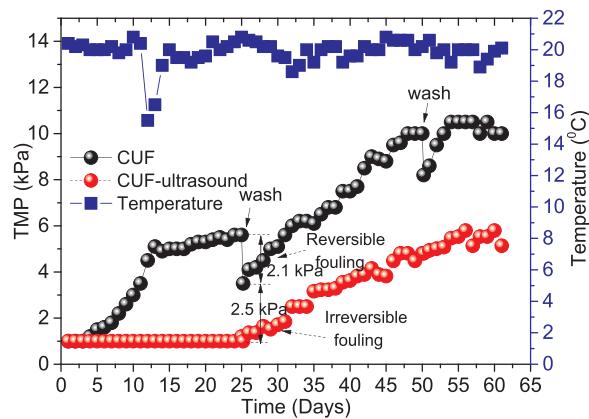


Fig. 1. Temporal variation of trans-membrane pressure (TMP) in the two membrane systems during the operation period (CUF membrane was briefly removed at days 25 and day 50 and washed by high pressure tap water, while for the CUF-ultrasound system, the membrane was washed by ultrasound for 3 min every three days, except at day 30 and 33 when the washing period was 10 min).

after the water wash, which corresponded to the removal of fouling material represented by the cake layer (reversible fouling). However, the irreversible fouling steadily increased with time, and corresponded to approximately 80% of the total TMP (7 kPa) at day 50; this could not be removed solely by backwashing with high pressure water.

In contrast, the intermittent application of ultrasound had the effect of substantially reducing the development of TMP, and therefore, the extent of membrane fouling. While there was little increase of TMP before day 25, indicating that the ultrasound could limit the membrane fouling to a low level (irreversible and reversible fouling); the TMP increased gradually after day 25, from 1 kPa to 6.0 kPa from day 25 to day 60 (0.14 kPa/day). As the slope/gradient of the TMP increase (TMP rate) can be used to indicate the fouling rates [39,40], the greater TMP rate observed in the CUF system indicated that intermittent application of ultrasound was highly beneficial in mitigating both irreversible fouling and reversible fouling. Overall, the avoidance of the need to wash the membrane, and the relatively low TMP (~5 kPa) at the end of 60 days of operation represented a major enhancement in membrane performance over pre-treatment by coagulation alone.

3.2. Particles, organic matter and bacteria in the membrane systems

The formation of a cake layer on the membrane surface or accumulation of organic matter in the membrane pores is mainly caused by the accumulation of substances in the membrane tanks, such as unsettled suspensions/particles, biopolymers (EPS) and other organic matter. Therefore, the presence of such materials in the membrane tank, specifically particles, dissolved organic matter and bacteria, was considered in detail. The results showed that there was a much greater concentration of suspended particles/flocs (expressed as turbidity) in the two membrane tanks, compared to the raw water (Fig. 2a), representing unsettled coagulant flocs and cake layer material (from

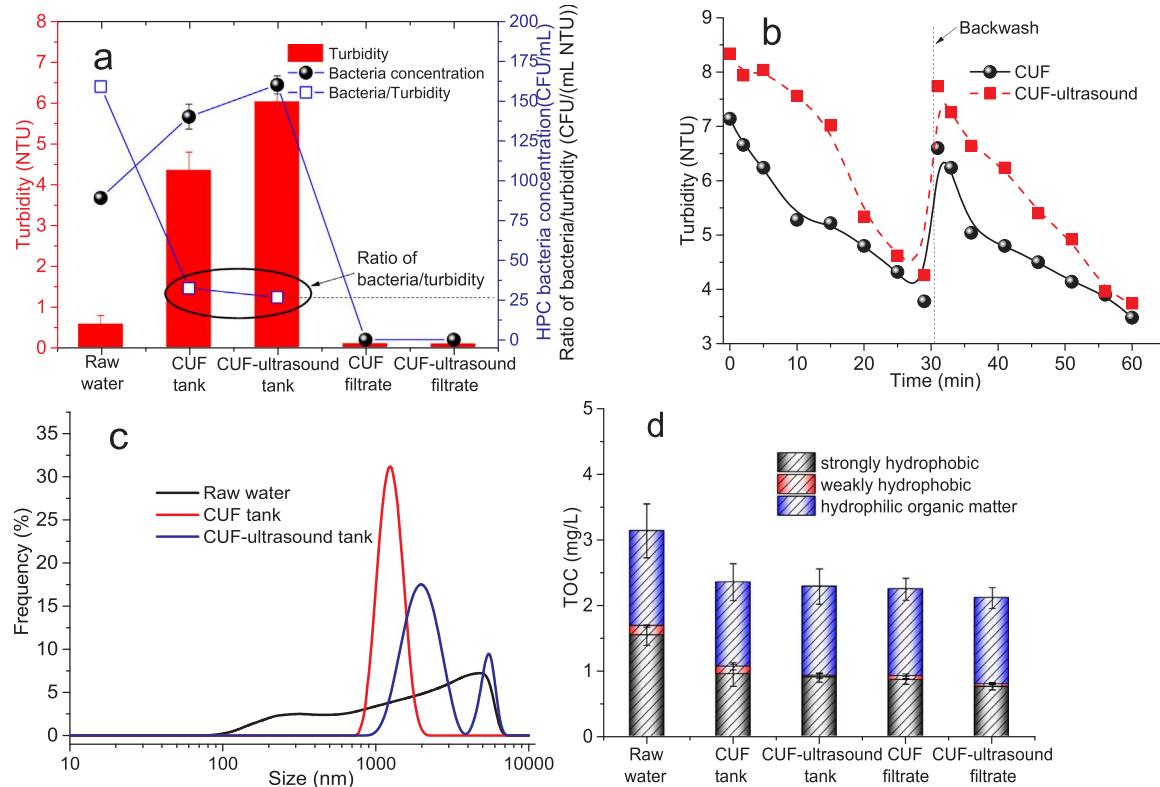


Fig. 2. (a) Turbidity and HPC bacteria concentration (average value) in the membrane systems (sampled at day 15, 30 and 45), (b) typical variation of turbidity in the two membrane tanks within two cycles, (c) size distribution of particles (sampled at the middle of a cycle, day 30), (d) nature of dissolved organic matter in the membrane systems (these results are representative for the period of testing).

backwashing) that accumulated in the membrane tank. Comparing the two membrane tanks, the particles concentration was greater in the CUF-ultrasound tank than in the CUF tank.

The typical variation of particle concentration (turbidity) in the two membrane tanks over two cycles is shown in Fig. 2b. The higher turbidity in the CUF-ultrasound membrane tank after water backwash indicated that the particles related to the cake layer are much easier to be washed away from the membrane surface than the CUF tank. However, the turbidity was approximately the same for the two systems at the end of each cycle showing that more particles were removed (through settling) in the CUF-ultrasound tank. This suggests that the intermittent ultrasound substantially reduced the bonding strength and extent of suspensions (particles) attached to the membrane surface, possibly because some materials (such as EPS) were reduced in the cake layer. It is likely, therefore, that more particles accumulated on the CUF membrane surface, and contributed to the greater fouling rate.

In addition to the particle concentration in the membrane tanks, the particle size distributions were also determined (Fig. 2c). It can be seen that the size distribution of particles (including biopolymers) in the model water covered a range between 80 nm and 7000 nm, which would cause significant membrane fouling if applied directly to the UF membrane. However, the effect of coagulation was the removal of the small particles/biopolymers, which have the greatest effect on fouling, leaving particles and small aggregates/clusters suspended in the tanks of a size $\geq 1 \mu\text{m}$. The size of particles in the CUF tank was clearly smaller than that in the CUF-ultrasound tank, which should result in a higher degree of reversible fouling owing to a greater density of cake layer, as was observed (Fig. 1). The different particle size distributions were probably related to the connection of EPS in the cake layers, as the EPS can improve the connection of particles to the membrane surface; since more particles were backwashed away from the membrane surface into the CUF-ultrasound tank, this would explain the larger size distribution of particles in the CUF-ultrasound tank.

The viable bacteria (HPC) concentration was also considered in the two membrane systems, as an indication of microbial effects and a source of EPS, which are known to be the prominent contributors to the membrane fouling. The bacteria concentration in the membrane tank accumulated or grew in both membrane tanks, and reached a maximum of approximately 140 CFU/mL in the CUF membrane tank and 160 CFU/mL in the CUF-ultrasound tank; the bacteria concentrations represent the net growth within the tanks and on the membrane surfaces and lost/removed with settled flocs in the tank. When the results are expressed as the bacteria/SS (turbidity) value, this was slightly lower in the CUF-ultrasound tank, which further indicated that the particles/cake layer on the CUF-ultrasound membrane surface was more easily detached from the membrane during the backwash process.

As a further indicator of the relative water quality within the membrane tanks, the hydrophilic and hydrophobic properties of organic matter were investigated (Fig. 2d). It was evident that the coagulation process removed some of the strongly hydrophobic organic matter from the raw water, but there was little change in hydrophilic organic matter removed during this process. Comparing the water quality within the membrane tank with the filtrate, the results suggested some organic matter was removed (Fig. S2), both hydrophilic and hydrophobic (Fig. 2d), and this was slightly greater for the CUF-ultrasound system, but the amounts were small and close to the limits of experimental error. However, the accumulation of small quantities of organic matter on, and within, the UF membranes over long periods of operation can have a significant impact on their performance. Therefore, the nature and quantity of the organic matter retained by the membrane is an important contributor to the membrane fouling (especially irreversible fouling), and this is described subsequently.

3.3. EPS on the membrane surface (cake layer)

In order to investigate the membrane fouling for the two systems,

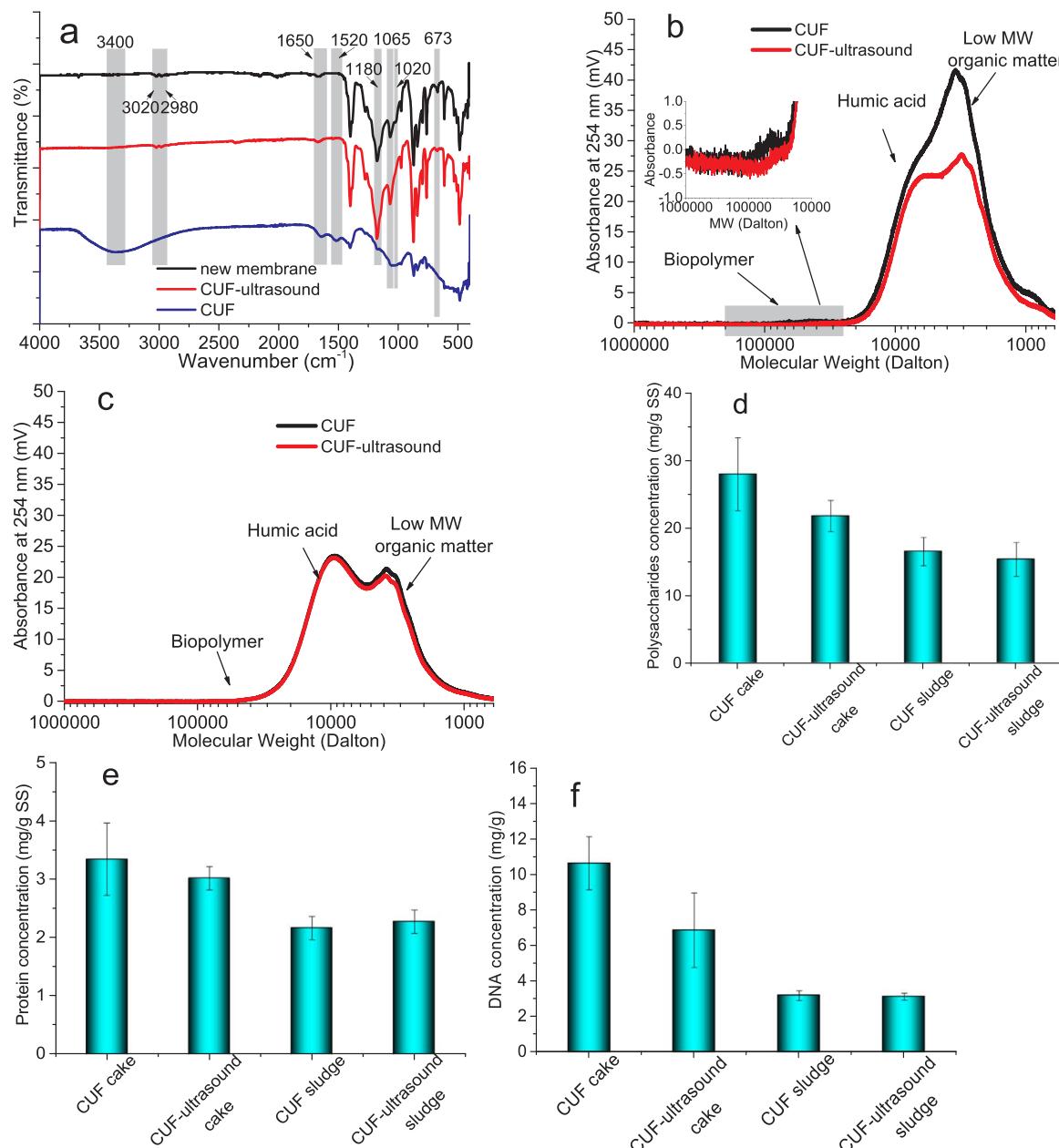


Fig. 3. Characteristics of organic material from UF systems: FTIR spectra of fouled membrane (a); MW distribution of organic matter extracted from cake layer (b) and sludge (c); polysaccharide (d), protein (e) and DNA (f) concentrations extracted from cake layer and sludge.

samples of fouled membrane were examined by FTIR analyses. As illustrated in Fig. 3a, peaks at 1650 and 1520 cm^{-1} may correspond to C=O and –N-H bonds [41], and these were evident for the CUF sample, but not for a new membrane, nor the CUF-ultrasound sample. The influent organic matter used in the tests contained C=O bonds, such as carboxylic acid (e.g. in the humic acid), which may adsorb into the CUF membrane pores. Also the –N-H peak may be ascribed to proteinaceous material accumulated in the membrane pores, which is produced by bacteria. The peak at 3400 cm^{-1} from the fouled CUF membrane indicated that some hydrophilic organic matter containing the –OH bond was present on the membrane. The intensities of PVDF absorption peaks at 763, 870, 1016, 1174, and 1400 cm^{-1} corresponding to CF₂ and CH₂ chemical bonds, were reduced in the spectra of the CUF membrane, most likely through the adsorption of organic substrates and flocs [42]. In contrast, the peaks for the membrane with ultrasonic treatment were nearly the same as those for the new PVDF, except the peaks at 1020 cm^{-1} and 673 cm^{-1} , which meant that some residual

organic substrate was still adsorbed on the CF₂ bonds and not removed by the intermittent ultrasound treatment. These results indicate that the ultrasound was able to remove hydrophilic organic matter and polysaccharide materials (at least part of them) on the membrane surface and in the membrane pores.

Large MW organic matter, such as EPS, can improve the interaction between particles in the cake layer or particles and the membrane surface, as well as block the membrane pores and increase the density of the cake layer. Therefore, the organic matter in the cake layer and sludge were extracted and their MW distributions were compared. The quantity of organic matter (at least UV-active organic matter) from the CUF cake layer was slightly greater than that of the CUF-ultrasound layer, in respect of the high MW (biopolymer; 50–100 kDa) and low MW organic matter (< 10 kDa), while for the sludge the amount and MW distribution were nearly the same (Fig. 3b and c), and it was similar to that washed by NaClO [43]. The greater EPS (biopolymer) concentration in the CUF cake layer is probably related to the gradual

accumulation of the cake layer, in which bacteria and EPS increased with increasing operation time. In contrast, the membrane cake layer in the CUF-ultrasound system was removed every 3 days, thereby preventing the accumulation of EPS in the cake layer.

The specific EPS content in the form of polysaccharides and proteins in the two systems was also compared (Fig. 3d and e). For the CUF system, the amount of polysaccharide in the cake layer (28 µg/gSS) was more than that in the sludge (16 µg/gSS); while for the CUF-ultrasound system, the amounts were 22 µg/gSS and 15 µg/gSS, respectively. However, there was little difference in the amount of protein between the cake layers on the two membrane surfaces, although the amounts in the cake layers were higher than in sludges. Comparing the relative concentrations of polysaccharides and proteins, the results suggest that the accumulation of organic material, and therefore membrane fouling, seems to be attributed to polysaccharides, as the ratio of the two (polysaccharide to protein) was approximately one order of magnitude.

The results of the DNA analysis for the two systems showed that the bacteria concentrations in the sludges of the two systems were nearly the same, with both at a low level, while the concentrations in the two cake layers were much higher. As most of cake layer was removed during the ultrasonic process, the bacteria were probably removed together with cake layer, which induced a lower DNA concentration for the CUF-ultrasound cake layer (Fig. 3f). Also, the cake layer on the CUF-ultrasound membrane was much less than that on the CUF membrane as a result of the ultrasound, and the total DNA (bacteria) in the CUF cake layer was dramatically higher than in the CUF-ultrasound cake layer. Therefore, the bacteria that grew and accumulated on the surface of the CUF membrane may have induced a higher EPS concentration in the membrane pores.

3.4. Materials detached from membrane by ultrasound

It is suggested that the effect of intermittent ultrasound on fouled membranes causes the adsorbed organic matter to detach from the membrane surface and within membrane pores, thereby reducing the accumulation of fouling material (Fig. 1). The characteristics of the organic matter removed by ultrasound were investigated by consideration of its MW distribution, hydrophilic and hydrophobic properties (Fig. 4), and FTIR absorbance spectra (Fig. 5b).

It is evident from the MW distribution results that most of the organic matter detached by the ultrasound comprised biopolymers (MW~100 kDa) and only relatively little HA and small MW organic matter (< 5 kDa). Application of the ultrasound process for a longer period (10 min, instead of 3 min) was able to detach more organic matter from the membrane, but this greater release was relatively minor (Fig. 4a). As mentioned earlier, this is consistent with previous studies which showed that the most vigorous particle disruption was achieved in the initial period of sonication, and subsided subsequently [23]. It was also evident that most of the organic matter detached was hydrophilic and only a small proportion (~10%) was strongly hydrophobic and weakly hydrophobic (Fig. 4b). The hydrophobic fraction has a greater affinity to adsorb on the surface, or in the membrane pores, of the hydrophobic PVDF membrane, and so this gradually accumulated on the membrane; while in contrast the attraction between the hydrophilic organic matter (e.g. biopolymers) and the membrane surface is not strong enough to prevent this fraction from being removed by the physical effects of the ultrasound (Fig. 4b).

3.5. Organic matter washed by NaOH from membrane pores

In addition to the materials forming the cake layer, and subsequently detached or washed by ultrasound and backwashing, there is an accumulation of materials within the membrane pores during the operational period for both membranes. Samples of these were extracted by NaOH, and analysed by SEC, FTIR and TG-DTA methods (Fig. 5). It was clear that a major difference in the organic matter from

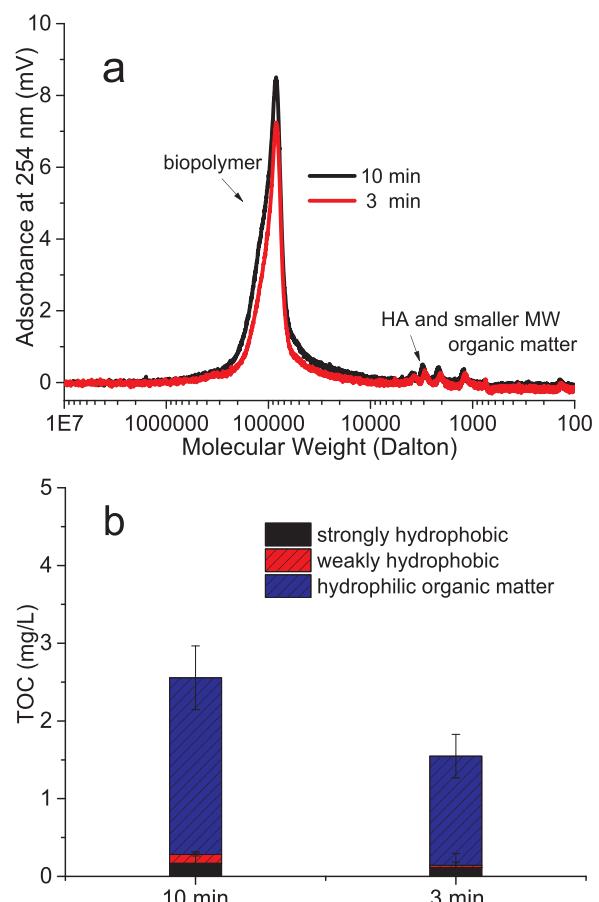


Fig. 4. MW (a) and hydrophilic/hydrophobic nature (b) of organic matter detached by ultrasound from CUF-ultrasound membrane (placed in 200 mL DI water) for different durations of ultrasound.

the pores of the two membranes was the biopolymer fraction (Fig. 5a), which suggested that this fraction of the EPS is effectively detached from the membrane by the intermittent ultrasound. In comparison there was no significant change in the low MW (< 5 kDa) organic matter indicating that ultrasound had little effect on this. However, the reduced membrane fouling observed in the CUF-ultrasound system confirms the important contribution that biopolymers make to deposits within the membrane pores. Comparing Fig. 5a with Fig. S2, the adsorbed biopolymers were probably formed in the membrane tank, but not from the raw water (at least this UV absorbance fraction). Therefore, control of the accumulation and growth of bacteria in the membrane tank is of great importance.

The FTIR spectra of the NOM adsorbed within the membrane pores after NaOH extraction (and freeze drying), are shown in Fig. 5b. The band at around 3400 cm^{-1} is generally indicative of $-\text{OH}$ stretching [44] and the band at around 2910 cm^{-1} is attributed to aliphatic C-H, C-H₂, and C-H₃ stretching. The peaks at 1635 cm^{-1} may correspond to C=O bonds [41,45]. Organic matter containing C=O bonds, such as carboxylic acid, or $-\text{CONH}-$ groups, may correspond to proteinaceous material (such as EPS) adsorbed in the membrane pores, which is produced by bacteria. Therefore, the ultrasonic process could detach the proteinaceous materials adsorbed or accumulated within the membrane pores. Thus, the band intensity of materials at around 1410 cm^{-1} , 1100 cm^{-1} , 870 cm^{-1} , indicated that the C-H deformation of aliphatic and CH₃ groups (1410 cm^{-1}), the C-O stretching of esters, ethers, and phenols (1100 cm^{-1}), and C-C anti-symmetric ring stretching of epoxides (870 cm^{-1}) [45,46]. The result further confirmed that hydrophilic polysaccharides (C=O bond from alcohol and ester) could be removed from the membrane by ultrasound. Some hydrophobic

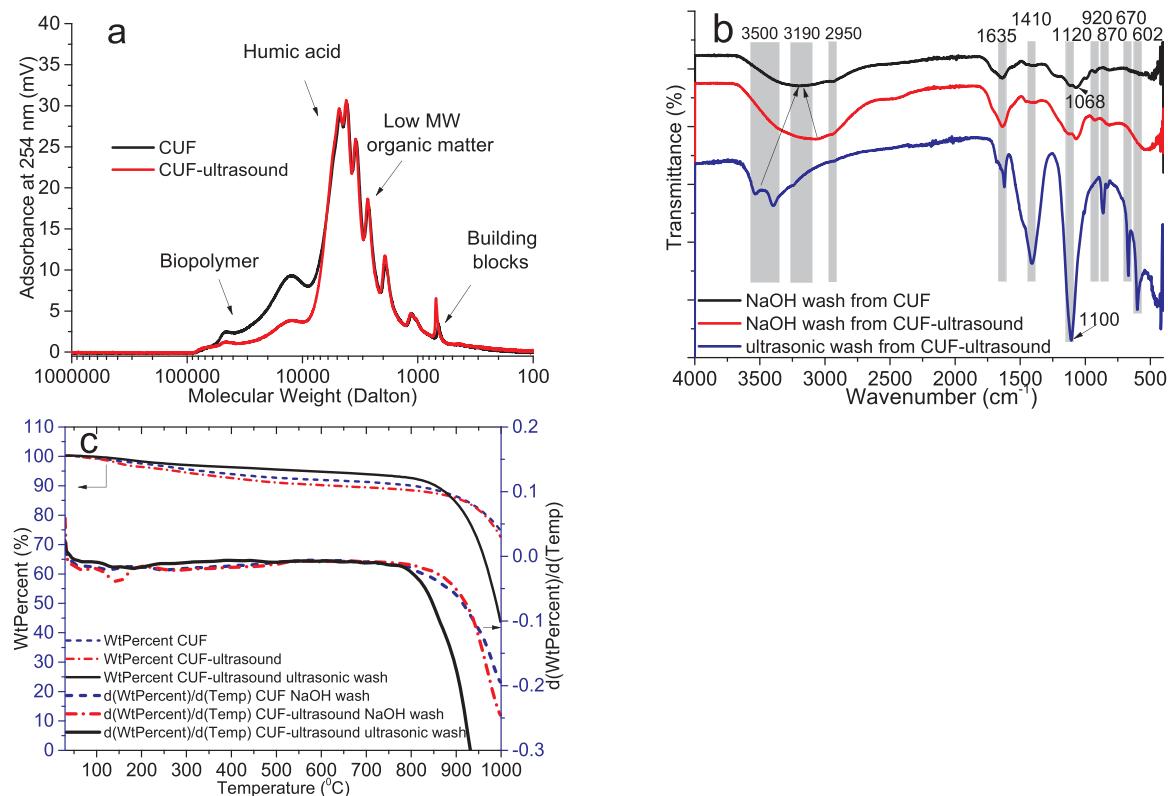


Fig. 5. Characteristics of organic matter in the membrane pores extracted by 0.1 M NaOH: (a) MW, (b) FTIR, (c) TG-DTA (for FTIR and TGA, samples were adjusted to pH 2, and HCl volatilized during the freeze-drying process; organic matter detached from CUF-ultrasound by 3 min ultrasound was compared here).

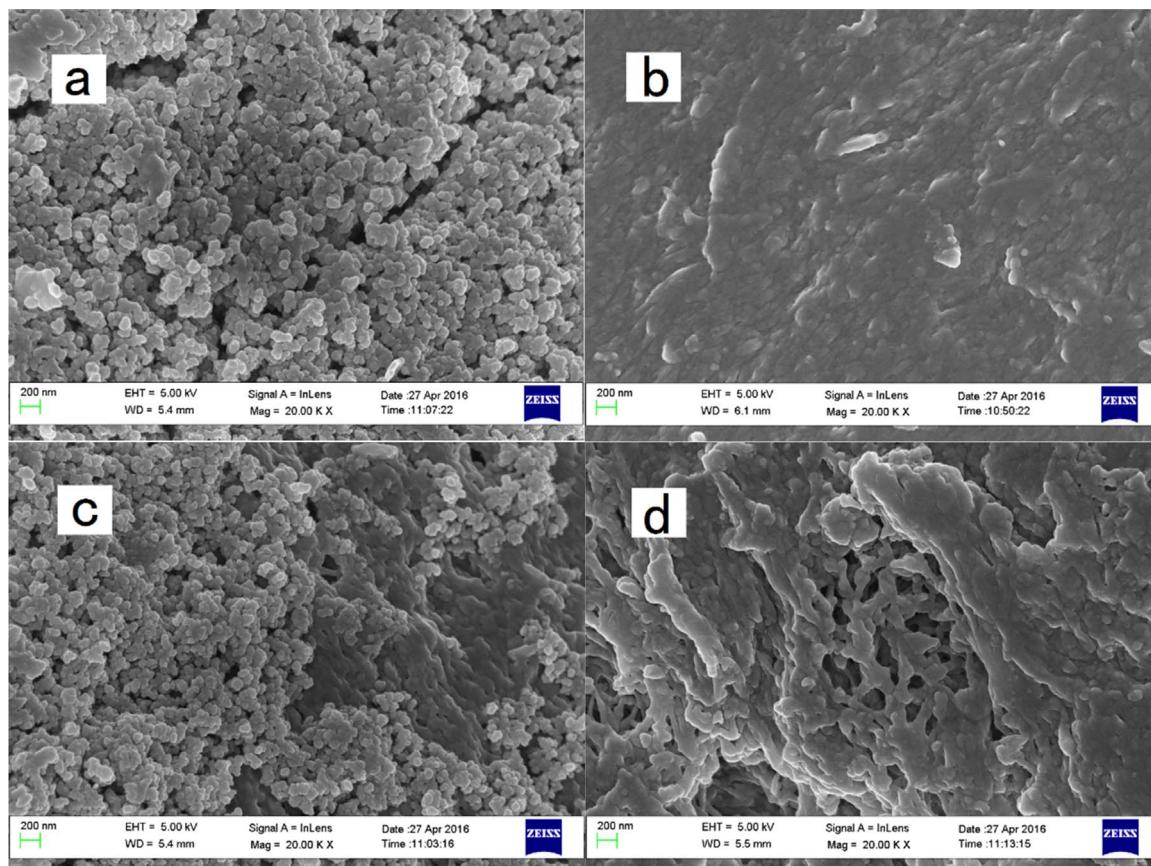


Fig. 6. SEM images of membrane taken at the end of the operation (day 61): CUF membrane with/without cake layer (a and b), CUF-ultrasound membrane with/without cake layer (c and d).

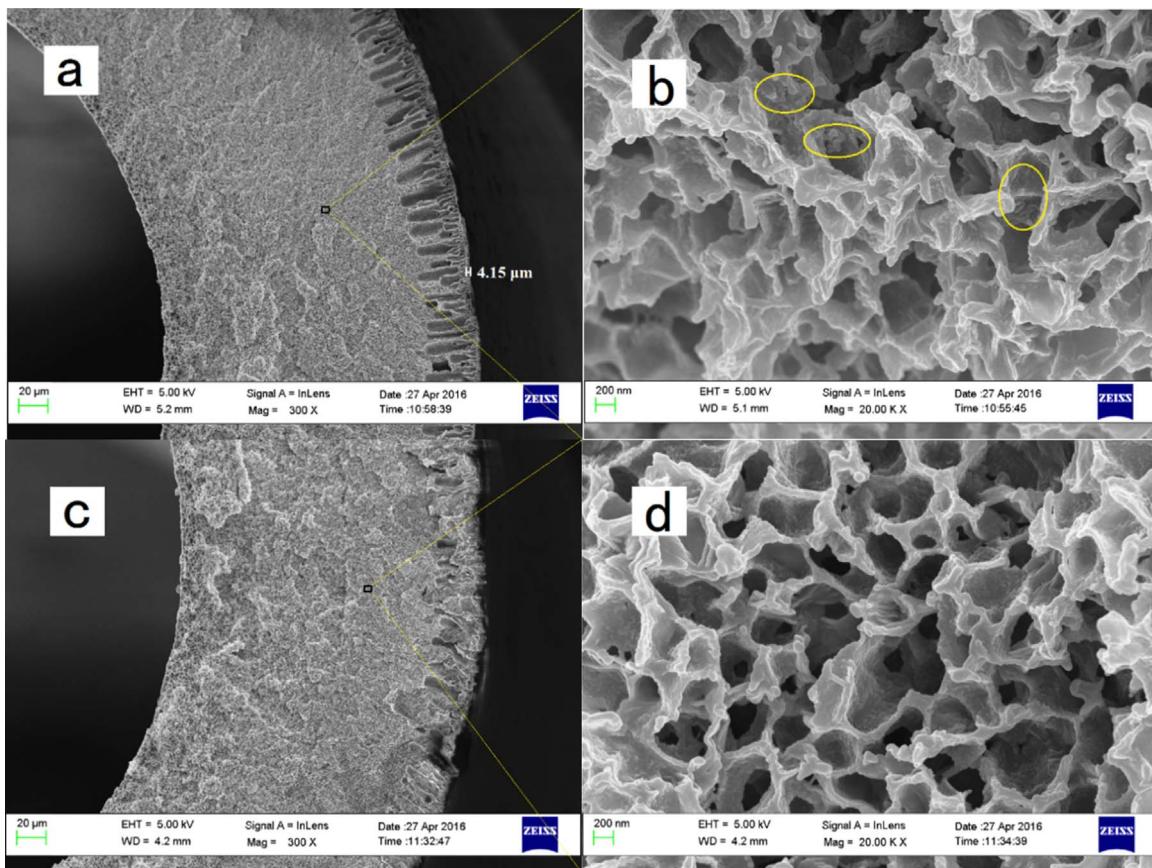


Fig. 7. SEM images of membrane cross-sections taken at the end of the operation (day 61): CUF membrane (a and b) and CUF-ultrasound membrane (c and d).

organic matter was adsorbed in both membrane pores (around 2950 cm^{-1} is attributed to aliphatic C–H, C–H₂, and C–H₃ stretching), and ultrasound was unable to remove much of this from the membrane, which further confirmed the results shown in Fig. 4.

The organic matter was also characterized by thermogravimetric (TG-DTA) analysis (Fig. 5c). The TG-DTA analysis revealed that the principal weight loss occurred at temperatures in three ranges of 100–200 °C, 200–500 °C and > 750 °C for all the samples. For the lowest temperature range (100–200 °C), the weight loss of the NOM washed by ultrasound and NaOH in CUF-ultrasound system was lowest and highest, respectively, and the weight loss from the CUF system was between them. For the temperature range of 200–500 °C, the result was similar to that for the temperature between 100 °C and 200 °C. The result observed at the higher temperature range of > 750 °C was different to that at 100–200 °C and 200–500 °C in terms of the greatest weight loss for the organic matter detached by ultrasound from the CUF-ultrasound membrane, which meant some of the large MW organic matter was detached from the CUF-ultrasound membrane by ultrasound. These results further confirmed that the large MW organic matter was removed by the ultrasonic process as indicated in Fig. 5a.

3.6. SEM

Fouled membranes with their cake layers or the cake layer removed from the membrane surface were further characterized by scanning electron microscopy, to compare visually the differences in the membrane fouling in the two systems after operating for 61 days (Fig. 6). An SEM image of a new UF membrane can be found in a previous paper [2]. Comparing the new and fouled membranes, it can be seen that a cake layer was formed on the surface of the membranes by continuous filtration of flocs, comprising numerous nano-particles (approximately 30–50 nm, Fig. 6a). The cake layer on the surface of the

CUF membrane was much thicker than that on the CUF-ultrasound membrane (Fig. 7). This indicated that the ultrasonic process removed most of the nano-particles/flocs (cake layer) on the membrane surface (ultrasound washing operated every 3 days resulted in only a minor presence of particles on the membrane surface). Also, the fouled membranes after washing were characterized by SEM and it was evident that more membrane pores were visible for the CUF-ultrasound membrane than for the CUF membrane, and that more substances had been detached from the membrane (Fig. 6b and d). The roughness of the new and fouled membrane surface is shown in Fig. S3. It was evident that the roughness was much higher for the used membrane compared to the new membrane, and ultrasound decreased the roughness of the used membrane. The result further confirmed that ultrasound was able to remove foulants on the membrane surface, and therefore reduced the extent of membrane fouling.

The SEM images of the CUF membrane and CUF-ultrasound membrane in cross-section are shown in Fig. 7 and Fig. S4. These clearly showed that the thickness of the cake layer on the CUF membrane surface (around 3–4 μm, operated for 12 days from day 50 to day 62) was much greater than that of the CUF-ultrasound membrane (nearly zero). Also it was apparent that there was retained material in the inner CUF membrane (Fig. 7b), but not in the inner CUF-ultrasound membrane (Fig. 7d). These results further confirmed that some organic substances accumulated in the inner membrane when the membrane was operated for a long time, but an intermittent ultrasonic process could remove these materials/organic matter from the inner membrane. Therefore, the ultrasound washing can mitigate external and internal membrane fouling.

4. Conclusions

This study has evaluated the effect of applying intermittent ultra-

sound following conventional coagulation as a method of reducing long term UF membrane fouling in water treatment. The results from bench scale tests conducted in parallel with a control UF process (no ultrasound) have shown the following:

1. The application of intermittent ultrasound during the UF operation (3 min/10 min every 3 days), reduced substantially reversible and irreversible membrane fouling, corresponding to a ~50% lower development of transmembrane pressure over 60 days. It is acknowledged that the higher level of cleaning comes at the cost of more frequent interruption and higher downtime of the membrane operation.
2. Intermittent ultrasound led to a much thinner cake layer, which contained less EPS concentration (polysaccharides (g/g) and proteins, per unit mass of extracted matter), as well as DNA concentration.
3. Application of the ultrasound process for a longer period (10 min, instead of 3 min) was able to detach more organic matter from the membrane, but this greater release was relatively minor.
4. Ultrasound removed predominantly hydrophilic, high molecular weight organic matter, such as polysaccharides, from the membrane surface and the membrane pores. However, ultrasound had less impact on the accumulation of smaller MW organic matter.

Acknowledgements

This work was supported by the Engineering and Physical Sciences Research Council [grant number EP/N010124/1], and by a Marie Curie International Incoming Fellowship (FP7-PEOPLE-2012-IIF-328867) within the 7th European Community Framework Programme for Dr. Wenzheng Yu.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.memsci.2017.04.031>.

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