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# Investigating the feasibility and the optimal location of pulsed ultrasound in surface water treatment schemes

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#### ABSTRACT

The deterioration of surface water quality due to extreme weather events and increasing human activities has exacerbated the common problems in drinking water production such as filtration fouling and DPBs formation. This in turn has urged for exploring alternative methods for the traditional treatment methods that are able to improve the removal of contaminants with minimal impact on environment and human health. In this study, the application of pulsed and continuous ultrasound for improving the quality of natural water with fresh natural organic matter (NOM) mainly driven from vegetation has been evaluated. The evaluation was performed using cost-effective and quick measurements such as specific UV-vis absorbance, COD<sub>Mn</sub>, alkalinity and conductivity. The changes in the characteristics of NOM induced by ultrasound were used to develop a framework for evaluating ultrasound performance in improving conventional surface water treatment processes and to identify the best fit of ultrasound within the treatment scheme. Results of this study showed that pulsed ultrasound was as effective as or in some cases better than continuous ultrasound in improving water quality. According to the adapted assessment criteria supported by an extensive literature survey, the most effective location of ultrasound treatment within surface water treatment scheme was found to be prior to coagulation/flocculation.

Keywords: Pulsed ultrasound; Continuous ultrasound; NOM; Filtration fouling; DBPs

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### 1. Introduction

Surface water is a major resource for drinking water production [1]. The contamination levels, particularly, of natural organic matter (NOM) in surface water resources have recently increased due to climate change and progressive human activities [2–4]. Increasing surface water contamination results in operating and health problems such as frequent filtration fouling [5,6] and formation of hazardous materials in finished water (e.g. disinfection by-products, DBPs). To find effective solution for the challenges of surface water treatment, the problems encountered in individual treatment processes within the treatment scheme need to be carefully identified.

Generally, surface water treatment systems consist of three main operational units; coagulation/flocculation, filtration and disinfection. Fig. 1 illustrates a schematic of surface water treatment scheme with emphasis on the problems associated with the main treatment processes. Coagulation/flocculation processes remove organic materials and pathogens via various mechanisms such as adsorption and charge neutralization. The common problem in coagulation/ flocculation processes is the residual of coagulants. The residual coagulants (e.g. aluminium) are involved in technical and health problems, such as increasing turbidity, filtration fouling, interfering with disinfectants and causing neuropathologic disorders and neurological diseases [7–9]. Filtration removes metals and other contaminants under the effect of physiochemical interaction and sieving capacity of filters. Fouling of filtration media is another challenge commonly encountered by the operators of surface water treatment systems. Fouling is the deposition of solids, organic/inorganic and micro-organisms onto the interactive surface of the filtration media [10]. The accumulation of organic and microbial foulants on the filtration media is of particular concern when membranes are used as filtration media [5]. The adhesion of organic and microbial foulants to filters inflicts extra cost and delay to filtration process as well as reduction in the quality of the product [11,12].

Disinfection is the last process in the surface water treatment scheme and it is applied to remove biological contamination and control the regrowth of micro-organisms in the distribution network. This process usually suffers from the formation of the hazardous DBPs [13]. DBPs are caused by the reaction between the chemical disinfectants (e.g. chlorine and ozone) with NOM [14–16]. DBPs include a wide spectrum of carcinogenic and mutagenic chemical complexes that pose a threat to human health and the environment. Epidemiological and toxicological studies indicate human exposure to chlorinated water-containing high concentrations of DBPs increases the risk of serious health problems such as bladder cancer [17] and congenital diseases [14].

It is clear that if the dosages of coagulants and disinfectants used in water treatment are not carefully

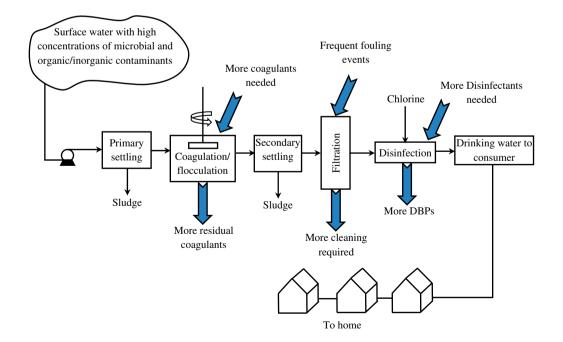


Fig. 1. Typical surface water treatment system.

manipulated, they can exacerbate the problems of surface water treatment systems. Hence, the key solution to reduce surface water treatment challenges is by reducing the amounts of chemicals added to water without compromising the quality of the finished water. This can be achieved by applying physical treatment methods capable of improving the quality of surface water. The use of ultrasound as a physical treatment method has been suggested in this study. Ultrasound has the ability to reduce the common problems of surface water treatment by destroying micro-organisms and oxidizing organic and inorganic contaminants [18-20]. Ultrasound has the advantage of having minimal impact on the environment and human health and is simple to implement in water treatment systems [21,22].

The high energy demand and rapid temperature rise associated with the use of continuous ultrasound in water treatment systems are of concern [5]. To overcome these problems, the use of pulsed ultrasound will be investigated in this study. In continued sonication, some bubbles grow to a bigger size through rectified diffusion mechanisms [20,23]. Large bubbles are not able to produce powerful shock waves and shear stress [20], and they absorb part of ultrasonic energy. Additionally, the existence of large bubbles in the liquid hinders the transfer of ultrasound waves through the liquid (shielding effect) [24]. In pulsed ultrasound treatment, the problem of stable bubbles is less as the size of such bubbles reduces during the interval period (Off period of pulsed ultrasound) due to the dissociation of the gases. This in turn decreases the shielding effect and reduces the energy that could have been absorbed by stable bubbles in the subsequent pulse train. The use of pulsed ultrasound for water treatment can also lessen the needs for extensive cooling process during the treatment, which may introduce additional cost.

Ultrasound has the potential to be effectively integrated into the existing surface water treatment schemes (Fig. 1), however, with which treatment process can ultrasound perform the best is a question that has not been addressed yet. In addition, Most of the studies on ultrasound implantation for water treatment used synthetic waters which focuses on particular contaminants and does not reflect the real case in water treatment plants. The practical evaluation to ultrasound application in water treatment requires the use of natural water samples [25]. It is also important to investigate the effect of ultrasound on DBPs formation [26,27].

It is known that ultrasound wave propagation causes an increase in bulk temperature of water due to friction produced from agitation and liquid circulation as well as cavitation. To separate the effect of bulk temperature rise on water properties from that of the cavitational effects of ultrasound, thermal treatments that are identical to ultrasound treatments in their temperature profile will be performed using electrical heater operated with DC. Comparison between the performances of pulsed ultrasound at different pulse/interval ratios with that of continuous ultrasound will also be carried out using rapid evaluation techniques such as dissolved organic carbon (DOC), specific UV–vis absorbance (SUVA), COD<sub>Mn</sub>, alkalinity and conductivity.

The criteria that will be used to assess the application of ultrasound in surface water treatment will consider the effect of ultrasound on the characteristics of the water that influence the proclivity of its NOM to (1) the removal by coagulation/flocculation, (2) filtration media fouling and (3) formation of DBPs. The outcome of this study will provide guidelines that help in choosing the most suitable location for ultrasound treatment within surface water treatment schemes.

### 2. Materials and methods

### 2.1. Water samples

Pittaway pond water located at the south-east Queensland was selected as a model for surface waters of Queensland,Australia in this study. Pittaway pond is an ephemeral, small pond containing highly coloured water with fresh NOM mainly produced by decomposition of tree leaves and bark litter.

Water samples were collected and stored frozen in polyethylene bottles at  $-10^{\circ}$ C until the experimental work commence. Table 1 shows the physiochemical properties of the collected water samples expressed in

Table 1 Characteristics of Pittaway pond water

Physiochemical prop	Measured values	
pH, 25℃		$8.2 \pm 0.20$
DOC (mg/L)		$6.5 \pm 0.15$
Specific COD <sub>Mn</sub> (mg	$O_2/mg$ DOC)	$0.54 \pm 0.06$
SUVA (L/mg.cm)	254	$0.038 \pm 0.007$
-	260	$0.036 \pm 0.009$
	280	$0.029 \pm 0.0010$
	250/365	$4.56\pm0.12$
	254/204	$0.35 \pm 0.050$
	254/colour 436	$15.45 \pm 1.64$
Alkalinity (meq/L)		$2.99 \pm 0.013$
Conductivity (mS/cn	n), 25℃	$0.16 \pm 0.006$
Iron (mg/L)		$0.12\pm0.0014$
Nitrate (mg/L)		$0.47 \pm 0.02$
Chloride (mg/L)		$67.3 \pm 3.9$

mean value  $\pm$  the standard of error of the mean of three measurements.

### 2.2. Analytical methods

### 2.2.1. DOC measurements

The DOC of untreated and treated water samples was measured using Total Carbon Analyser (TOC-V<sub>CSH</sub>, SHIMADZU, Australia). The DOC of each sample was measured in duplicate. At least three injections of each measured sample were made, which resulted in coefficient of variance (CV) lower than 0.02. Water samples were filtered through 0.45  $\mu$ m glass-fibre filters using syringe filter holder prior to DOC measurements.

### 2.2.2. UV-vis spectroscopy analysis

UV absorbance of the sample is directly related to the concentration of the absorber (i.e. DOC) [28].

Table 2 Measured UV–vis wavelengths with interpretation

Therefore, to better express the change in the nature of the NOM, the UV absorbance of a sample will be standardized by DOC of water sample (SUVA). JENWAY UV/Vis spectrophotometer, model 6705 with a single cell holder was used for measuring the absorbance of untreated and treated water samples at UV and visible ranges. Quartz cuvette with path length of 1 cm was used in the UV measurements. The water samples were filtered through 0.45  $\mu$ m glass-fibre filter prior to UV analysis. The samples were scanned in a wavelength range of 200–500 nm to measure the absorbance at 204, 250, 254, 260, 280, 365 and 436 nm. Table 2 details the indicative characteristic of the NOM that corresponds to each measured wavelength. Distilled water was used as a baseline.

UV absorbance of water samples is sensitive to pH and the content of interfering species, such as iron, nitrate, nitrite, chloride and bromide [29,30]. Under acidic conditions (pH < 2), some of the NOM such as humic acids precipitate resulting in a bias judgement to the change of UV–vis absorbance [29]. To eliminate

Wavelength (nm)	Indicative characteristics of water
254	UV absorbance at 254 nm will be used as an indicator for humic fraction in aquatic DOC [32,33], as it reveals the electronic structure of DOM especially detecting the presence of conjugated structure [34] much as these times are accurately and the improvement of DOM [25].
260	such as those in aromatic compounds. It inversely correlates to the aliphatic carbon content of DOM [35] The absorbance at 260 nm will be used to detect the change in the hydrophobic fraction of NOM [31,36]. The use of SUVA <sub>260</sub> as indicator for the hydrophobicity will be strictly applied to estimate the effect of the treatments on the hydrophobicity of the aromatic compounds in the treated water samples as some of the hydrophobic treatment of the hydrophobic treatment of the LWA is the LWA in the treatment of
280	of the hydrophobic acids moieties are aliphatic [37] which do not absorb the UV light [38] SUVA <sub>280</sub> will be applied as an indicator for the bulk aromaticity of aquatic NOM [39]. The electron delocalization in the pi orbital of the conjugated structure of some of the aromatic compounds such as phenolic arenes, benzoic acids, aniline derivatives, polyenes and polycyclic aromatic hydrocarbons [40] occurs at UV range 270–280 nm is the basis behind the application of this wavelength as measure for aromaticity
254/204	The quotient SUVA <sub>254</sub> /SUVA <sub>204</sub> will be adapted as a measure for the degree of functionality of the aromatic ring [41]. This ratio represents the proportional composite absorbance of the chromophores of NOM at electron transfer (ET) band to benzenoid (Bz) band [30], sometimes denoted as $A_{ET}/A_{Bz}$ . This ratio can be used as an indicator to the prevalence of aromatic compounds substituted with oxygen-containing functional groups such as hydroxyl, carboxyl, ester and carbonyl which are mostly involved in adsorption and complexation processes [30,42]
250/365	This ratio is commonly known as $E_2/E_3$ ratio and it will be used as indicative for the proportion of low to high molecular size organic compounds in the treated water [40,43–45]. The use of $E_2/E_3$ will be applied in this study as alternative to the expensive and time-consuming laborious techniques such as high-pressure size exclusion chromatography, vapour pressure osmometry and ultracentrifugation [46,47]
254/436	The absorbance ratio 254/436 will be used to detect the change in the UV-absorbing groups to colour- forming groups of NOM in the treated water [42]. The absorption at 436 nm represents the functional groups that produce the yellow to brown colour in water samples [42,45,48]. Absorbance at 436 nm is a recommended spectrophotometric method for measuring water colour in the Australian Drinking Water Guidelines [49]

the effect of pH on UV absorbance, pH of water samples was adjusted to pH range of 6–7 using 0.1 N of HCl or NaOH as this range is suitable for the applied UV–vis measurements [29,31,32]. Titration workstation TitraLab, TIM 845 (Radiometer-Analytical, Australia) was used to measure pH of the samples during the adjustment.

The concentrations of nitrate, nitrite, chloride and bromide in water samples were measured using Ion Chromatography system ICS-2000 according to the standard method 4110 B detailed in Ref. [29]. The iron content of the water was quantified using Atomic Absorption Spectrophotometer (AAS) model AA-7000 (SHIMADZU, Australia) by following the standard method 3111 B, direct air-acetylene flame method explained in Ref. [29]. Anions such as chloride and nitrite are unlikely to interfere with UV measurements in this study. The minimum detection limit of chloride in UV measurements is 500 mg/L, which is higher than the concentration of chloride of the water sample (Table 1), and it only causes change in the absorbance peaks at  $\lambda < 200$  nm, while nitrite is unstable and mostly oxidized to nitrate [50]. The concentration of bromide was not detectable in the applied measurement method, which indicates that the concentration of bromide is under the method detection level set by the standard methods [29] (i.e.  $14 \mu g/L$ ). So the effect of bromide on UV absorbance was neglected in this study. The concentrations of iron and nitrate in water samples were lower than the effective limit of these minerals which is between 0 and 0.5 mg/L for iron [32] and 5 mg/L for nitrate [50] as shown in Table 1. The UV absorbance measurements were performed in triplicate for each water sample.

#### 2.2.3. $COD_{Mn}$ , alkalinity and conductivity

The  $\text{COD}_{\text{Mn}}$  of the water samples was measured following the standard procedure described in Ref. [51].  $\text{COD}_{\text{Mn}}$  can be expressed as the amount of permanganate oxidized per one litre of the water sample or the amount of oxygen consumed in the oxidation of one litre of water sample [52], and this measurement unit will be adapted in this study. This procedure is valid for water samples with chloride concentration of less than 300 mg/L as it is the case of Pittaway pond water (Table 1). The alkalinity of the untreated and treated samples was measured using autotitrator, workstation TitraLab, TIM 845 (Radiometer-Analytical, Australia).

Ion analyser, MeterLab model ION-450 supplied by Radiometer-Analytical, Australia was used for measuring the conductivity of water samples.  $COD_{Mn}$ , alkalinity and conductivity measurements for Pittaway water were performed in triplicate.

### 2.3. Ultrasound treatments

A commercial ultrasonic horn device (Branson Sonifier 450) with variable input power and fixed frequency of 20 kHz was used in this study. The probe tip is made of titanium with diameter ( $\emptyset$ ) of 19 mm.

Fig. 2 shows a schematic illustration of the laboratory set-up used in conducting the experimental work. Ultrasound and thermal treatments were performed in a batch mode. A 400 mL Pyrex beaker was used to contain water samples. The temperature rise caused by ultrasound treatments was measured using calibrated thermocouple type *K*. The signals from thermocouple were recorded at a rate of 40 samples/s using A/D card and Lab-View software.

Ultrasound treatment variables such as power, treatment time and depth of the probe in the treated water were set at  $21.5 \text{ W/cm}^2$ , 4 min and 1 cm, respectively. The effect of continuous and pulsed ultrasound at three pulse/interval ratios (denoted as *R*) of 0.5/0.5, 0.6/0.3 and 0.6/0.2 s correspond to *R*1:1, *R*2:1 and *R*3:1, respectively. In order to compare the effect of pulsed ultrasound to that of continuous ultrasound, the applied acoustic power has to be equal for both cases. This can be achieved by applying longer treatment time for pulsed ultrasound at certain value of *R* as shown in below equation [53].

$$t = t_0 \left( 1 + \frac{1}{R} \right) \tag{1}$$

where *t* is the treatment time of pulsed treatments and  $t_o$  is the treatment time of continuous ultrasound. From Eq. (1), the treatment time of the pulsed treatments *R* 1:1, 2:1 and 3:1 was calculated to be 480, 360 and 320 s, respectively.

The frozen water samples were thawed and mixed well before ultrasound and thermal treatments. The beaker was filled with 200 mL of the sample and immersed in an ice bath to bring down the temperature of the sample to approximately 2°C prior to the treatments. Ultrasound treatments were conducted in triplicates for each water sample.

### 2.4. Temperature mimicry (thermal treatments)

Ultrasound treatment of water especially for small to moderate volume samples (the most probable case in the laboratory investigations) usually induces a rapid heat rise in the samples. In the case of this study, the temperature rise was minimized by immersing the water sample in an ice bath to reduce the starting temperature to around 2°C. In spite of using the ice bath, water temperature increased to a

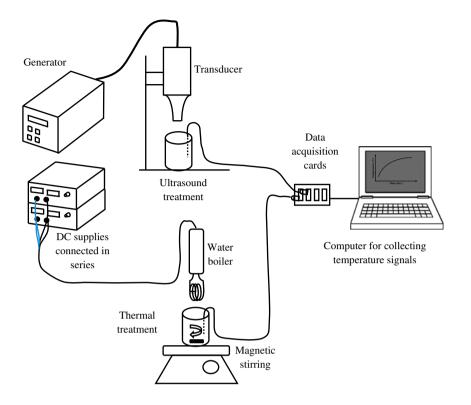


Fig. 2. Graphical representation of the experimental set-up.

maximum of  $11^{\circ}$ C in the most heat-inducing ultrasound treatment (i.e. continuous). The increase in the bulk temperature of the samples within the range of 2–11°C may affect the physiochemical properties of the NOM in water samples.

To investigate the thermal effect of ultrasound treatments on the properties of NOM, thermal treatments that simulate the range and pattern of temperature during ultrasound treatments were designed. A water boiler was used as a heat source in thermal treatments. Tap water was used as a medium in the temperature mimicry experiments. The heated water was continuously stirred to obtain homogeneous temperature rise. The temperature profile of tap water under ultrasound and thermal treatments was obtained with the aid of data acquisition system as shown in Fig. 2.

### 2.5. Statistical analyses

Analysis of variance (one way ANOVA) was performed to each set of experiments (ultrasound and heat experiments) separately to determine any significant change in the dependent variables (water characteristics) at p < 0.05. The experiments of heat and ultrasound treatments were conducted in four levels; R 1:1, R 2:1, R 3:1 and continuous. Least significant difference (LSD) post-hoc test was applied to compare the differences between the treatment levels (pulsed and continuous treatments) when there is an overall significant change in the studied characteristic. Statistical analyses were carried out using SPSS 19 statistics.

### 3. Results and discussion

### 3.1. Mimicry of temperature rise and its effect on water samples characteristics

Fig. 3 shows the temperature rise of ultrasound treatments with their corresponding thermal treatments. The voltages that successfully resulted in temperature increase analogous to that of ultrasound treatments; R 1:1, 2:1, 3:1 and continuous were 75, 79, 82 and 90 V, respectively. The effect of ultrasound pulsation on temperature rise curve appears clear in the temperature fluctuation in Fig. 3. To match the temperature fluctuation of pulsed ultrasound, the corresponding temperature mimicry experiments were performed in pulsation with On/Off ratios same as R of pulsed ultrasound treatments. The obtained levels of voltage were applied in continuous and pulsing modes in the thermal treatments for surface waters.

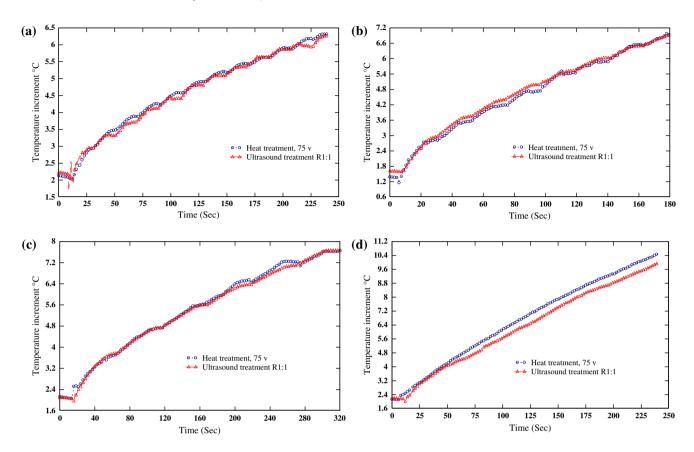


Fig. 3. Temperature rise vs. time for the treatments ultrasound (O) and thermal treatments ( $\Delta$ ); (a) ultrasound *R* 1:1 and heat at 75 v, (b) ultrasound *R* 2:1 and heat 79 v, (c) ultrasound *R* 3:1 and heat at 82 v and (d) continuous ultrasound and heat at 90 v.

The analysis of variance and the descriptive statistics for the overall effect of ultrasound and heat treatments on the characteristics of Pittaway pond water are presented in Tables 3 and 4, respectively. The mean values in Tables 3 and 4 represent the average of the measured characteristics of the treated samples normalized by that of the untreated samples. *p*-value lower than the considered significant level (0.05) indicates significant change. Table 3 illustrates that ultrasound treatment significantly altered six characteristics

Table 3 Descriptive statistics and summary of analysis of variance (ANOVA) for ultrasound treatment of Pittaway pond water

Normalized characteristics	Mean	SD	<i>F</i> -value	<i>p</i> -value
SUVA <sub>254</sub>	0.8897	0.0420	3.223	0.082
SUVA <sub>260</sub>	0.8834	0.0362	1.500	0.287
SUVA <sub>280</sub>	0.8963	0.0371	4.921	$0.032^{*}$
$E_2/E_3$	1.0861	0.0348	11.407	$0.003^{**}$
SUVA <sub>254</sub> /SUVA <sub>204</sub>	0.9825	0.0156	7.929	$0.009^{**}$
SUVA <sub>254</sub> /Color <sub>436</sub>	1.0422	0.0246	0.440	0.731
COD <sub>Mn</sub>	0.9336	0.0363	4.281	$0.044^{*}$
Alkalinity	0.6635	0.1236	63.480	6.4E-06***
Conductivity	2.0094	0.5306	75.678	3.3E-06***

\*\*\*p < 0.001; \*\*p < 0.01; \*p < 0.05.

Descriptive statistics and summary of analysis of variance (ANOVA) for heat treatment of Pittaway pond water

Normalized characteristics	Mean	SD	<i>F</i> -value	<i>p</i> -value
SUVA <sub>254</sub>	0.9974	0.0109	0.204	0.891
SUVA <sub>260</sub>	0.9904	0.0282	0.009	0.999
SUVA <sub>280</sub>	0.9770	0.0321	0.507	0.688
$E_2/E_3$	1.0034	0.0544	0.004	1.000
SUVA <sub>254</sub> /SUVA <sub>204</sub>	0.9984	0.0039	0.153	0.925
SUVA <sub>254</sub> /Color <sub>436</sub>	1.0073	0.0028	2.819	0.107
COD <sub>Mn</sub>	0.9972	0.0221	0.024	0.994
Alkalinity	0.9944	0.0687	0.003	1.000
Conductivity	1.0042	0.0147	0.030	0.993

Table 4

of Pittaway pond water, while the changes in the remaining three characteristics namely SUVA<sub>254</sub>, SUVA<sub>260</sub> and SUVA<sub>254</sub>/SUVA<sub>436</sub> were not significant. Table 4 shows that the temperature rise from 2 to 11°C during ultrasound treatments has a negligible effect on the characteristics of the treated water. Similar findings were reported by Destaillats et al. [54], who found that the increase in the bulk temperature of the treated water by ultrasound from 2 to 12°C led only to a marginal change in the concentration of dichloromethane by less than 2-4% of the initial concentration. Hence, it can be concluded that the significant change in the properties of the treated water is solely attributed to ultrasound effects. The concomitant thermal effect of ultrasound treatment and the insignificant changes of SUVA254, SUVA260 and SUVA<sub>254</sub>/SUVA<sub>436</sub> will not be discussed in terms of their implications on the surface water treatment train.

### 3.2. Comparison between pulsed and continuous ultrasound treatments

Table 5 shows the analysis of LSD post-hoc test for the significantly changed water characteristics of

Pittaway pond water. The significance level considered in this table is p < 0.05. It can be seen from Table 5 that in all the significantly changed characteristics except SUVA<sub>254</sub>/SUVA<sub>204</sub>, there is at least one pulsed ultrasound treatment that is not significantly different in its effect to the continuous treatment. In fact, for some characteristics such as alkalinity, the change caused by pulsed ultrasound R 3:1 exceeded that of continuous ultrasound. This means that applying pulsed ultrasound treatment in this study resulted in a comparable or in some cases better effect as compared to continuous ultrasound treatment. This finding is in agreement with the observations reported in Refs. [55,56] as Xiao et al. [55] reported a higher reduction of carbamazepine with pulsed ultrasound by 6% as compared to the reduction with continuous ultrasound. Similarly, Yang et al. [56] observed that the degradation rate constant of sodium 4-octylbenzene sulphonate under pulsed ultrasound was nearly twice the degradation rate of continuous ultrasound. The high efficiency of pulsed ultrasound as opposed to continuous ultrasound in terms of water characteristics alteration is attributed to the occurrence of shielding effects more pronouncedly in continuous ultrasound than in pulsed ultrasound [20].

Table 5

Descriptive statistics and summary of analysis of variance (ANOVA) for ultrasound treatment of Pittaway pond water; comparison between treatment levels

Treatment levels	R 1:1		R 2:1		R 3:1		Continuou	s
Normalized characteristics	Mean	SD	Mean	SD	Mean	SD	Mean	SD
SUVA <sub>280</sub>	0.9390a	0.0438	0.9015ab	0.0144	0.8843b	0.0188	0.8605b	0.0130
$E_2/E_3$	1.0373a	0.0180	1.0889b	0.0124	1.1003b	0.0268	1.1179b	0.0078
SUVA <sub>254</sub> /SUVA <sub>204</sub>	0.9955a	0.0063	0.9879a	0.0019	0.9857a	0.0057	0.9610b	0.0162
COD <sub>Mn</sub>	0.9451a	0.0125	0.9629a	0.0152	0.8891b	0.0272	0.9373ab	0.0408
Alkalinity	0.8472a	0.0443	0.6318b	0.0253	0.5262c	0.0102	0.6488b	0.0261
Conductivity	1.1450a	0.0144	2.2990b	0.2283	2.2750b	0.0187	2.3188b	0.0062

Note: Means in the same row that do not share the same letter are significantly different (p < 0.05) by LSD post-hoc test.

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It can also be noticed from Table 5 that the change in SUVA<sub>254</sub>/SUVA<sub>204</sub> was the only case where pulsed ultrasound *R*1:1 was not significantly different from the other pulsed treatments. The low efficiency of pulsed ultrasound *R* 1:1 could be due to the long offperiod in this treatment as opposed to the other pulsed treatments which could result in the disappearance of ultrasonic effects. This in turn leads to a subsequent pulse with fewer cavitation sites in the case of *R* 1:1 as compared to the other treatments.

### 3.3. Spectroscopic properties analysis

### 3.3.1. SUVA<sub>280</sub>

The change in SUVA<sub>280</sub> is related to the change in the bulk aromaticity of the water samples as explained in Table 2. Fig. 4 demonstrates the effect of pulsed and continuous ultrasound treatments on the bulk aromaticity of Pittaway pond water. The normalized UV absorbance in Fig. 4 and other water characteristics in the following figures of this study are expressed by the mean of the measurements, and the error bars represent the standard error of the mean. The results obtained from the UV analysis for Pittaway pond water at 280 nm (Fig. 4) demonstrate that ultrasound treatments in its different levels destroyed the aromatic structure of the organic compounds presented in Pittaway pond water. Fig. 4 shows that as the pulse length increases, the reduction of aromaticity increases. However, the difference between continuous treatment and pulsed treatments (R 2:1 and R 3:1) is not statistically significant (Table 5). These results are in agreements with earlier work conducted by Naffrechoux et al. [57] that illustrated the capacity of ultrasound on destructing phenol as model for aromatic compounds. Equally, some other studies presented the ultrasonic degradation of other aromatic compounds such as polycyclic aromatic compounds [58]. The ultrasonic decaying of bulk aromaticity is attributed to two possible mechanisms, the cleavage of the aromatic rings [58,59] or the destruction of the aromatic side chain of the organic compounds [60].

Aromaticity is an important property of the aquatic organic matter that can be utilized to estimate the behaviour of water contaminants with the treatment processes. It was noted that the amenability of the organic matter to the removal by coagulation increases with increasing the aromatic moieties of the organic matter [61,62]. The other important aspect in water treatment is the blockage of filtration media on account of organic materials accumulation on filters. Fan et al. [63] examined the effect of the NOM properties of three Australian surface waters on fouling tendency of MF membrane and observed that water with high aromaticity caused a greater permeate flux decline as compared to other waters. In another investigation for the mechanisms of humic acid fouling to UF membrane, Yuan and Zydney [64] noticed that Suwannee River humic acid solution that was less aromatic than Aldrich humic acid solution caused less flux decline than its comparative Aldrich humic acid solution. The increase in flux declines as the aromaticity of the foulants' increases is attributed to the strong ring structure of the aromatic compounds that increase the hydraulic resistance of the fouling layer. The aromaticity indicated by SUVA<sub>280</sub> has also been frequently correlated to the formation of DBPs [65-67]. SUVA<sub>280</sub> has been also applied to predict the reaction sites of NOM with chlorine [68].

Since ultrasound decreased the SUVA<sub>280</sub> of Pittaway pond water, it can be deduced that this water has become less aromatic under the effect of ultrasound. Less aromaticity means that the NOM of Pittaway pond water has less amenability to coagulation removal, membrane fouling and DBPs formation.

### 3.3.2. $E_2/E_3$ (SUVA<sub>250</sub>/SUVA<sub>365</sub>)

The modification occurs in the  $E_2/E_3$  of water samples implies change in the molecular size distribution of the NOM presented in the samples. Fig. 5 shows that ultrasound treatments increased  $E_2/E_3$  of Pittaway pond water. The increment in  $E_2/E_3$  is directly proportional with the pulse length. Nevertheless, the differences between continuous and pulsed ultrasound treatments, *R* 2:1 and *R* 3:1, were found to be insignificant as presented in Table 5. The molecular size of NOM is directly correlated to the aromaticity (SUVA<sub>280</sub>) [42,43,46,47], so when the aromaticity decreases,  $E_2/E_3$  increases. Such relationship has been observed in this study as it is illustrated in Fig. 6 ( $R^2 = 0.967$ ).

The molecular size distribution of the NOM has a significant effect on the sequential treatment processes of surface water (Fig. 1). Starting from coagulation/flocculation processes, several researches have elaborated that NOM with intermediate to large molecular size are the most susceptible compounds to the removal by coagulation [69]. A study conducted by Nissinen et al. [70] on various Finnish waterworks confirmed that coagulation using common coagulants successfully removed the largest molecular size humic fraction from the tested waters.

Filtration fouling by NOM is largely affected by its molecular size distribution. The effect of the molecular size of NOM on the membrane fouling and rejection to these contaminants emanates from the fact that the membrane capacity in separating pollutants from water relies on two mechanisms, sieving effects and physiochemical interaction (i.e. repulsion) [5,71]. The general consensus in the literature indicates that NOM with hydrophobic characteristic and high molecular weight are regarded as the major contributors to membrane fouling [72,73]. More specifically, organic materials with high molecular size are mostly associated with the cake layer fouling of the membrane [74,75], whereas the low molecular weight NOM causes pore plugging fouling [76]. However, the molecular size of NOM is governed by the solution chemistry characteristics such as pH, ionic strength and the presence of mono- and multi-valence species [73].

The reactivity of NOM with disinfectants does not have a conclusive correlation with the molecular size distribution. For example, Kitis et al. [77] reported that out of two surface waters that were investigated for their potential to form Trihalomethanes (THMs) and Haloaceticacid (HAAs), the results of one of the water resources showed that DPBs increased with increasing the molecular size, whilst the results of the other water resource showed the opposite. Zhao et al. [78] explored the generation of THMs from the reaction of different DOC-sized fractionates with chlorine and chlorine dioxide. Their findings showed that generally the smaller the size of the DOC fractionate, the higher the THMs formed. Nevertheless, the formed THMs with chlorine dioxide did not show clear trend and it was independent of the DOC molecular size. Amy et al. [79] pointed to the decrement of the reactivity of organic matter with chlorine when converted to a lower molecular weight compounds. Similarly, Amy et al. [80] observed that the destruction of organic materials of ground water into smaller fractions by ozone did not increase THM formation potential (THMFP) of the water.

The results obtained from the quotient  $E_2/E_3$  in this study suggest that ultrasound treatments for 4 min were sufficient to bring about a small change in the molecular size of the NOM for Pittaway pond water. The increase of  $E_2/E_3$  ratio of Pittaway pond water may negatively affect the amenability of NOM to the removal by coagulation. It also indicates that the treated water would more likely cause pore blocking than cake layer fouling. The effect of the molecular size distribution of NOM on the DBPs formation was not decisive from the knowledge available in the literature. Therefore, the interpretation regarding the effect of NOM molecular size change due to ultrasound on the potential of waters to form DBPs has not been discussed herein.

### 3.3.3. $SUVA_{254}/SUVA_{204}$ ( $A_{ET}/A_{Bz}$ )

The change of SUVA<sub>254</sub>/SUVA<sub>204</sub> reflects a change in the concentration of aromatic compounds with oxygen-containing functional groups [30] as explained in Table 1. The impacts of ultrasound treatments on the SUVA<sub>254</sub>/SUVA<sub>204</sub> of Pittaway pond water is shown in Fig. 7. The general trend of Fig. 7 is in mutual agreement with that of Fig. 4 as both reveal a reduction in the aromatic compounds of Pittaway pond water. It can be noted from Figs. 4 and 7 that the extent of ultrasound effect on SUVA254/SUVA204 (maximum decrease of 4%) is less than its effect on SUVA<sub>280</sub> (maximum decrease of 14%). This means that small portion of the destructed aromatic compounds by ultrasound was activated aromatic rings of oxygencontaining functional groups. These results are comparable with the results obtained by Chen et al. [81], as the latter showed that the acidity of organic matter was slightly reduced when treated with low frequency ultrasound. Since the acidity of natural organic matter is attributed to the presence of carboxylic and phenolic groups [82], the slight deterioration in the acidity of organic matter in Chen et al. [81] study can be accounted for the degradation of ultrasound to the phenolic and carboxylic groups which agrees with findings of this study.

SUVA<sub>254</sub>/SUVA<sub>204</sub> can be used as an indication for the tendency of NOM to involve in adsorption and complexation reactions [30]. The absorption intensity of SUVA<sub>254</sub>/SUVA<sub>204</sub> ratio is related to the presence of aromatic rings substituted with oxygen-containing functional groups [30]. These functional groups play a significant role in the NOM adsorption to coagulants and its potential to form DBPs [83–85]. Korshin et al. [30]

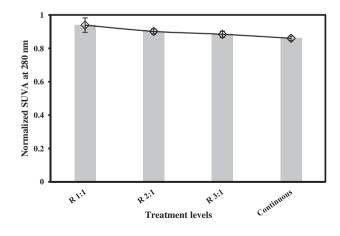


Fig. 4. Normalized SUVA<sub>280</sub> of Pittaway pond water after exposure to ultrasound  $(21.5 \text{ W/cm}^2)$  for effective treatment time of 4 min.

observed that coagulation with alum selectively removes aromatic compounds substituted with oxygen-containing functional groups. This can be interpreted as water with high SUVA254/SUVA204 exhibits high NOM removal by coagulation with metallic salts. On the other hand, recent reports on the correlation between SUVA<sub>254</sub>/SUVA<sub>204</sub> and DBPs formation potential [16,42,86] asserted the existence of direct correlation between DBPs formation and SUVA<sub>254</sub>/SUVA<sub>204</sub>, the higher the SUVA<sub>254</sub>/SUVA<sub>204</sub> of the water, the more DBPs form in the disinfected water by chlorine. The adsorption tendency of NOM could also be adapted as an index for its fouling potential to filtration medium. Sotto et al. [87] showed that some of the aromatic compounds with substituted hydroxyl groups (e.g. 2-nitrophenol and 2-chlorophenol) have the potential to adsorb onto RO and NF membranes, causing a decline in the permeate flux.

Taking lead from the findings of the reviewed literature above, one can deduce that ultrasound has slightly decreased the aromatic compounds with oxygen-containing groups in Pittaway pond water, which in turn can reduce the risk associated with these compounds in terms of membrane fouling and DBPs formation. However, such decrease in the oxygencontaining groups may adversely affect the coagulability of Pittaway pond water by metallic salts.

### 3.4. Effect of ultrasound treatments on $COD_{Mn}$

The change in  $\text{COD}_{Mn}$  implies alteration in the oxidabizality and/or reactivity of the water pollutants. Since the  $\text{COD}_{Mn}$  of the samples depends on the amount of carbon in the samples [88], the  $\text{COD}_{Mn}$  of the treated water samples was standardized by the DOC of the samples and referred to as specific  $\text{COD}_{Mn}$ , expressed as mg O<sub>2</sub>/mg C.

Fig. 8 depicts the effect of ultrasound treatments on the oxidant demands of Pittaway pond water. Fig. 8 shows that the specific  $COD_{Mn}$  of the Pittaway pond water decreased after ultrasound treatments. It can be noticed that the decrease in  $COD_{Mn}$  in Fig. 8 did not follow a regular pattern, and this is attributed to the superiority of pulsed ultrasound effect (*R* 3:1) on  $COD_{Mn}$  as compared to other treatments. The results of this study are consistent with those obtained by Naffrechoux et al. [57], who reported 50% reduction of COD of wastewater after ultrasound and UV treatments.

It was reported that potassium permanganate reacts preferentially with the aromatic ring-structured organic compounds of large molecular weight [52]. This means that the  $COD_{Mn}$  is related to aromaticity and  $E_2/E_3$  ratio. It can be noticed from the general

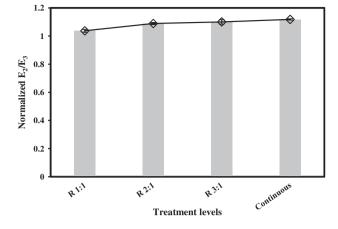


Fig. 5. Normalized  $E_2/E_3$  of Pittaway pond water after exposure to ultrasound (21.5 W/cm<sup>2</sup>) for effective treatment time of 4 min.

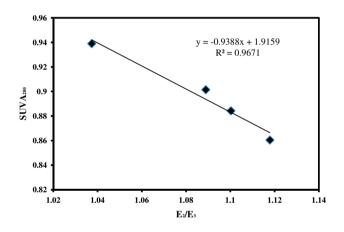


Fig. 6. Relationship between  $E_2/E_3$  with SUVA<sub>280</sub> for the treated Pittaway pond water.

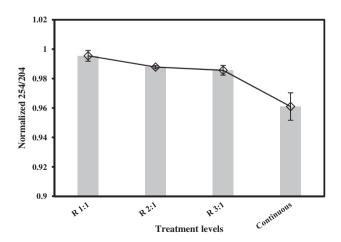


Fig. 7. Normalized SUVA<sub>254</sub>/SUVA<sub>204</sub> of Pittaway pond after exposure to ultrasound  $(21.5 \text{ W/cm}^2)$  for effective treatment time of 4 min.

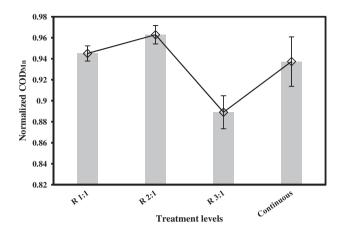


Fig. 8. Normalized COD<sub>Mn</sub> of Pittaway pond water after exposure to ultrasound ( $21.5 \text{ W/cm}^2$ ) for 4 min.

trend of Figs. (4, 5 and 8) (regardless of the variation in the results) that  $COD_{Mn}$  exhibited a direct correlation with  $SUVA_{280}$  and inverse correlation with  $E_2/E_3$ , which agrees with Pittaway and Ancker statement [52]. The results obtained in this work are also in agreement with the findings of Mrkva [89] that underlined a direct relation between  $SUVA_{254}$  and  $COD_{Mn}$ (both exhibit reduction, Table 3).

With regard to the effect of COD<sub>Mn</sub> change on the performance of coagulation process, it appears from the literature that there is no obvious relationship between COD<sub>Mn</sub> and coagulability of NOM. For instance, the results of Ma and Liu [90] showed that the turbidity removal with metallic coagulants did not exhibit a consistent trend with the initial  $COD_{Mn}$ of the treated water. Hence, the prediction of coagulability of the treated water depending on the COD<sub>Mn</sub> results is not discussed in this study. The COD<sub>Mn</sub> was found to have fair direct correlation (R = 0.587) with THMs [91]. This means that ultrasound reduced the potential of Pittaway pond water to form THMs. With regard to filtration performance, to the knowledge of the authors no linkages have been established between the performance of filtration and COD<sub>Mn</sub> of water.

### 3.5. Effect of ultrasound treatments on alkalinity

The normalized alkalinity of the treated Pittaway pond water by ultrasound is presented in Fig. 9. It appears from Fig. 9 that ultrasound treatments dropped the alkalinity of the treated water. These results are in agreements with the findings of Suresh et al. [92] who also observed a reduction in water alkalinity under the effect of ultrasound. Pulsed ultrasound *R* 3:1 showed more effective alteration of

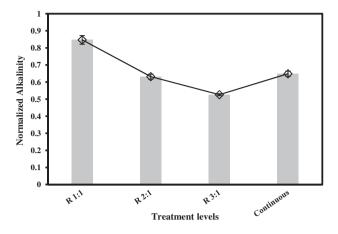


Fig. 9. Normalized alkalinity of Pittaway pond water after exposure to ultrasound  $(21.5 \text{ W/cm}^2)$  for 4 min.

alkalinity than the other treatments (also supported by Table 5).

The decrement in the treated water alkalinity in this study is a result of destruction of the alkalinityforming agents (bicarbonates (HCO<sub>3</sub>), carbonates (CO<sub>3</sub>) or hydroxyl anions (OH<sup>-</sup>)). Since the pH of Pittaway pond was below 10 (Table 2), the alkalinity of this water is mainly caused by carbonates and bicarbonates [93], and thus it can be appropriately said that ultrasound has destroyed the carbonate and bicarbonate species in the treated water. The mechanism via which ultrasound causes destruction to water forming alkalinity agents is the production of highly reactive radicals (i.e. OH<sup>•</sup>) that are able to oxidize the carbonate and bicarbonate producing  $H_2O$  and  $CO_2$ .

Alkalinity has a strong influence on water treatment process through its buffering effects. In coagulation process, alkalinity can alter the charge of the NOM by changing the pH of the bulk water. When the pH of the water exceeds or becomes lower than the isoelectric point of the NOM molecules, the molecules' charge alters to negative or positive [5]. Similarly, the change in pH has an influence upon the hydrolysis of the metal salts and their charge production [61,94]. For instance, Edzwald and Tobiason [95] reported that the charge of aluminium hydrolysis species reduces from +1.5 Al(OH)<sub>1.5</sub> to +0.5 Al(OH) $^{+0.5}_{2.5}$ when the pH rises from 5.5 to 6.5. So, decreasing the alkalinity to some extent as a result of ultrasound treatment should have a positive impact on coagulation, especially when the water is very alkaline (the case of this study, Table 1) [61,96].

Similar to coagulation process, the separation of contaminants from water via filtration is affected by the charge of the contaminants [5]. In addition to the effect of alkalinity on pH and subsequently on the charge of contaminants, the carbonate alkalinity may interact with cations presented in water such as  $Ca^{+2}$ and forms  $CaCO_3$ . Such interaction could have a positive effect on water purification if it takes place at the stage of coagulation, as  $CaCO_3$  may improve the retention of sludge produced by coagulation [97]. However, the production of calcium carbonate in the filtration feed water can impose risk of filters' scaling [98]. The other concern of high alkalinity is the promotion of membrane filters fouling with silica [99]. It has been suggested by number of studies that decreasing alkalinity can be applied to alleviate the problems of scaling in filtration processes [100,101].

There is also a possibility of alkalinity being a trigger to the formation of DBPs [102]. Adedapo [103] observed an increase in the formation of some classes of DBPs such as dichloroacetonitrile and chloroform when the alkalinity of the water increased. Amy et al. [104] pinpointed a positive direct correlation between alkalinity and bromate formation. Additionally, since alkalinity affects the hydrolysis of coagulants [105] and the charge of substances in water, it is a crucial factor that determines the ability of treatment processes that proceed the disinfection step in removing DBPs precursors. In conclusion, decreasing the alkalinity by ultrasound treatments in this study suggests that ultrasound can be used to alleviate the scaling problems caused by cations, promote the removal of contaminants in coagulation process and hinder the formation of some DBPs classes.

### 3.6. Effect of ultrasound treatments on conductivity

The change that occurred in the conductivity of Pittaway pond water on account of ultrasound treatments can be seen in Fig. 10. Fig. 10 illustrates that ultrasound noticeably increased the conductivity of Pittaway pond water. Continuous and pulsed ultrasound R 2:1 and R 3:1 treatment had the same effect on the conductivity. The increase in the conductivity of water due to ultrasound can be explained as the extreme conditions inside the bubble and in its vicinity promote the concurrent decomposition and binding of dissolved gasses and subsequently, produce acids that makes the water more conductive [106,107]. The observed conductivity increase in this study is in agreement with data reported in Naddeo et al. [25], as the latter showed an increase in the conductivity of humic acid solution as a model for aquatic NOM after ultrasound treatment.

The conductivity of water gives an indication to the tendency of contaminants to adsorb to surfaces such as coagulants and filters. It is important to

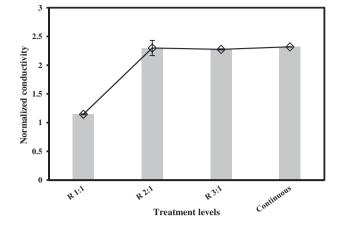


Fig. 10. Normalized conductivity of Pittaway pond water after exposure to ultrasound  $(21.5 \text{ W/cm}^2)$  for 4 min.

elaborate here the link between conductivity and adsorption of pollutants to surfaces. Conductivity is directly related to the ion strength [108], and increasing the ionic strength of water reduces the thickness of electrical double layer leading to a reduction in the magnitude of electrical double layer interaction [109,110]. Electrical double layer interaction is one of three physiochemical interactions that govern the stability of the particles in the solution. These interactions include Lifshitz-van der Waals, Electrical double laver and Lewis acid-base [111-113]. When the total free energy ( $\Delta G$ ) of the combined three interactions is negative, the adsorption of molecules or living organisms to surfaces is favourable, otherwise the adsorption is unlikely to occur when  $\Delta G$  is positive [109,112]. So, the increase in the conductivity of Pittaway pond water under the effect of ultrasound reduces the thickness of electrical double layer between the suspended contaminants and surfaces. This in turn can improve contaminants removal by coagulation through adsorption and enmeshment mechanisms. Kobya et al. [114] and Bazrafshan et al. [115] noticed an enhancement in the removal of organic compounds from water by electrocoagulation when water conductivity increased.

The change of ionic strength of water also has an influence on membrane filtration performance [6]. Increasing ionic strength increases the thickness and compactness of the fouling layer, and thereby increases the hydraulic resistance of fouling layer [73]. Decreasing the electrical double interaction increases the adsorption of the NOM and micro-organisms to the membranes which in turn increases the thickness of the fouling layer [109,116]. Similarly, the increase of ionic strength causes a conformational change in the

structure of organic materials. With increasing the ionic strength, the humic and fulvic acid molecules behave like rigid spherocolloids, while decreasing ionic strength makes these molecules behave like flexible linear colloids [117]. The spherical shape of the NOM molecules makes the fouling layer more compact. In addition to the membrane fouling, the increase of ionic strength decreases the rejection of salts and DBPs due to the increase in the osmotic pressure [118]. The enhancement of fouling as a result of increasing the conductivity of water has been confirmed by several researchers [119,120]. So, increasing the conductivity of the treated Pittaway pond water can exacerbate the fouling problem and decrease the rejection rate of DBPs.

In relation to the effect of ionic strength on the formation of DBPs, some studies observed that ionic strength is inversely correlated to DBPs formation. For example, Siddiqui and Amy [121] reported a decrease in the CHBr<sub>3</sub> from 43 to  $36 \,\mu\text{g/L}$  when the ionic strength increased from 0.006 to 0.075 M. However, technically it is hard to establish links between the formation of DBPs and ionic strength, as the latter reflects the ionic content of water with no specific information on the concentration of particular ions. In addition, the ionic strength affect equally the physiochemical interactions of NOM with disinfectants and the dissociation of disinfectants [122,123], which makes evaluating the effect of ionic strength on DBPs formation hard to perform through a literature survey. In summary, it can be said that the relationship between ionic strength and DBPs formation is dependent on treatment conditions and the physicochemical properties of water and can be established experimentally.

## 4. Overall evaluation for ultrasound application in surface water

The effects of ultrasound on the characteristics of an Australian surface water with fresh organic materials have been investigated along with their implications on the performance of conventional treatment processes. In this section, an assessment table (Table 6) has been developed to help choosing the most suitable location of ultrasound in surface water treatment systems depending on UV–vis absorbance,  $COD_{Mn}$ , alkalinity and conductivity. Only the significantly changed characteristics have been considered in the

 Table 6

 Assessment scheme for ultrasound treatment in surface water system

Treatment process	Measured characteristics		Maximum change (%)	Effect of change	Net effect	Suitability
Coagulation/flocculation	Specific UV absorbance (SUVA),	280	14 <sup>D</sup>	_	+	
0	$Lmg^{-1} cm^{-1}$	250/365	11.7 <sup>I</sup>	_		
		254/204	$4^{\mathrm{D}}$	_		
	Specific permanganate index (mg $O_2/mg$ DOC)		11 <sup>D</sup>	*		
	Alkalinity (meq/L)		47.3 <sup>D</sup>	+		
	Conductivity, 25°C		131 <sup>I</sup>	+		
Filtration	Specific UV absorbance (SUVA),	280	$14^{\mathrm{D}}$	+	_	×
	$Lmg^{-1} cm^{-1}$	250/365	11.7 <sup>I</sup>	#		
		254/204	$4^{\mathrm{D}}$	+		
	Specific permanganate index (mg $O_2/mg$ DOC)		11 <sup>D</sup>	*		
	Alkalinity (meq/L)		47.3 <sup>D</sup>	+		
	Conductivity, 25°C		131 <sup>I</sup>	_		
Disinfection	Specific UV absorbance (SUVA),	280	$14^{\mathrm{D}}$	+	+	
	$Lmg^{-1}cm^{-1}$	250/365	11.7 <sup>I</sup>	*		
	0	254/204	$4^{\mathrm{D}}$	+		
	Specific permanganate index (mg DOC)	O <sub>2</sub> /mg	11 <sup>D</sup>	-		
	Alkalinity (meq/L)		47.3 <sup>D</sup>	+		
	Conductivity, 25°C		131 <sup>I</sup>	*		

Notes: (-) Negative effect; (+) Positive effect; (\*) inconclusive effect; (#) neutral effect; (I) increment; (D) decrement.

assessment. The assessment criteria are based on the effect of the water characteristics change on the performance of coagulation, filtration and disinfection.

The symbols that have been used in the assessment table to indicate the effects of the change on a certain treatment process are; (-) possible adverse effect, (+) possible positive effect, (\*) inconclusive effect and (#) indefinite effect. It should be mentioned here that although the decrease of SUVA<sub>280</sub> of Pittaway pond water is marked as possible negative change for coagulation process, ultrasound has a positive effect represented by the decrease of DOC concentration (Table 7). The effect is marked as inconclusive (\*) when there is no scientific explanation available in the literature. The hash symbol was used to describe situations where the change in the characteristic cannot be regarded positive or negative (i.e. indefinite). For example, the effect of  $E_2/E_3$  alteration on filtration performance is indefinite, as both small and large molecules have the potential to foul the membrane.

To establish an acceptable assessment strategy using the measured characteristics, we assumed that all characteristics have the same weight in terms of their effect on the treatment processes. The net effect of the change was determined by combining the maximum percentage of the change occurred in the characteristics with their signs excluding the inconclusive and the indefinite effects. If the net effect of the changes on a particular treatment process is positive, the use of ultrasound as pre-treatment for this process is suitable  $(\mathbf{\nu})$ , otherwise the application of ultrasound is not suitable, indicated by a cross sign. It is clear from Table 6 that ultrasound is suitable pre-treatment for coagulation/flocculation and disinfection processes for Pittaway pond water. Contrarily, ultrasound is not suitable as a pre-treatment for filtration process when organic fouling is concerned. However, it is worth mentioning that when bio-fouling and inorganic fouling are considered, ultrasound is an effective pre-treatment technique due to its disinfection and oxidizing effects [18,19,124].

Table 7	Ta	ble	7
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DOC concentration of Pittaway pond water (initial concen-
tration of $6.5 \pm 0.15$ ) after ultrasound treatments

Treatments	DOC concentration of Pittaway pond water (mg/L)
R 1:1	$5.76 \pm 0.08$
R 2:1	$5.31 \pm 0.12$
R 3:1	$5.3 \pm 0.11$
Continuous	$5.25 \pm 0.06$

Implementing ultrasound as pre-treatment for coagulation process is the best arrangement for ultrasound application in surface water treatment as ultrasound has no residual effect [5] and its application prior to disinfection can be ineffective practice. In addition to the positive effect of ultrasound in enhancing the amenability of organic contaminants towards removal by coagulation, ultrasound destruction of micro-organisms and oxidizing of inorganic species can improve the coagulation and subsequent treatment processes. For instance, the disintegration of micro-organisms and the release of intracellular products may enhance the coagulation as cell products may act as non-ionic polyelectrolytes that aid the removal of organic compounds by coagulation [125]. Moreover, the oxidation of inorganic species such as iron and manganese by ultrasound can be harnessed as a replacement for the pre-chlorination prior coagulation that is normally adapted for oxidizing metals [124,126]. This in turn reduces the formation of DBPs by reducing the amount of added chlorine to water.

### 5. Conclusions and recommendations

In this work, the effect of ultrasound treatment (pulsed and continuous) on UV–vis absorbance,  $COD_{Mn}$ , alkalinity and conductivity of an Australian surface water with fresh NOM mainly driven from vegetation was investigated. The bulk temperature rise of the water that accompanied ultrasound treatments was recorded and subsequently used to perform thermal treatments that had the same temperature rise pattern as ultrasound treatments. ANOVA of the obtained results revealed that thermal treatments had no significant effect on the properties of the treated water and the changes occurred were mainly attributed to ultrasonic effects.

LSD post-hoc analysis showed that pulsed ultrasound treatments (R 2:1 and R 3:1) had similar or in some cases stronger influence on the properties of the treated water as compared to continuous treatment. However, pulsed ultrasound with equal pulse and interval periods was significantly less effective than the continuous ultrasound in terms of the treatment effect on water properties. This confirms that pulsed ultrasound can conveniently be used as a replacement for continuous ultrasound in water treatment with less requirement for cooling process (Fig. 2).

An assessment based on experimental observation backed by extensive literature survey was carried out to identify the best location of ultrasound in surface water treatment schemes. The outcomes of the assessment indicated that implementing ultrasound before coagulation/flocculation (Fig. 1) is the most beneficial location for ultrasound in surface water treatment system. The effect of ultrasound as pre-treatment on coagulation performance with various coagulants at various operating conditions is recommended to be experimentally investigated in the future. It is also important for the future work to explore the down-stream effects of ultrasound as pre-treatment for coagulation on the efficiency of filtration and disinfection processes in terms of fouling and DBPs formation.

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