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Pulsed ultrasound as an energy saving mode for ultrasound treatment of surface water with terrestrial aquatic carbon

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ABSTRACT

The use of ultrasound technology in water treatment has gained great popularity in recent years owing to its benign environmental effects. The evaluation of this technology for water treatment purposes has mostly been conducted using synthetic water samples. This study however investigated the use of ultrasound for treating natural water with organic carbon predominantly derived from terrestrial sources. Ultrasound treatments were applied in continuous and pulsed modes with a range of On: Off ratios (R) and power intensity of 21.5 W/cm^2 for 4 min. Physio-chemical and spectroscopic measurements were applied to determine the effect of ultrasound treatments on the concentration and structure of dissolved organic carbon (DOC) in the treated water. Post-hoc statistical analysis at a significance level of 0.05 showed that the performance of pulsed ultrasound treatments at least at one of pulse settings was better than that of continuous treatment. Overall, it was found that ultrasound treatments decreased DOC in the treated water and altered its nature to become more reactive towards oxidation and electrochemical reactions. Energy and cost analysis for DOC removal have also been conducted and results showed that applying the appropriate pulse settings can reduce the cost of the treatment by more than a half.

Keywords: Pulsed ultrasound; DOC; Physio-chemical properties; Spectroscopic properties; LSD post-hoc analysis

1. Introduction

The nature of dissolved organic carbon (DOC) in water governs its behavior towards treatment processes. The structural characteristics of aquatic organic matter depends on source materials, geology and topography of the catchment [1]. There are three main categories of DOC that are of concern to drinking water treatment; allochthonous, autochthonous and anthropogenic [2]. Allochthonous DOC is originated from the vegetative decomposition and terrestrial sources. Autochthonous DOC is derived mostly from algal and microbial activities. The source of anthropogenic DOC is human activities and microbial products that result from the biological treatment of wastewater. The differentiation between the above-mentioned DOC categories is a challenging task that involves the use of advanced chemical techniques. For example, the differentiation between allochthonous and autochthonous DOC requires the use of Fourier transform ion cyclotron resonance mass spectrometry (FTICRMS) coupled with electro spray ionization (ESI) [3]. Similarly, estimating the concentration of anthropogenic carbon in natural water requires the application of isotopes with a complicated aquatic carbon modelling [4,5].

The water resources that are utilized for drinking water production mostly contain allochthonous and

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autochthonous carbon [6]. However, the occurrence of autochthonous DOC in water resources depends on the hydraulic residence time of water in the reservoirs, and this would naturally reduce its contribution to carbon budget of the water. Thus, focusing on the enhancement of allochthonous DOC removal would be of more importance to drinking water treatment practices as compared to other DOC types.

Generally, DOC can be removed from drinking water through sequential processes of coagulation/flocculation and filtration. However, some DOC can still reach the disinfection step and react with disinfectants leading to an inefficient microbial inactivation and the formation of pernicious disinfection by-products (DBPs) [7]. The common classes of DBPs are trihalomethanes (THMs) and haloacetic acids (HAAs). DBPs are potential carcinogenic and mutagenic complexes that can cause serious health issues [7]. Since chemical treatments produce harmful by-products, the use of chemical-free techniques such as ultrasound is needed to be sought.

Ultrasound technology is an attractive method for DOC removal owing to its benign environmental effects and its simple implementation [8]. Ultrasound capacity to remove DOC lies in its physical and chemical effects. The passage of ultrasonic wave through water generates micro-bubbles in the negative swing of the pressure wave (rarefaction) and these bubbles collapse in the subsequent positive swing of the pressure wave (compression). The movement of ultrasonic wave in water along with bubbles' oscillation and collapse are the source of the physical and chemical effects of ultrasound [7]. The physical effects of ultrasound include acoustic streaming, micro streaming, micro-jets, turbulences and shock waves [9]. The chemical effect of ultrasound is represented by the generation of highly oxidative chemicals such hydroxyl and atomic oxygen radicals and hydrogen peroxide [10]. Both physical and chemical effects of ultrasound are capable of destructing DOC structure [11].

Applying ultrasound technology for DOC removal may require high energy [12], hence, ways of reducing energy requirement in this technology should be explored. One of the energy-saving ways for running ultrasound is the pulsed mode operation. Pulsed ultrasound refers to the intermittent wave irradiation. In sono chemistry, the ratio of On: Off is denoted as *R*. A portion of ultrasonic energy is normally wasted in continuous ultrasound operation due to the formation of a cloud of bubbles near the irradiating surface that scatters the waves in different directions (shielding effects). This phenomenon decreases significantly in the pulsed operation as such bubbles dissolve into smaller sized bubbles during the Off period serving as cavitation nuclei in the next pulse. However, the extent of energy recovery in pulsed ultrasound depends largely on choosing the suitable pulses and quiescent periods.

In this work, the effect of pulsed ultrasound at three different pulse settings of R = 1, 2 and 3 on DOC concentration and structure in natural water samples was investigated and compared to the standard continuous operation. It is important to use natural water samples in studying the efficiency of ultrasound, as the use of synthetic samples may lead to performance mis-assessment of the technology. Also, the effectiveness of ultrasound is usually measured based on the quantity of DOC removed while the structural change of DOC is not taken into consideration. The structural change of DOC due to ultrasound treatments was also evaluated using surrogate measurements such as conductivity, alkalinity, chemical oxygen demand (COD), single wavelength UV absorbance and UV ratios. The use of surrogate measurements is a common practice for evaluating the performance of water treatment processes [13]. Single wavelength measurements included absorbance at 254 and 280 nm as indicators for humic and aromatic fractions of DOC [8]. Single wavelength measurements were normalized by DOC concentration to produce the so-called specific UV absorbance (SUVA) that is normally used to detect the structural change of DOC rather than the change in DOC concentration. UV absorbance ratios of A_{250}/A_{365} known as E_2/E_3, A_{254}/A_{204} and A_{254}/A_{436} were applied as measures for the change in the molecular size, presence of aromatic compounds with functional groups (e.g., hydroxyl, carboxyl, etc.) and the ratio of UV absorbance to colour forming DOC moieties, respectively [8]. A denotes absorbance. The above-mentioned physio-chemical and spectroscopic measurements were applied in this study due to their reliability in research investigations and common use in water treatment industry. Statistical analyses were applied to determine the significance of the change in DOC concentration and structure, and also to compare between the treatments.

2. Materials and methods

2.1. Water sample

Logan water was selected in this study as a model for Southern East Queensland (SEQ) water bodies. Logan water is an agricultural storage with natural organic matter (NOM) mainly driven from soil and grass degradation. The characteristics of Logan water are shown in Table 1.

2.2. Ultrasound treatment

Fig. 1 shows a schematic representation for the experimental set-up. A low frequency 20 kHz ultrasonic horn device equipped with a titanium probe of 19 mm diameter (digital Branson sonifier 450 W) was used for treating water samples. In a typical experimental run, 200 ml of water sample in a Pyrex beaker was treated ultrasonically with an immersed horn for a depth of 1 cm. An ice bath was used for reducing temperature rise during ultrasound treatment. The temperature of the water sample being treated by ultrasound was measured using a calibrated thermometer.

Ultrasound treatments for both modes continuous and pulsed were conducted at power intensity of 21.5 W/cm^2 for 4 min. Ultrasonic power was measured calorimetrically applying the techniques reported in [10].

The pulsed mode was performed at three R ratios of 1, 2 and 3. The logic behind choosing the applied R ratios is to test the performance of pulsed ultrasound as oppose to continuous ultrasound with a systematic increment of R ratio and a reasonable length of operation time (maximum of 8 min). In order to apply the same amount of ultrasonic energy in the pulsed mode as that of the continuous mode,

Table 1
Characteristics of Logan water

Water properties		Measured values
pH, 25°C		9.10 ± 0.30
DOC (mg/L)		8.57 ± 0.17
Specific COD Mn (mg O_2/mg DOC)		1.17 ± 0.13
Total suspended solids (TSS) (mg/L)		44.00 ± 1.20
SUVA (L/mg·cm)	254	0.046 ± 0.005
	280	0.033 ± 0.004
	250/365	5.36 ± 0.55
	254/204	0.33 ± 0.02
	254/436	17.9 ± 1.2
Alkalinity (meq/L)		3.00 ± 0.26
Conductivity (mS/cm), 25°C		0.3 ± 0.04
Iron (mg/L)		0.060 ± 0.008
Nitrate (mg/L)		1.02 ± 0.1
Chloride (mg/L)		44.0 ± 2.7
Sulphate (mg/L)		0.94 ± 0.07
Phosphate (mg/L)		<0.1*
Bromide (mg/L)		<0.1*

*Below the detection limit of the standard method 4110 B using ICS-2000 ion chromatography.

ultrasonic system was operated for a longer time in the case of pulsed mode. The treatment time required for applied pulse mode settings was calculated based on the treatment time of continuous mode as well as the set *R* ratio using Eq. (1) [8].

$$t_p = t\left(1 + 1/R\right)$$

where t_p is the treatment time of pulsed treatments and t_o is the treatment time of continuous ultrasound (= 4 min). Short treatment time of 4 min was chosen in this study due to its energy efficient removal of DOC in natural water [14]. The treatment time of the pulsed treatments with *R* ratios of 1, 2 and 3 was found to be 480, 360 and 320 s, respectively. It is worth mentioning that ultrasound treatments were conducted in triplicates.

2.3. Analytical methods

A range of physio-chemical and spectroscopic properties of water samples were measured before and after ultrasound treatments applying the following analytical techniques. These techniques were applied to evaluate the effect of ultrasound treatments on DOC concentration and structure. It is important to note here that all the measurements were conducted in triplicate for each water sample.

2.3.1. Dissolved organic carbon

The DOC of water samples was measured applying the standard high temperature combustion method [15]. Water samples were filtered through 0.45 µm prior to DOC measurements. A total Carbon Analyser (TOC-VCSH, SHIMADZU, Australia) equipped with an auto-sampler (ASI-V) was utilised for DOC measurements. Three replicate injections were made that resulted in coefficient of variance of < 0.02.

2.3.2. UV-vis absorbance

The spectrophotometric absorbance of water samples was measured using JENWAY UV/Vis spectrophotometer, model 6705. Quartz cuvette of 1 cm path length was used to carry filtered water samples through 0.45 µm. Water samples were scanned for a wavelength range of 200–500 nm with distilled water being used as a base line. Absorbance of water samples at selected wavelengths of 204, 250, 254, 280, 365 and 436 nm was recorded.

The effect of the interfering ions on UV measurements was ignored in this study due to their low concentration (see Table 1). For instance, the maximum effective range of iron and nitrate are 0.5 mg/L and 5 mg/L, respectively [8], which is higher than the concentrations of these species in

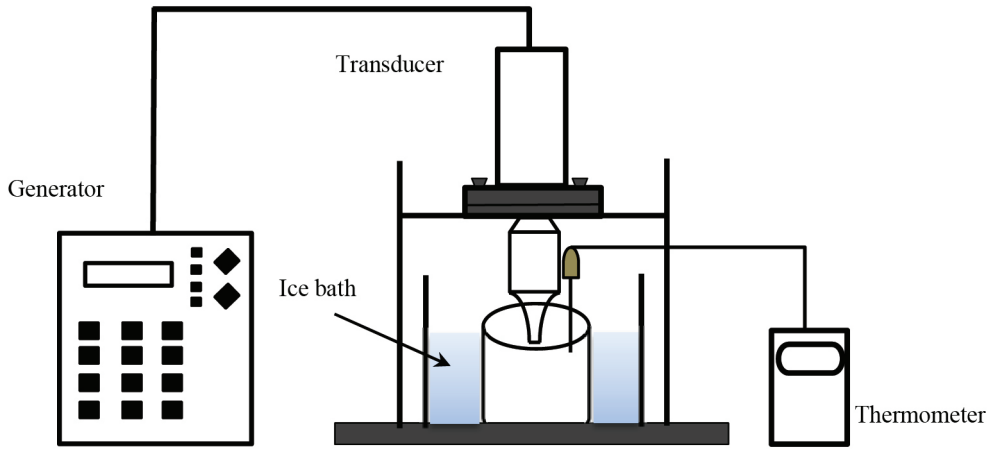

Fig. 1. Schematic of the experimental set-up.

Logan water. Chloride and sulphate only have a tangible absorbance at wavelength <200 nm [16].

2.3.3. Permanganate chemical oxygen demand (COD_{Mn})

The permanganate chemical oxygen demand (COD_{Mn}) was applied in this study to measure the oxidation potential of DOC in water before and after ultrasound treatment. COD_{Mn} is a suitable technique for measuring DOC reactivity after exposure to photo-degradation [17] which has a similar oxidation mechanism as ultrasound (free radicals degradation) [18,19]. COD_{Mn} was measured following the procedure detailed in [20].

2.3.4. Alkalinity and conductivity

The alkalinity and conductivity of water samples was measured using titration workstation TitraLab, TIM 845 and ion analyser, MeterLab model ION 450 (Radiometer-Analytical, Australia).

2.4. Statistical analyses

To evaluate the significance of the change occurs in DOC characteristics due to ultrasound treatments, analysis of variance (one-way ANOVA) was carried out for the measured characteristics at $P < 0.05$ using SPSS 19 statistics software. Only when there is an overall significant change observed in the measured characteristic, least Significant Difference (LSD) Post Hoc test was performed to compare the differences in water characteristics for continuous and pulsed treatments.

3. Results and discussions

3.1. Overall effect of ultrasound treatments

Table 2 presents the overall effect of ultrasound treatments on the measured characteristics of the treated water. The values in Table 2 represent the mean of characteristics of triplicate treatments normalized by their counterparts of the untreated water. The significance level applied in this study was 0.05, so the normalized change of a characteristic with a P-value of less 0.05 is considered significant otherwise the change is insignificant. Applying this criteria, one can clearly see that ultrasound treatments had insignificant effect on normalized $SUVA_{254}$ and $SUVA_{280}$, whereas the other characteristics were significantly altered by ultrasound treatments. The slight increment in $SUVA_{254}$ and $SUVA_{280}$ is in agreement with the results reported by Naddeo, Belgiorno [21]. Such agreement is attributed to the structure resembling between the carbon source of Logan water (i.e. terrestrial) and that used in [21] (i.e. Aldrich humic acid) as both known to be highly aromatic [22]. The slight increments in $SUVA_{254}$ and $SUVA_{280}$ can be explained in two possible scenarios; sonication extraction of humic acids from suspended soil particles [23] or alteration of UV absorbing moieties under the effect of ultrasound [21]. The presence of high TSS level in Logan water (44 ppm) as compared to the usual TSS levels in natural waters (i.e. 10–20 ppm) [24] supports the second scenario. If the increase in SUVA at 254 and 280 nm is not accompanied by increase in DOC, then the second scenario becomes valid only if the extracted DOC from suspended solids is of aromatic nature and the destructed DOC by ultrasound is of aliphatic nature and the destruction rate is higher than the extraction rate. In this case, the DOC concentration decreases while SUVA at 254 and 280 nm increases as the UV absorbing fraction of DOC (i.e. aromatic) increases and the non-absorbing DOC fraction (i.e. aliphatic [25]) decreases. Since the changes in $SUVA_{254}$ and $SUVA_{280}$ were found to be statistically insignificant, so it will not be discussed further in this study and the attention will rather be focused on the significantly changed characteristics.

Table 2
Analysis of variance (ANOVA) and descriptive statistics for overall effect of ultrasound treatments

Normalized characteristics	Mean	SD	P-value
DOC	0.953	0.0245	0.000
$SUVA_{254}$	1.113	0.0167	0.140
$SUVA_{280}$	1.107	0.0222	0.137
A_{250}/A_{365}	1.110	0.0757	0.037
A_{254}/A_{204}	1.125	0.0259	0.010
A_{254}/A_{436}	0.873	0.1180	0.009
COD_{Mn}	1.024	0.0240	0.033
Conductivity	1.043	0.0143	0.030
Alkalinity	0.888	0.0661	0.019
pH	0.890	0.0183	0.030

3.2. Comparison between ultrasound treatments

The significance of the difference between treatments effects on water characteristics was evaluated applying LSD post-hoc analysis at significance level of 0.05 as shown in Table 3. The mean and standard deviation values in Table 3 were calculated from averaging the normalized change of the treated water characteristics for three replicates of each treatment. The percentage variations in the normalized change of characteristics achieved with pulsed treatments with respect to the continuous treatment are also presented in Table 3 to highlight difference between the effect of pulsed and continuous treatment on the quality of the treated water.

It can be seen from Table 3 that the effect of pulsed treatment with R ratio of 1 on the treated water characteristics was not significantly different from that of continuous ultrasound except for A_{250}/A_{365} and conductivity. This could be due to the long quiescent period of $R = 1$ (0.5 s) treatment as compared to other treatments. For instance, Orzechowska and Poziomek [26] found that continuous ultrasound caused significantly higher increment in conductivity of different solutions as compared to pulsed ultrasound with 60% duration (i.e. 0.6:0.4 s, $R = 3/2$). However, increasing the pulse duration to 80% in [26] resulted in a similar effect on conductivity as that of the continuous treatment and this is in agreement with the observations of this study.

The effect of pulsed treatment of R ratio of 3 on water characteristics was also not significantly different from that of continuous treatment for most of the characteristics except for DOC, A_{250}/A_{365} and $A_{254}/Color_{436}$. This indicates that shortening the quiescent period of pulsed ultrasound with having a

Table 3
Descriptive statistics and LSD post-hoc comparison between ultrasound treatments

Treatment levels	*R* = 1			*R* = 2			*R* = 3			Continuous	
Normalized characteristics	Mean	SD	(%) variation~	Mean	SD	(%) variation~	Mean	SD	(%) variation~	Mean	SD
DOC	0.978[a]	0.0053	0.7	0.923[b]	0.0017	4.9	0.938[c]	0.0035	3.4	0.971[a]	0.0035
A_{250}/A_{365}	1.040[a]	0.0297	14.5	1.100[a]	0.0287	9.6	1.084[a]	0.0316	10.9	1.217[b]	0.0555
A_{254}/A_{204}	1.136[a]	0.0183	1.4	1.089[b]	0.0006	5.5	1.124[a]	0.0011	2.4	1.152[ac]	0.0039
A_{254}/A_{436}	0.934[a]	0.0437	8.0	0.784[b]	0.0411	22.8	0.757[b]	0.0411	25.4	1.015[a]	0.0389
COD_{Mn}	1.010[ac]	0.0006	3.1	0.998[c]	0.0043	4.2	1.047[b]	0.0027	0.5	1.042[ab]	0.0229
Conductivity	1.022[a]	0.0047	3.0	1.052[b]	0.0047	0.2	1.044[b]	0.0117	0.9	1.054[b]	0.0023
Alkalinity	0.949[a]	0.0466	2.4	0.796[b]	0.0094	14.1	0.882[a]	0.0287	4.9	0.927[a]	0.0078
pH	0.913[a]	0.0008	1.8	0.871[b]	0.0047	2.9	0.879[bc]	0.0155	2.0	0.897[ac]	0.0062

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

~ Variation in the normalized values of the pulsed treatments with respects to continuous treatment.

relatively high pulse period brings the effect of the pulsed treatment closer to that of continuous treatment.

The effect of pulsed treatment of *R* ratio of 2 on most of the treated water characteristics was significantly different than those of the other treatments. This highlights that this treatment falls in the pulsed cavitation peak range for the applied power level in this study. The pulse cavitation peak is described to be the pulsed cavitation conditions during which the maximum cavitation activity is generated [27]. To achieve pulsed cavitation peak conditions, the suitable pulse and quiescent periods need to be applied otherwise pulsed ultrasound would result in similar or less effects than the continuous ultrasound. The corresponding pulse and quiescent periods for pulsed cavitation peak is normally identified through experimental work as demonstrated in [19,27].

The higher effect of pulsed cavitation peak conditions as compared to other treatment conditions is believed to be due to the clarification effect of pulsed ultrasound (i.e. reduction of shielding effects). During the quiescent period of pulsed ultrasound, the density of bubbles in the irradiating liquid decreases and this reduces the coalescence between bubbles leading the formation of bubbles with spherical shape [27]. These bubbles would then act as source for the transient cavitational bubbles in the subsequent pulse. The collapse of spherical bubbles generates physical and chemical effects with higher energy than that of deformed bubbles. There are other mechanisms that can explain the superiority of pulsed ultrasound effects as compared to continuous ultrasound such as time availability for species diffusion into collapsing bubbles during the quiescent period, effect of residual pressure on driving cavitation activities during the quiescent period and spatial enlargement of the active zone [19].

3.3. Ultrasonic effect on DOC physio-chemical properties

3.3.1. DOC

The average normalized DOC of Logan water treated with different ultrasound treatments is shown in Fig. 2. It

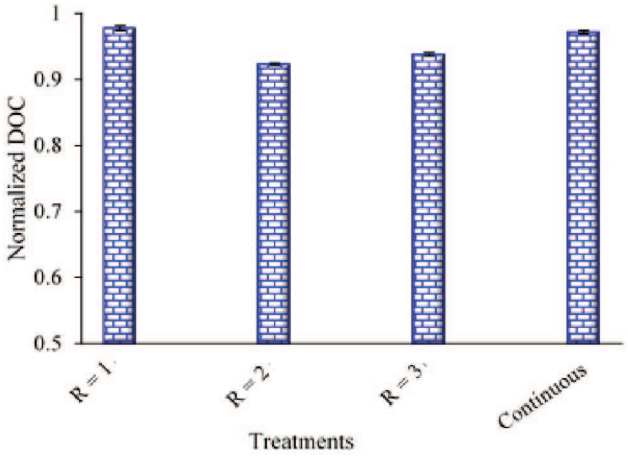

Fig. 2. Normalized DOC of ultrasound treatments, initial DOC = 8.57 mg/L.

can be seen from Fig. 2 that DOC removal of the applied ultrasound treatments was in the order of $R = 2 > R = 3 >$ continuous $> R = 1$. DOC removal levels obtained in this study were consistent with the ones reported in previous studies. For instance, Stepniak, Kepa [28] reported a DOC removal of <10% in natural water treated with continuous ultrasound. Two of the pulsed treatments had a better DOC removal than continuous treatment, while the other pulsed treatment had lower DOC removal. Such variation in pulsed ultrasound performance is likely to be due to the selection of pulse settings as explained in earlier sections.

Ultrasound destructs/alters DOC through chemical and mechanical effects. The prominent chemical effect of ultrasound is the cleavage of aromatic rings under the effect of oxidative radicals [29]. The mechanical effects of ultrasound represented by powerful shear forces produced from cavitation and streaming effects [30]. The shear degradation is focused in the regions with high agitation. Such regions form in the adjacent area of bubbles where

oscillation and collapse cause energetic turbulences and shock waves. Decreasing DOC concentration should alleviate common treatment problems such as organic and biological fouling [7,31] and DBPs formation (e.g. THMs) [32].

3.3.2. COD_{Mn}

Fig. 3 illustrates the change in COD_{Mn} of Logan water with various ultrasound treatments. Fig. 3 presents an interesting trend as COD_{Mn} of the treated water increased with most of ultrasound treatments except for the treatment with *R* ratio of 2 where there was a slight decrease in COD_{Mn}. The overall trend indicates that ultrasound treatment generally increases the oxidant demand for the treated water. Potassium permanganate reacts preferentially with DOC of aromatic structure [33] and this is consistent with the results presented in Table 2 (increase in SUVA at 254 and 280 nm). There is a limited number of studies that investigated the effect of ultrasound on COD of water. The results of previous studies were inconsistent. For instance, Naffrechoux, Chanoux [12] obtained a 50% reduction in COD of water samples treated with a combination of ultrasound and UV radiation, whereas another study observed COD increment with ultrasound [34]. The limited number of studies and their inconsistent observations makes it hard to establish links between our results and what has been reported. Hence, based on the obtained COD and other characteristics results one can conclude that for water with similar properties to those of Logan water, ultrasound increases COD and the slight decrease in COD_{Mn} with ultrasound treatment of $R = 2$ can only be regarded as an outlier.

The alteration of Logan water COD_{Mn} under the effect of ultrasound treatments can give an indication to the tendency of contaminants towards the involvement in oxidation reactions. El-Shafy and Grünwald [35] reported that there is a weak correlation between the formation of THMs and COD_{Mn} of the water ($R^2 = 0.587$). This means that the alteration of COD_{Mn} after sonication treatments might not cause any change in the tendency of the treated water to form DBPs.

3.3.3. Alkalinity

The alteration of Logan water alkalinity under the effect of ultrasound treatments is presented in Fig. 4. The alkalinity of Logan water decreased after the exposure to ultrasound treatments. It can be seen from Fig. 4 that pulsed ultrasound of $R = 2$ resulted in the highest reduction of alkalinity ~ 20% followed by the treatment of *R* ratio of 3, continuous and *R* ratio of 1 at approximate reduction percentages of 12%, 7% and 5%, respectively. Alkalinity reduction of treated water is attributed to the reaction of bicarbonates with the hydroxyl radicals produced from collapsing bubbles as illustrated in Eq. (2) [36]. It should be noted that although hydroxide ions (alkalinity boosting species) are produced from the proposed reaction pathway for hydroxyl radicals and bicarbonates, the chemically active environment surrounding the ions can drive them to undergo further reactions to produce more reactive species [Eq. (3)] [37].

$$HCO_3^- + HO^\cdot \rightarrow HCO_3^\cdot + OH^- \quad (2)$$

$$OH^- + OH^- \rightarrow H_2O_2 + 2e^- \quad (3)$$

Alkalinity plays a crucial role in most of water treatment processes, however its effect is usually studied in conjunction with pH. Hence, the effect of ultrasound treatment on pH of the treated water was also measured and the results are presented in Fig. 4. The pH reduction trend is similar to that of alkalinity. However, the reduction of pH was more pronounced than the reduction of alkalinity for all treatments except for $R = 2$.

Alkalinity consumes hydrogen ions in water affecting the pH and redox reactions. The surface charge of contaminants in water is affected by the pH. If the pH of a solution exceeds the isoelectric point (IES) of existing contaminants, the charge of these contaminants becomes negative, and if it drops below IES, the charge of contaminants turns positive [7]. The pH level can also influence the solubility of metals and organic matter in water.

Ultrasound reduction of Logan water pH could positively affect its coagulability as it brings the pH level closer to the optimum level for DOC removal (6.5–5.5

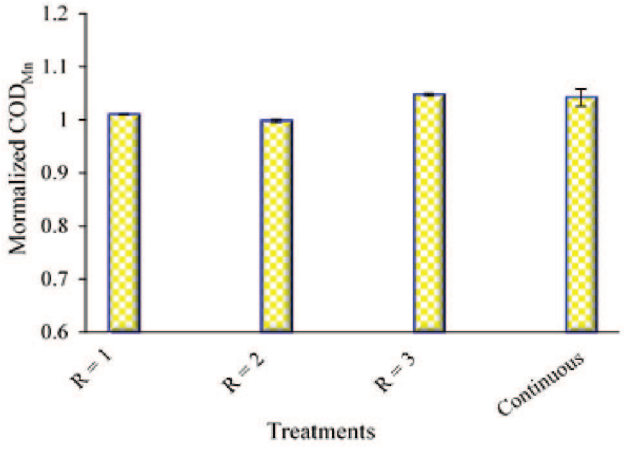

Fig. 3. Normalized permanganate index of ultrasound treatments, initial COD_{Mn} = 1.17 (mg O_2/mg DOC).

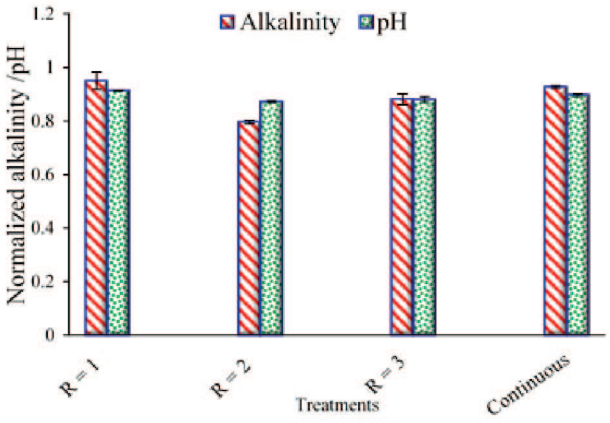

Fig. 4. Normalized alkalinity and pH of ultrasound treatments, initial alkalinity and pH are 3 meq/L and 9.1, respectively.

[38]) with zero addition of chemicals. Also, reducing water alkalinity due to ultrasound treatment can be useful particularly for water with high alkalinity. In this case, the addition of coagulant would be sufficient to bring the pH to the optimum level for DOC removal without adding pH reducing agents. The reduction of pH and alkalinity of treated water could also affect the filtration process owing to the dependence of filtration on surface charge of contaminants [7]. Decreasing the alkalinity may help in alleviating inorganic fouling in filtration [8]. Alkalinity was found to have a direct correlation with the formation of Haloacetonitriles and dichloroacetic and trichloroacetic acids [39], hence reducing it could potentially reduce the risk of DBPs formation in the treated water.

3.3.4. Conductivity

The normalized conductivity of the treated Logan water with different ultrasound treatments is shown in Fig. 5. Generally, the conductivity of Logan water increased after ultrasound treatment. The increment of water conductivity upon ultrasound treatment can be attributed to the gaseous reactions occur in the thermolytic centre of transient bubbles producing acid in the adjacent areas to the collapsing bubbles [8]. The observed conductivity increase with ultrasound treatments is consistent with the results reported by Naddeo, Belgiorno [21] who found that the conductivity of humic acid solution increased after ultrasound treatment. The variation in conductivity of the treated water with pulsed and continuous ultrasound treatments was found be insignificant except for *R* ratio of 1 treatment as compared to other treatments (Section 3.2).

Conductivity plays a crucial role in contaminants response to treatment processes. For instance, the adherence of contaminants to filtration media or metal complexes (coagulants) is affected by the electrical double layer interaction [40]. Increasing the conductivity of Logan water indicates either an increase in the concentration of charged contaminants or an increase in their charge density. In either way, the thickness of the electrical double layer decreases and the affinity between contaminants and filters or coagulants complexes increases [40]. Based on the conductivity results presented here, ultrasound treatment can promote the coagulability of Logan water, but at the same time may increase fouling potential of filtration media. Effect of conductivity on DBPs formation is complex as such characteristic cannot only affect electrochemical interactions between disinfectants and DOC, but also affects dissociation and recombination reactions of disinfectants [41].

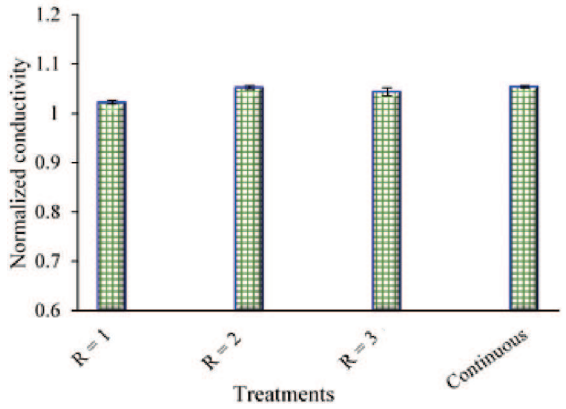

Fig. 5. Normalized conductivity of ultrasound treatments, initial conductivity = 0.3 mS/cm.

3.4. Ultrasonic effect on spectroscopic properties

The impact of ultrasound treatments on UV ratios of Logan water is presented in Fig. 6. It can be noticed from this figure that ultrasound treatments increased the proportion of small sized molecules to large sized molecules, and these results are in agreement with previous studies that were conducted on synthetic organic solutions and wastewater samples [42]. It is also clear that the continuous treatment has higher effect on DOC molecular size compared to pulsed treatments. Among pulse treatments, the treatment with *R* ratio of 3 resulted in the highest A_{250}/A_{365} increment. The large increment of A_{250}/A_{365} in continuous treatment as opposed to pulsed treatments suggests that molecular size degradation under the effect of ultrasound depends on the mechanical effects more than chemical effects. This statement is supported by the findings of Henglein and Gutierrez [43], as the latter reported that the size destruction of polymers was favoured at bubbles coalesce conditions which occur mostly in continuous operation. The unremitting agitation in the continuous treatment could also play a role in the observed A_{250}/A_{365} results, as such agitation produces high level of shear stresses capable of breaking down molecules into smaller sized ones.

Fig. 6 also shows that ultrasound treatments increased the ratio A_{254}/A_{204} of Logan water. Increasing A_{254}/A_{204} reflects an increase in the bulk aromaticity of the treated water and this is consistent with the results presented in Table 2. The increase of aromatic compounds with oxygen containing functional groups is believed to be mainly due to the alteration in DOC structure caused by ultrasound treatment as explained in Section 3.1. Fig. 6 reveals that pulsed ultrasound treatment of *R* = 3 had the least effect on

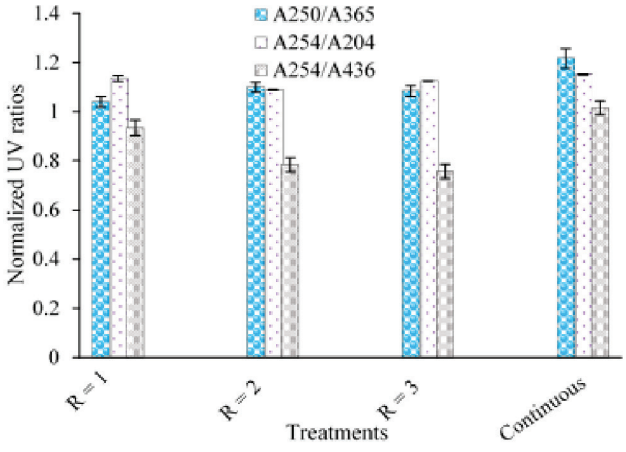

Fig. 6. Normalized UV ratios of ultrasound treatments, initial A_{250}/A_{365}, A_{254}/A_{204} and A_{254}/A_{436} are 5.36, 0.33 and 17.90, respectively.

A_{254}/A_{204}, and continuous treatment had the highest effect, while the other two treatments had effects fall in between these two ranges.

Interestingly, continuous ultrasound treatment increased A_{254}/A_{436}, while pulsed ultrasound treatments decreased this ratio as shown in Fig. 6. This trend suggests that pulsed ultrasound was more effective in removing UV absorbing portion of DOC than colour forming moieties of DOC. This could be ascribed to the nature of DOC moieties, as moieties that absorb UV light are likely to be of a hydrophobic nature, while the colour forming moieties are mostly of autochthonous origin that possesses a hydrophilic nature [44]. In general, ultrasound favourably destructs DOC of hydrophobic nature, however this destruction can be more pronounced with pulsed treatments as opposed to continuous treatment due to the time given to these compounds to diffuse into the collapsing bubbles or their vicinity in pulsed treatments. The change in A_{254}/A_{436} with ultrasound treatments can be explained as ultrasound oxidation altered the structure of treated DOC in a way that changes its tendency to absorb UV or form colour. For instance, the oxidation of phenol that shows UV absorbance in the range 210–285 nm [45] leads to the production of colour forming compounds [46]. The results presented in Fig. 6 suggest that continuous ultrasound is more active in driving similar alteration in such DOC compounds.

The size spectrum of DOC has an important effect on its removal via common treatment processes. Some studies showed that the larger the size of DOC molecules, the higher the removal of DOC can be achieved with coagulation process [47]. Although that ultrasound treatment of Logan water decreased the size of DOC molecules, the number of the broken molecules increased which would increase the chance of these molecules collision with coagulants and ultimately increases their removal [48]. The abundance of oxygen containing functional groups in DOC promotes adsorption and complexation reactions [49]. This implies that the increase of A_{254}/A_{204} after sonication can potentially increase the amenability of DOC towards coagulation. The preferential removal of colour forming moieties with continuous ultrasound or UV absorbing moieties in pulsed ultrasound would not affect the performance of any of the treatment processes as both portions can form organic fouling and THMs [50,51]. However, knowing the portion of coloured DOC might help in choosing the right coagulant, as coloured DOC is more effectively scavenged by polymer based than metallic salt coagulants [52].

4. Energy and cost analysis

This study showed that the operation mode of ultrasound can play a significant role in DOC removal and structural alteration. This observation is important from environmental point of view, however from water treatment industry perspective, the DOC change needs to be gauged against its energy and cost requirements. Hence, the energy and cost required for the obtained levels of DOC removal were calculated applying Eqs. (4) and (5). It should be noted that the price for one kWh was based on the price range of electricity in Queensland, Australia [53]. Table 4 shows the calculated energy and cost requirements for the applied ultrasonic treatments. It can be seen from this table that pulsed ultrasound treatments with *R* ratio of 2 and 3 required less cost as opposed to continuous treatment for removing 1 mg of DOC from surface water. The cost required for removing 1 mg of DOC using pulsed ultrasound treatment with *R* ratio of 1 was the highest among all treatments. This is expected as the previous sections showed that the performance of pulsed treatment of $R = 1$ was the poorest in comparison to other treatments. The results presented in Table 4 highlight the potential of pulsed mode to significantly reduce the operational cost of ultrasound treatment for DOC removal.

$$E = \frac{P_U \times t}{DOC_i - DOC_T} \tag{4}$$

$$C = \frac{\text{Cost of } 1 kWh}{(DOC_i - DOC_T)/kWh} \tag{5}$$

where *E* is ultrasonic operational energy required for 1 mg DOC removal (kJ/mg DOC removed), *t* is the effective treatment time (s), *DOC* with subscripts *i* and *T* is the amount of dissolved organic carbon before and after the treatment in (mg), respectively and *C* is the operational cost of the treatment for 1 mg DOC removal ($/mg DOC removed).

5. Conclusions

The effect of pulsed and continuous ultrasound treatments on concentration and structure of natural DOC originated mainly from terrestrial sources was investigated in this study. All the changes occurred in water properties were statistically significant except for SUVA at 254 and 280 nm. On average, ultrasound treatments decreased DOC, alkalinity, pH and A_{254}/A_{436} by 4.7%, 11.2%, 11% and 12.7%, respectively and increased SUVA at 254 and 280 nm, A_{250}/A_{365}, A_{254}/A_{204}, COD_{Mn} and conductivity by 11.3%, 10.7%, 11%, 12.5%, 2.4%, and 4.3% respectively. Pulsed treatments of *R* ratios of 3 and 1 were statistically similar to continuous treatment in their effects on treated water properties. Pulsed treatment of *R* ratio of 2 was significantly different than other ultrasound treatments in terms of its effect on DOC concentration and properties. The maximum DOC and alkalinity removal and pH drop of 7.7%, 20.4% and 12.9% was achieved with ultrasound treatment of $R = 2$. In comparison, continuous ultrasound treatment resulted in the maximum increase in A_{250}/A_{365}, A_{254}/A_{204} and conductivity 21.7%, 15.2% and 5.4%, respectively. The change in A_{254}/A_{436} and COD_{Mn} varied with treatments.

Table 4
Energy and cost figures for operating ultrasound treatments

Treatments	Ultrasonic energy (kJ/mg DOC removed)	Treatment cost ($/mg DOC removed)
Continuous	1176.73	0.085
$R = 1$	1551.15	0.112
$R = 2$	443.18	0.032
$R = 3$	550.40	0.040

The alteration of Logan water properties due to ultrasound treatments indicates that the treatment improves the coagulability of the water through reducing DOC concentration and alkalinity and increasing conductivity and aromatic compounds with oxygen containing functional groups. However, some of these changes such as increment of conductivity and aromaticity might increase the potential of fouling and DBPs formation of the water. Applying pulsed mode reduced the energy requirement for DOC removal with ultrasound.

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