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Tracking ultrasonically structural changes of natural aquatic organic carbon: Chemical fractionation and spectroscopic approaches

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HIGHLIGHTS

- Natural surface water samples were treated with pulsed and continuous ultrasound.
- DOC structural alteration was monitored using chemical fractionation and UV–vis.
- Hydrophobic DOC decreased while hydrophilic DOC somewhat increased.
- Pulsed ultrasound degraded aromatic humic-like DOC.
- Most of UV–vis indices showed strong correlations with DOC fractions.

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ABSTRACT

In this study, the structural alteration to DOC for a range of ultrasound treatments was investigated with chemical fractionation and UV–vis spectroscopic measurement. Ultrasound treatments were applied in continuous and pulsed modes at power levels of 48 and 84 W for effective treatment times of 5 and 15 min. Overall results show that the ultrasound treatments tended to degrade the hydrophobic aromatic fraction, while increasing the hydrophilic fraction to a lesser extent. The highest recorded reduction of hydrophobic DOC (17.8%) was achieved with pulse treatment of 84 W for15 min, while the highest increase in the hydrophilic DOC (10.5%) was obtained with continuous treatment at 84 W and 5 min. The optimal ultrasound treatment conditions were found to be pulse mode at high power and short treatment time, causing a minimal increase in the hydrophilic fraction of 1.3% with moderate removal of the hydrophobic fraction of 15.52%. The same treatment conditions, with longer treatment time, resulted in the highest removal of $SUVA_{254}$ and $SUVA_{280}$ of 17.09% and 16.93, respectively. These results indicate the potential for ultrasound treatments in DOC structural alteration.

The hydrophobic fraction showed strong and significant correlations with UV absorbance at 254 and 280 nm. A_{254}/A_{204} also exhibited strong and significant correlations with the hydrophobic/hydrophilic ratio. The other UV ratios (A_{250}/A_{365} (E_2/E_3) and A_{254}/A_{436}) had weak and insignificant correlations with the hydrophobic/hydrophilic ratio. This confirms the applicability of UV indices as a suitable surrogate method for estimating the hydrophobic/hydrophilic structure.

1. Introduction

The presence of DOC in surface water resources is a major concern for the drinking water production industry due to its involvement in many technical, aesthetic and health related problems (Xing et al., 2012). DOC can adsorb onto the filtration media causing one of the major fouling problems known as organic fouling (Al-Juboori and Yusaf, 2012a). It can also block the pores of the adsorption media that are designed to remove specific synthetic pollutants (Xing et al., 2012). DOC has the capability to bind to heavy metals and micro-pollutants forming complexes that are difficult to be remove by standard water treatment processes (Kim

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et al., 2015). If DOC is not completely removed during the final stages of water treatment, it can also promote the formation of biofouling in the distribution systems (Soh et al., 2008). In addition, the occurrence of DOC in water can cause odour colour and taste issues (Audenaert et al., 2015). The most concerning issue from a community health perspective is the reaction of DOC with disinfectants to produce hazardous disinfection by-products (DBPs) (Zhang et al., 2005; Richardson et al., 2007; Richardson and Postigo, 2012; Pan and Zhang, 2013; Al-Juboori et al., 2015b). The extent of detrimental effects on drinking water quality by DOC in water treatment systems is largely dependent on the concentration and nature of DOC present.

A fair proportion of DOC can be conventionally removed from surface water by applying a standard coagulation/flocculation process followed by filtration (typically multi-media gravity filtration). However, downstream problems (e.g. DBPs) are still common with these conventional methods of DOC removal (Lavonen, 2015). To solve this problem chemical oxidation prior to coagulation has been proposed, however, the pre-oxidation process was found to have some drawbacks such as formation of DBPs and mass transfer limitations (Chemat et al., 2001). Hence, chemical-free techniques for removing DOC such as ultrasound are being investigated. Zero chemical DOC degradation is not the only positive trait of ultrasound technology, it also has the advantage of simple installation/retrofitting and ease of maintenance (Patist and Bates, 2008). To date, the work on this technology for DOC removal from natural surface water tends to focus on DOC removal levels with little published on DOC structural changes due to ultrasound treatment. In addition, while operating ultrasound in pulsed mode has been shown to be more energy efficient than continuous ultrasound for removing water contaminants (Al-Juboori et al., 2015a, 2015c, 2016). The effect of pulsed ultrasound on the structure of natural DOC has yet to be examined. Hence, this work is devoted to investigating and comparing the effects of ultrasound in pulsed and continuous modes on the DOC structure prevalent in natural surface water samples.

An in-depth understanding of the transformation of DOC structure caused by a particular treatment technique is critical for the design of an efficient treatment scheme. The change of DOC structure induced by ultrasound treatments was analysed by applying rapid chemical fractionation and UV–vis spectroscopic measurements. The rapid chemical fractionation technique, introduced by Chow et al. (2004) was based on full fractionation processes proposed by Croue et al. (1993) and Bolto et al. (1999). In this fractionation procedure, the DOC is divided into four fractions: very hydrophobic acids (VHA) which adsorbs to DAX-8 resin at pH 2, slightly hydrophobic acids (SHA) which adsorbs to XAD-4 resin at pH 2, hydrophilic charged (CHA) which adsorbs to IRA-958 resin at pH 8 and hydrophilic neutral (NEU) that does not adsorbe to any of the aforementioned resins. This fractionation process serves as a valuable tool for studying the response of different DOC fractions in different treatment processes (Chow et al., 2004; Liu et al., 2008). In addition to looking at the change in DOC polarity through chemical fractionation, the change in DOC chemical structure such as alteration of aromatic contents or molecular weight was inspected using a range of UV–vis indices. Absorbance at 254 and 280 nm was applied for evaluating the change in humic-like aromatic DOC. UV absorbance at 254 nm is used to study the electronic structure of DOC as it specifically detects the conjugated structure of DOC which is prevalent in humic DOC (Silverstein, 1974). The electron delocalization in the pi orbital of the conjugated structure of some of the aromatic compounds such as phenolic arenes, benzoic acids and polycyclic aromatic hydrocarbons falls within the UV absorbance range of 270–280 nm (Uyguner and Bekbolet, 2005a), therefore absorbance at 280 nm is used as a measure for DOC bulk aromaticity. Absorbance ratios of 254/204 and 250/365 (E_2/E_3) nm were utilized to determine the respective changes in aromatic DOC with oxygen containing functional groups and DOC molecular weight, while 254/436 nm was used to measure the ratio of UV absorbing to colour forming DOC (Al-Juboori et al., 2015b). The correlation between the applied UV–vis indices and chemical fractions was also investigated to explore the possibility of using UV–vis indices for detecting change in DOC polarity.

2. Materials and methods

2.1. Water sample

Natural water samples were collected from Narda lagoon located in Southeast Queensland, Australia. The samples were collected during July–September 2014 using 5 L pre-cleaned plastic containers. Prior to the application of ultrasound, the samples were screened through a 0.5 mm sieve to simulate standard water treatment practices (Food Safety and Regulatory Activities Victorian, 2009; Van Nieuwenhuijzen and Van der Graaf, 2011). The DOC concentration and chemical fractionations of Narda water along with other characteristics are presented in Table 1.

2.2. Sonication treatments

The description of the system used for performing ultrasonic treatments is provided in our previous work (Al-Juboori et al., 2015a). Briefly, the system consists of a digital Branson sonifier model 450 operating at 20 kHz with rated electrical power of 400 W (Branson, USA). Ultrasonic energy was delivered sample through a titanium horn (⌀ = 19 mm) into a 500 mL Pyrex beaker filled with the screened water sample. The temperature of water samples was maintained at approximately 20 °C using a cooling bath with dimensions of 335 × 275 × 140 mm (l × w × h) and centrifugal submersible pump. The temperature was monitored using a calibrated digital thermometer (Hanna instruments, Australia).

The operating parameters for the experimental work were selected depending on both the economic viability of the treatment and our prior knowledge of the effective ranges (Phull et al., 1997; Al-Juboori et al., 2015c, 2015d). The water samples were treated with two ultrasonic modes i.e. continuous mode and pulsed mode. Two pulse settings were tested; *On*:*Off* ratio (*R*) of 0.1:0.6 s and 0.2:0.1 s. Only the results of the first pulse setting will be presented in this work, while the latter results will be used for validation of the statistical analysis. The effects of continuous and pulsed treatments of $R = 0.1{:}0.6$ s on DOC fractions and spectroscopic properties were used to construct a statistical model for predicting the change in DOC structure and properties under different experimental factors. The validity of the model was confirmed by testing the predicted changes of DOC structure and spectroscopic properties for pulsed treatment of $R = 0.2{:}0.1$ s against the experimental data with the same treatment conditions.

Two levels of ultrasonic calorimetric power and treatment time of 48 and 84 W, and 5 and 15 min (based on effective continuous operation), were applied. The details of calorimetric power measurements are detailed in our previous work (Al-Juboori et al., 2015d). It is important to note here that the applied power levels of 48 and 84 W correspond to power intensities and densities of 16.93 and 29.63 W/cm^2 and 96 and 168 W/L, respectively. The treatment time of pulsed treatments was determined based on the applied *R* ratios and the corresponding treatment time for the continuous treatments (referred to as effective treatment time) as follows (Gutierrez and Henglein, 1990):