Behaviour of natural organic mater during ultrasonic irradiation

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Abstract

Ultrasonic irradiation has been one of the advanced oxidation methods for natural organic matter (NOM) removal. Its application simplicity and no production of toxic by-products make the system attractive. It has been shown that high power ultrasound produces strong cavitation in aqueous solution causing shock wave and reactive free radicals by the violent collapse of the cavitation bubble. These effects should contribute to the physical disruption and inactivation of microbial structures as well as to the decomposition of toxic chemicals in the water. The objective of this research was to investigate the effectiveness of low frequency – high power sonication for NOM removal (measured by both means of UV_{254} absorbance and TOC) as well as controlling DBPs formation by varying irradiation time, light intensity, NOM concentration. Temperature, pH, conductivity, redox potential, and turbidity were monitored to evaluate the experimental study. The results indicate a strong capacity of sonication for NOM removal. The preliminary experiments showed that NOM removal is influenced by the intensity and time of sonication. Ultrasound, applied under such conditions, may be a realistic possibility for large-scale treatment; however, further studies should be performed to evaluate its effectiveness on different water sources.

Keywords: Natural organic matter (NOM); Humic acids; Ultrasound; TOC removal

1. Introduction

Natural organic matter (NOM) is used to describe the complex mixture of organic material, such as humic acids, hydrophilic acids, proteins, lipids, amino acids and hydrocarbons, present in all drinking water sources. The characterisation and removal of these dissolved organics are major issues faced by the water industry as they act as precursors for the formation of disinfection by-products (DBPs).

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Currently, the most used oxidants/disinfectants in drinking water treatment are free chlorine (chlorine gas and hypochlorites), chlorine dioxide and ozone. But these chemicals react with substances naturally occurring in drinking water resulting in formation of compounds harmful for human health. The reaction between free residual chlorine and NOM result in potential carcinogens compounds called trihalomethanes (THMs) [1–3].

Hence the control of NOM has been widely studied for the protection of public health.

The organic carbon content in water is used as a surrogate parameter to represent the NOM concentration. Additionally, UV absorbance at 254 nm is measured as an alternative surrogate to represent the concentration of NOM in water [6]. Recently, the specific UV absorption defined as UV_{254} per milligram of organic carbon ($SUVA_{254}$) has also been used as another surrogate of the DBP precursors. [8]

Thus, due to DBPs formation, alternative oxidation/disinfection processes are under investigation; among these ultrasound treatment was applied for both bacteria inactivation [6,7] and organic compound removal [9,10].

Ultrasonic irradiation is an attractive means to improve water quality because of the simplicity of the system and no production of toxic by-products, such as THMs, formed through chlorination. When US irradiation is applied in a liquid medium, extreme temperatures and pressures are generated as a result of acoustic cavitation. The result is solute thermolysis as well as the formation of hydroxyl radicals and hydrogen peroxide [17]. As a consequence of the cavitation phenomena, when a solid is present in an aqueous medium, the following phenomena can occur: (i) the analyte present in the solid may be partially or totally extracted into the liquid medium; and, (ii) the sample size of the particles is diminished if an US probe is used, increasing the total solid surface in contact with the liquid [17]. US irradiation may either destroy the organometallic species dissolved in water — so this may be used to distinguish between organic and inorganic species such as organic and inorganic mercury [9] — or leach organometallic compounds from solids [6].

These effects should contribute to the physical disruption of microbial structures and inactivation as well as decomposition of both organic and toxic compounds [4].

The overall objective of this research was to investigate the effectiveness of low frequency – high power sonication for NOM removal (measured by both means of UV254 absorbance and TOC) as well as controlling DBPs formation by varying irradiation time, light intensity, NOM concentration. Temperature, pH, conductivity, redox potential, and turbidity were monitored to evaluate the experimental study.

2. Materials and methods

Research analyses were conducted in the Environmental Engineering Laboratory of the University of Salerno, Fisciano (SA), Italy. An ultrasound device (Sonics & Materials VCX-750) equipped with a horn sonotrode (horn tip of 1.3 cm in diameter) was operated at 20 kHz (Fig. 1). Electrical power was applied in the range of 8–57 W. Calorimetric intensities ranged from 6.3 to 42.4 W/cm^2 while densities varied from 33 to 226 W/l, respectively. Ultrasound was transmitted into the 300 ml solutions containing of 5, 10, and 15 mg/l of humic acid (Aldrich) through the tip of the probe for 1, 2, 3, 5, 10, 15 and 20 min. 10 mg/L of nitrates were added at the same solution for another test series. The reactor was open to the atmosphere, and the probe was inserted into the centre of the reactor. To avoid any airborne contamination, the experiments were run inside of a waterproof sound abating enclosure. The samples were analyzed for temperature, NOM, ORP, turbidity, and conductivity. Absorption values of the samples were recorded at different wavelengths in the range of 220–620 nm on a Perkin Elmer spectrophotometer with 1.0 cm quartz cell. The
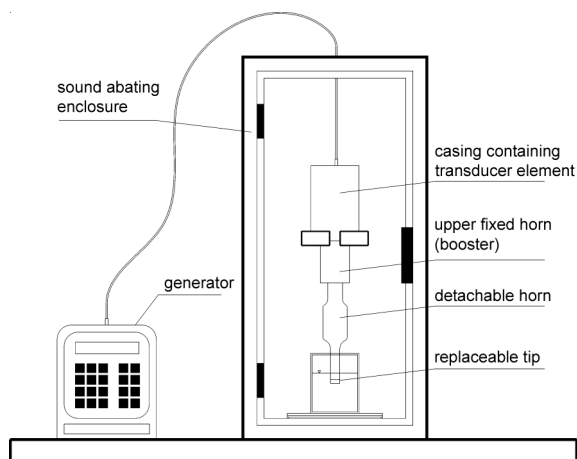
Fig. 1. Experimental set-up (Sonics & Materials VCX-750).

absorbance at 254 nm was expressed as UV254. TOC values of the samples were detected by SCHIMADZU 500 instrument. Source water parameters as pH, alkalinity, bromide and chloride were also measured according to the Standard Methods [1].

3. Results and discussion

3.1. Behaviour of water quality during ultrasonic irradiation

The influence of the intensity of sonication (7–42 W/cm^2), initial concentration of Humic Acid (5, 10, 15 mg/L), and the presence of nitrate (0–15 mg/L) on the main physical-chemical parameters are shown in Figs. 2, 3 and 4.

The changes in the pH and P.redox of the humic acids solution treated by ultrasonication are presented in Figs. 2 and 3. The results show that the pH of the solution decreased slightly at low intensity, the results are magnified in the presence of nitrate (Fig. 2b). Little change in the P.redox of the solution (on the average less than 10 mV) was observed as a result of ultra-sonication (Fig. 3a), but in the presence of nitrate the

variation increased strongly (average value 20 mV) (Fig. 3b).

The changes in the pH can possibly be attributed to the fact that, when the aqueous solution is irradiated by ultrasound, water vapour present in the ultrasound bubble is split to yield H• and OH• radicals. Humic acid molecules present in the vapour phase or in the surrounding liquid of the collapsing bubbles are subject to direct attack by OH• radicals, thus probably accelerating hydrolysis by several orders of magnitude in the presence of ultrasound. The acidic nature of humic acids is usually attributed to the ionization behaviour of –COOH and phenolic –OH groups [11].

The change in pH of the humic acid solution by ultrasonication implies that the ionization behaviour of the acidic functional groups of humic acids in an ultrasound field could be modified. Since, humic acids behave like weak-acid polyelectrolytes with a relatively high pH buffering capacity, changes in the pH of the humic acids would probably not be evident, even when the acidic functional groups of the humic acid molecules change. Oxidation, pyrolysis and/or the mechanical degradation of humic acid molecules could be expected in an ultrasonic field. Changes in the P.redox of the aqueous humic acid solution can mostly be attributed to electron transfer in the system, and therefore the negligible change in the P.redox of the humic acid solution suggests that no substantial electron transfer was stimulated between the radical species in the ultrasonic field and the reactive functional groups of the humic acids.

Obviously the initial values of temperature, conductivity and turbidity of the solution were increased by irradiation intensity, and at the same intensity energy these parameters were increased by acid (Figs. 4a, 4b, 4c). In the same conditions, solutions with nitrates amplify the growth of temperature, conductivity and turbidity, especially at the lower intensity (Figs. 4d, 4e, 4f). The main physical effect of powerful implosion of cavitation bubbles in the natural water is the fragmen-
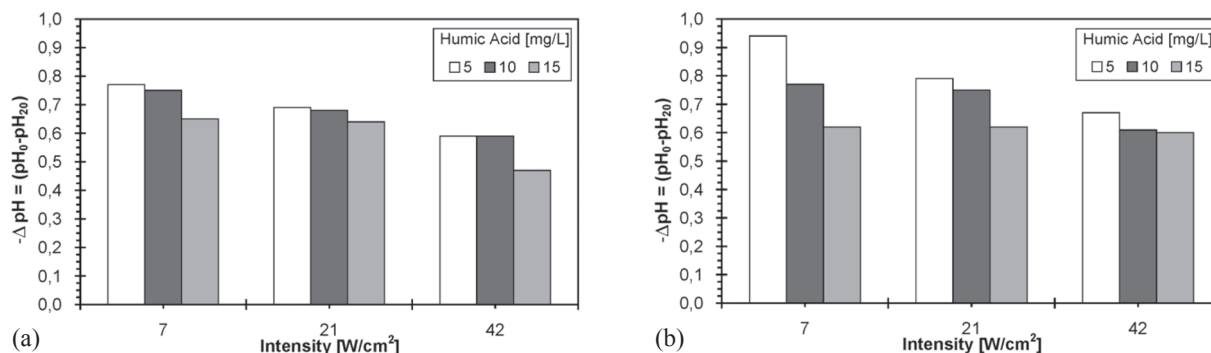
Fig. 2. pH behaviour in function of sonication intensity and humic acid concentration with (right side) or without (left side) 15 mg/L of nitrate.
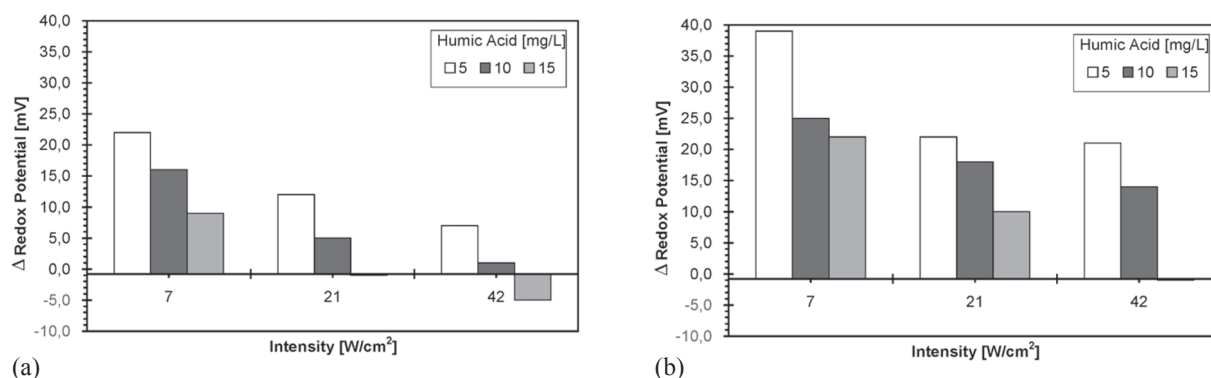

Fig. 3. P.redox behaviour in function of sonication intensity and humic acid concentration with (right side) or without (left side) 15 mg/L of nitrate.

tation of the suspended solids. This effect is easily measurable by turbidity growth.

3.2. The effect of sonication on the natural organic matter

The changes in the UV absorption levels are given in Fig. 5. The results show that the absorption of the humic acid solution first increased softly with ultrasonication at all tested wavelengths.

UV light absorption of humic acids appears to increase with an increase in: (a) the degree of condensation of the aromatic ring [12], (b) the total C content, (c) the molecular weight (MW), (d) the ratio of C in aromatic rings to C in aliphatic side chains [13], and (e) the pH of the solution [14]. The changes in UV absorption as a result of ultrasonication suggest that the structure and/or contents of chromophores, such as OH-, COOH-substituted benzene rings, the intramolecular electron donoracceptor complexes and complex unsaturated conjugated chromophores had changed in the ultrasound field. Comparing the changes in the UV_{254} absorption (Fig. 6) with the changes in the pH (Fig. 2), it is clear that ultrasonication could induce changes in disassociation or protonation of carboxyl and phenolic hydroxyl groups of the
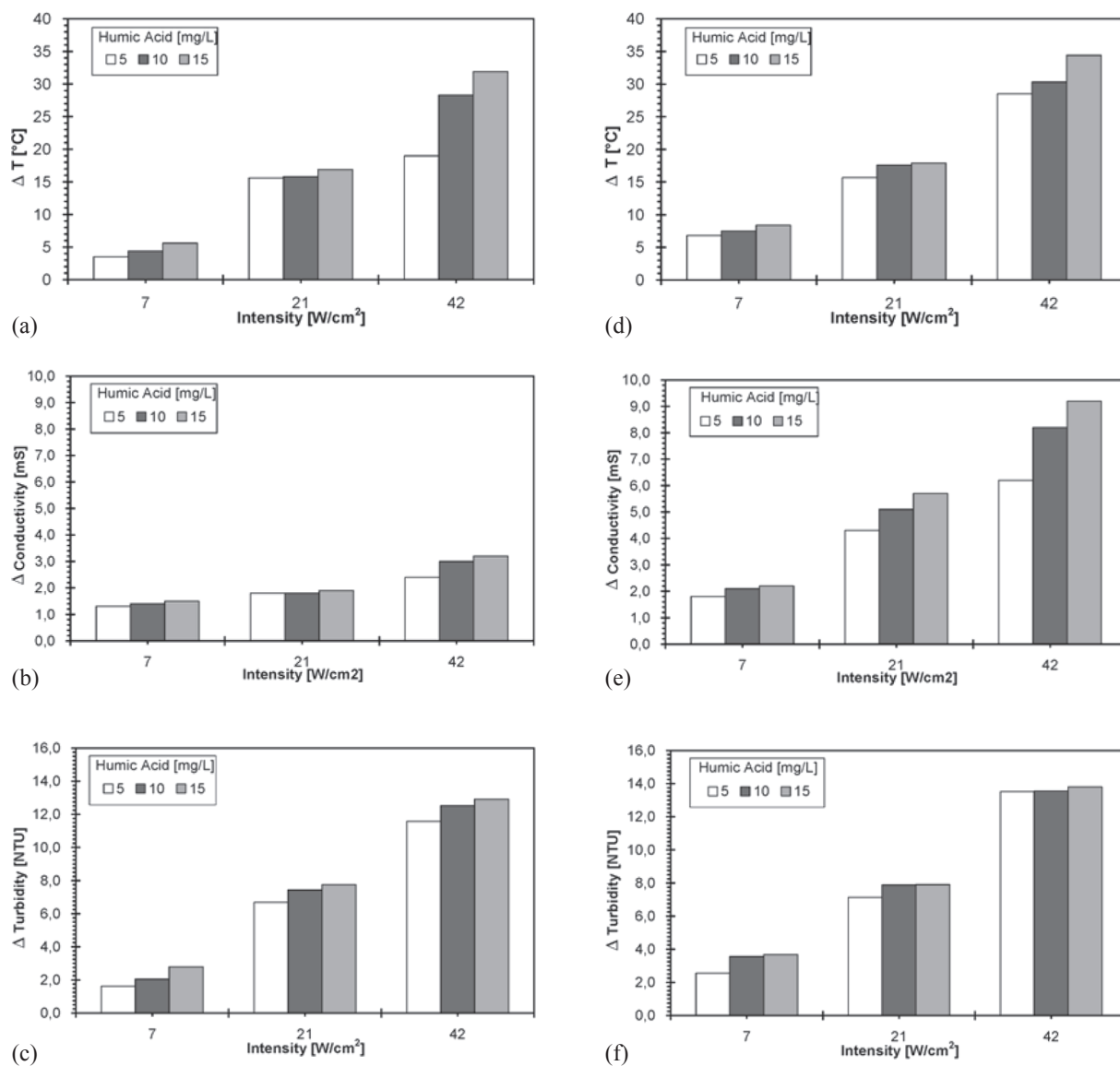
Fig. 4. Temperature, conductivity and turbidity behaviours in function of sonication intensity and humic acid concentration with (right side) or without (left side) 15 mg/L of nitrate.

humic acids. In addition, the macromolecular structure of the humic acids could have been altered, resulting in a greater or lesser exposure of chromophores to light, while auxochromes also could have been introduced into aromatic rings.

Measurements of TOC conducted during ul-

trasound treatment on synthetic water showed different behaviour in respect to absorbance measured at the same conditions.

In fact, after 20 min of sonication of humic acid solution, TOC concentration was reduced from 24.5 to 34.9%, and from 28.1 to 38.2% in
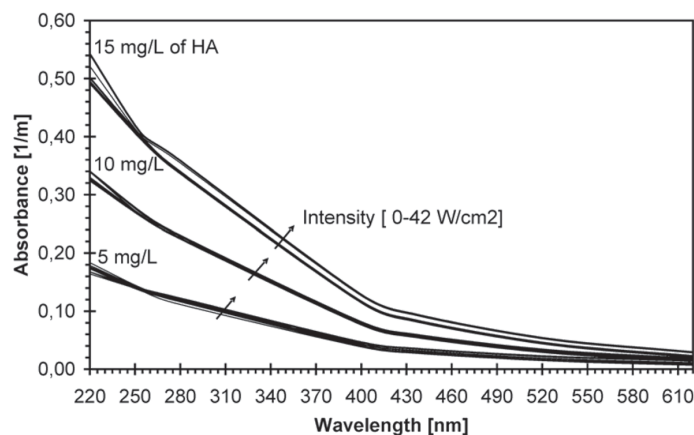
Fig. 5. Absorbance vs wavelength at different sonication intensity and humic acid concentration.
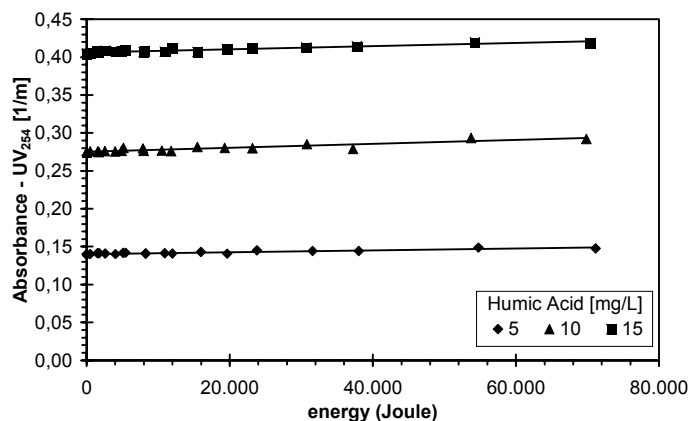

Fig. 6. Absorbance UV254 vs. sonication energy at different sonication intensity and humic acid concentration.

the presence of nitrate (Fig. 7). TOC removal increased slowly by the power supply during the treatment.

This different behaviour is explainable by a possible influence of suspended solids on adsorption values. To confirm this hypothesis, turbidity was measured for the same sample, in fact, turbidity increased with energy supply to the sample by US probe.

The apparent independence of absorbance increment by the power of treatment (Fig. 6) underlines that, in contrast to crumbling in suspended

NOM (turbidity increase), the formation of dissolved NOM relievable with absorbance measure was mainly dependent on time. This can be explained by the predominant sonochemical action on the dissolution of NOM, related to the formation of hydrogen peroxide.

4. Conclusions

The potential of ultrasound for the intensification of chemical and biological processes in water technology is very broad.
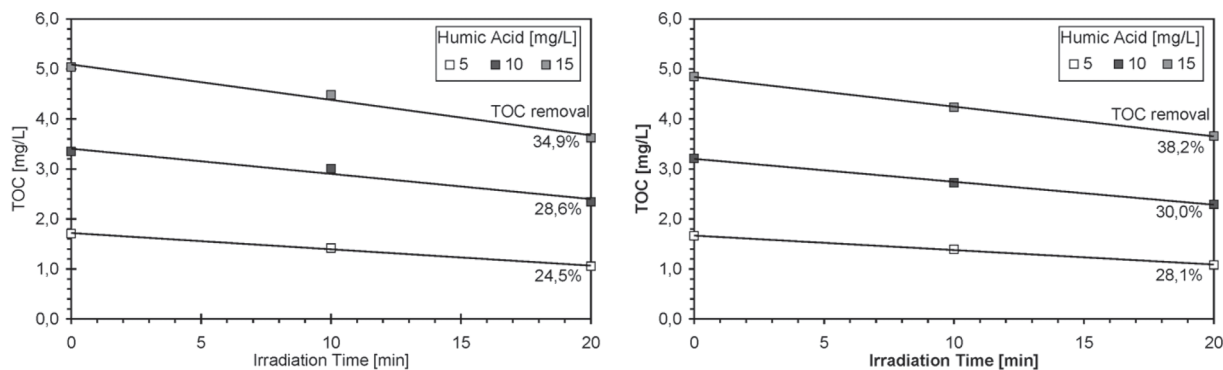
Fig. 7. TOC removal at 42 W/cm^2 in function of sonication time and humic acid concentration with (right side) or without (left side) 15 mg/L of nitrate.

Some incongruence was measured in respect to absorbance removal and TOC removal. The effects of ultrasonication on the humic acids could be explained by two mechanisms. One is the chemical degradation of the humic acids in the cavitation bubbles by oxidation. The other is the physical aggregation of humic acid fragments. The main physical effect of powerful implosion of cavitation bubbles in the natural water is the fragmentation of the suspended solids. This effect is easily measurable by turbidity growth. At the same time, high turbidity value influences positively the absorbance value, in contrast to TOC values, which are independent of turbidity.

The removal of natural organic matter from solution is influenced by parameters such as intensity and time of sonication. 20 min of sonication at 42 W/cm^2 provided the best performances with respect to TOC removal.

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