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Natural Organic Matter Degradation Using Combined Process of Ultrasonic and Hydrogen Peroxide Treatment

Degradação da Matéria Orgânica Natural Utilizando Processos Combinados de Ultrassom e Tratamento Com Peróxido de Hidrogênio

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Abstract

The purpose of this study was to explore and examine an advance oxidation process using ultrasonic (US)/H_2O_2 as a potential treatment and removal of humic acid (HA). The US power, HA concentration and H_2O_2 concentration enhanced removal process was performed by varying the irradiation time, the preliminary experiments demonstrated that natural organic matter (NOM) and HA removal was influenced by the power, HA concentration and time of sonication. The optimum conditions for HA and NOM removal were achieved by US irradiation of 110 W power, at 20 min contact time, and 20 mg.L^{-1} of HA concentration. Likewise, the optimum conditions for HA and NOM removal with hydrogen peroxide were obtained at 120 min time and 10×10^{-3} mol.L^{-1} of H_2O_2. The results indicated a strong capacity of sonication for NOM and HA removal, therefore by adding H_2O_2 to the aqueous solution increased NOM and HA removal by US. The HA removal efficiency of US/H_2O_2 (91.5%) was more than US (69.3%) and H_2O_2 (20%). US/H_2O_2 system proved to be the most effective. The sonochemical degradation with US/H_2O_2 can be an efficient method to remove the NOM from aqueous solution and may be a realistic possibility for large-scale treatment.

Keywords: Natural organic matter; Humic acid; Ultrasound; Hydrogen peroxide

Resumo

O propósito deste estudo foi explorar e examinar um avançado processo de oxidação utilizando (US)/H_2O_2 ultrasônico como um tratamento potencial e remoção de ácido húmico (HA). A potência do ultrassom, a concentração de ácido húmico e a concentração de H_2O_2 potencializa o processos de remoção pela variação do tempo de irradiação. Os experimentos preliminares demonstraram que a remoção da matéria orgânica natural (NOM) e do ácido húmico foram influenciadas pela intensidade, concentração de ácido húmico e tempo de exposição. As condições ideiais para a remoção do ácido húmico e matéria orgânica natural foram obtidas pela irradiação ultrassônica de 110 W, em 20 min de tempo de contato, e 20 mg.L^{-1} de concentração de ácido húmico. De forma semelhante, as condições ideais para a remoção de ácido húmico e matéria orgânica natural com peróxido de hidrogênico foram obtidas em um tempo de 120 min e 10×10^{-3} mol.L^{-1} de H_2O_2. Os resultados indicam a grande capacidade de uso de ultrassom para a remoção da matéria orgânica natural e ácido húmcio, ainda que pela adição de H_2O_2 na solução aquosa aumente a remoção da matéria orgânica natural e o ácido húmcio por ultrassom. A remoção de ácido húmico de forma eficiente pela ação US/H_2O_2 (91.5%) foi maior que US (69.3%) e H_2O_2 (20%). O sistema US/H_2O_2 provou ser o mais efetivo. A degradação sonoquímica com US/H_2O_2 pode ser um método eficiente para a remoção da matéria orgânica natural de soluções aquosas e pode ser uma possibilidade realística para o tratamento em larga escala.

Palavras-chave: Matéria orgânica natural; ácido húmico; ultrassom; peróxido de hidrogênio

1 Introduction

Natural Organic Matter (NOM) is used to describe the complex mixture of organic materials such as humic acids, hydrophilic acids, proteins, lipids, amino acids, and hydrocarbons that may be found in various sources of drinking water. The characterization and removal of these dissolved organics are a major issue in industrial water since they act as precursors for the formation of disinfectant by-products (Naddeo *et al.*, 2007). Wide varieties of commercial chemicals are using organic compounds and resulting in generation of different types of wastewater with significant amounts of organic waste compounds. The discharge of this wastewater into existing natural bodies of water is undesirable (Wang *et al.*, 2005; Amin *et al.*, 2013).

Advanced oxidation technologies (AOTs) are attractive alternatives for the traditional water treatments and have recently received considerable attention. These processes involve in generating hydroxyl radical ($^{\bullet}OH$) as the predominant species responsible for degradating of pollutants (Song & O'Shea, 2007). In the past, advanced oxidation processes (AOPs) involved in hydroxyl radicals have been applied as a promising new technology for organic pollutants degradation. The diverse methods used for generating these radicals are photocataysis and sonochemistry methods (Vinodgopal *et al.*, 1998). A new alternative sonochemistry approach offers a solution for combating the persistent water and wastewater organic pollutants (Méndez-Arriaga *et al.*, 2008).

Sonochemical degradation could be used for organic pollutant removal in aqueous solutions (Vinodgopal *et al.*, 1998). The advantages of using ultrasound irradiation are: 1- The simplicity of its use (Vinodgopal *et al.*, 1998), 2- The ultrasound does not require additional chemicals, and 3- It can be used for treatment of turbid solutions (Song & O'Shea, 2007).

The scattering of an ultrasound wave in a lead solution is determined as (Song & O'Shea, 2007; Vinodgopal *et al.*, 1998; Farshbaf Dadjour *et al.*, 2006; Méndez-Arriaga *et al.*, 2008; Chemat *et al.*, 2001; Hua & Thompson, 2000):

1- Forming and collapsing of cavitation bubbles that can spawn in extreme conditions of high temperature and pressure (5000°K and 1000 atm).

2- Dissociation of H_2 and production of the radical species such as $^{\bullet}OH$, $^{\bullet}HOO$ and etc. Based upon the equation 1, sonolysis generates hydroxyl radical from water dissociation:

$$\mathbf{H}_2O\ +))) \rightarrow {}^{\bullet}H + {}^{\bullet}OH \qquad (1)$$

The perhydroxyl radical is also formed as Eq. 2:

$$^{\bullet}H + O_2 \rightarrow {}^{\bullet}OOH \qquad (2)$$

From the combination of $^{\bullet}OH$ and $^{\bullet}OOH$ radicals, hydrogen peroxide simultaneously is released (Eq. 3&4).

$$2^{\bullet}OH \rightarrow H_2O_2 \qquad (3)$$

$$2^{\bullet}OOH \rightarrow H_2O_2 + O_2 \qquad (4)$$

During this process, three determinate zones can be described in these scattering levels: a) cavitations of bubbles, b) supercritical interface, and c) bulk of the dissolution.

3- In most cases, the reaction US pathways induced degradation of dissolved organic compounds in aqueous media involved in hydroxyl radical oxidation, pyrolysis and supercritical oxidation.

4- The US (US) propagation in a liquid causes a series of wave's compression and rarefaction. At sufficient high power, these bubbles grow and reach an unstable size and collapse violently.

5- Due to the concomitant release of heat, formation of hotspots are created.

6- By exposing dissolved gases in the water vapors to the organic substances in these extreme conditions, bond-rupture occurs.

7- Oxygen atoms are also produced in the gas phase.

Studies (Méndez-Arriaga *et al.*, 2008; Wang *et al.*, 2005; Wolski & Zawieja, 2012) reported that the application of ultrasound could improve extraction technology and industrial productivity of the various medicinal substances. Additionally, several studies have demonstrated the degradation of organic molecules, pharmaceuticals, pesticides, and dyes by US waves in water and wastewater (Méndez-Arriaga *et al.*, 2008; Cui *et al.*, 2011; Verma *et al.*, 2013). Cui *et al.* (2011) reported that US/O_3 could breakdown the HA and tannic acid molecules. In Cui *et al.* (2011) study, O_3 caused reduction in the pH of the solution (Cui *et al*., 2011). Zhang *et al.* (2011) reported that US/H_2O_2 process could remove bisphenol-A (BPA) from an aqueous solution. BPA removal was shown to be inhibited by the presence of HA during US irradiation. Results demonstrated the considerable enhancement of sonochemical destruction of green malachite in the presence of bromide (Moumeni & Hamdaoui, 2012). A number of researchers have proposed that the combination of an US process with an oxidant can enhance the decomposition of organic matter (Entezari *et al*., 2003; Kim *et al*., 2007; Cui *et al*., 2011).

Based on the impacts of US waves on removal efficiencies of the NOM illustrated in the literature, a new investigation of combined US and H_2O_2 was proposed to degrade the NOM in a solution. Therefore, the objective of this study was detecting the optimum condition for NOM removal by US and hydrogen peroxide and investigation the potential combination of US and H_2O_2 in optimal conditions.

2 Material and Methods

In this study, HA (Sigma Aldrich, USA) was used as a typical organic pollutant compound, found in water and wastewater. Water for the preparation of the solution was millipore quality with a minimum resistance of 12 MΩ-cm. Hydrogen peroxide (Merck Co., Germany) with a purity of 31.5% was applied based on its instruction as well as other chemicals.

2.1 US Setup

An ultrasound device (Sonopuls Bandelin HD3200, Germany) equipped with a horn sonotrode (horn tip with 5 mm diameter) was operated at 25 KHz (Figure 1). The source of US irradiation was fixed to a lab-build reactor. Applied US power was adjustable from 20 to 140 W, however, its frequency was fixed to 25 KHz. Additionally in this study, power varied from 30 to 130 W. Calorimetric intensities ranged from 150 to 60 $W.cm^{-2}$ while densities varied from 120 to 530 $W.L^{-1}$, respectively. Sonolysis was performed at six different powers 30, 50, 70, 90, 110, and 130 W. The reactor was open to the atmosphere. The US probe was inserted in the center of the 500 mL reactor with 8.5 cm internal diameter and 8.8 cm heights. The volume of aqueous in the reactor was 250 mL that horn was inserted in 2.5 cm from bottom of reactor. This setup was operated at laboratory temperature.

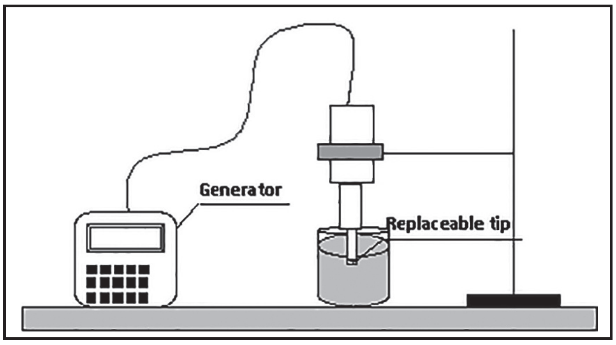

Figure 1 Experimental setup (Sonopuls Bandelin with 500 mL reactor).

2.2 Methodology

The study consisted of three phases. The optimal conditions such as power, time, and humic concentration for HA removal by US were detected in the first phase (Phase One). H_2O_2 concentration for HA removal by H_2O_2 and the optimal conditions for time were detected in the second phase (Phase Two). The optimal conditions of US/H_2O_2 were used for HA removal in the third phase (Phase Three). Ultrasound was transmitted into the 250 mL solutions of 10 $mg.L^{-1}$ of HA through the tip of the probe for 5 min at different power levels (30, 50, 70, 90, 110, and 130 W) in Phase One. The time varied from 5 to 30 min (5, 10, 15, 20, 25, and 30 min) with HA concentration as 10, 20, and 30 $mg.L^{-1}$ in Phase One. The effects of different hydrogen peroxide concentrations, 2.5×10^{-3}, 5×10^{-3}, and 10×10^{-3} $mol.L^{-1}$, were studied in Phase Two. In the third phase, optimal US and H_2O_2 conditions were used for HA removal.

Experiments were conducted in a 500 mL cylindrical water-jacketed glass reactor containing HA dissolved in deionized water (250 mL). The monitored parameters in each step were HA, NOM (as UV254 absorption), temperature (T), pH, conductivity, oxidation- reduction potential (ORP), salinity, total dissolved solid (TDS), and turbidity.

2.3 Experiments

For HA analysis, an isocratic mobile phase flow of phosphate buffer (0.1 $mol.L^{-1}$), sodium sulfate

(0.1 mol.L^{-1}) in Milli-Q water (made of 0.1 mol.L^{-1} phosphate buffer and 14.1 g of Na_2SO_4) were used. A HPLC (Jasko, UV 2.75 Plus-FP-2020, Japan) with a column Biosuit 5 µm HR SEC column (7.8×300 mm) at 25°C, 20 µl of volume injection and recorded at 280 nm was used for the quantification of HA.

Phosphate buffer with 0.1 mol.L^{-1} concentrations was prepared by dissolving 6.23 g of $Na_2HPO_4.2H_2O$ and 10.405 g of $NaH_2PO_4.2H_2O$ in 300 mL of Milli-Q water. This mixture was stirred to dissolve the salt and also was made up to reach the final volume of 1000 mL (McGrane *et al.*, 1998). The pH of the mobile phase adjusted to 6.8 by 0.1 mol.L^{-1} of HCl. The HPLC grade filters employed for filtration of the mobile phase.

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 parameter to represent the concentration of NOM in water (Naddeo *et al.*, 2007; Valencia *et al.*, 2012; Imoberdorf & Mohseni, 2011; Dubrawski *et al.*, 2013). For NOM analyzing, absorption values of the samples were recorded by DR 5000 with 1 cm quartz cell. The absorbance at 254 nm was expressed as UV 254. Water parameters including temperature (T), pH, conductivity, oxidation-reduction potential (ORP), salinity, total dissolved solid (TDS), and turbidity were also measured according to the standard methods (Eaton & Franson, 2005).

In order to obtain reproducible experimental results, all experiments were carried out at least 10 times.

3 Results and Discussion

3.1 US Optimum Condition

The most critical parameters for sonolysis application were the power, US time and concentration.

3.1.1 Effect of Ultrasound Power

Figures 2 and 3 depicts the effect of the applied US power on the conversion of NOM as increase UV 254 absorbance percent and HA removal percent.

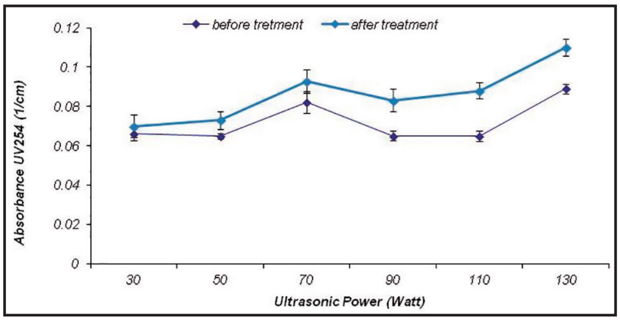

Figure 2 Effect of applied power on the UV 254 absorbance (5 min US and pH 7).

The UV light absorption of HA increased with increasing in condensation of the aromatic ring, the total C content, the molecular weight (MW), and the ratio of C in aromatic rings to C in aliphatic side chains (Naddeo *et al.*, 2007). The changes in UV absorption were the result of ultrasonication, which suggests that the structure and/or contents of chromophores such as OH$^-$, COOH$^-$ substituted benzene rings, the intramolecular electron donor acceptor complexes and complex unsaturated conjugated chromophores were changed in the ultrasound field. In addition, the macromolecular structure of the HA could have been altered, resulting in a greater or lesser exposure of chromophores to light, while auxochromes could have been introduced into aromatic rings.

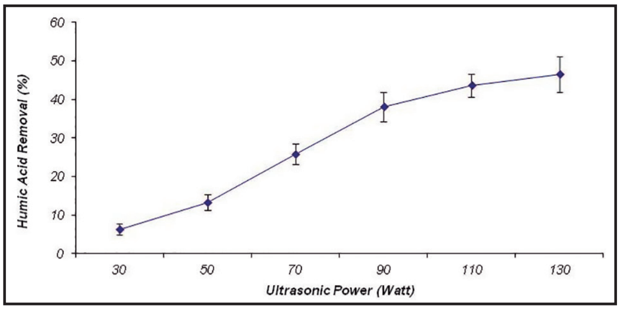

Figure 3 HA removal percent at different US powers (HA initial concentration 10 mg.L^{-1}, 5 min US, and pH 7).

As expected, a higher applied power lead to a higher degradation of HA. Similar results were reported in the Vincenzo Naddeo and Zhang experiments (Naddeo *et al.*, 2007; Zhang *et al.*, 2011). Although the highest degradation percentage was reached at the 130 W of the US power, its required energy versus the percent removal of HA, was greater. Therefore, it was recommended not to exceed the power level greater than 110 W. After conducting the experiment at 110 W power, 5 min contact time and initial concentration of 10 mg.L^{-1} of HA, the concentration of remained HA was 5.8±0.407 mg.L^{-1} HA. In this condition 43.6% of HA removed but UV 254 absorption increased to 2.2±0.47 m^{-1}.

Higher power density resulted in faster HA degradation because of increasing rate of cavitation in a unit volume of solution and producing more reactive radicals. Because of an increase in the power input, higher number of cavities were generated and caused higher magnitudes of total pressures pulses (pressure pulse due to the collapse of single cavity × number of cavities) (Pandit *et al*., 2001). Furthermore, this result can be explained by US intensity, which is defined by US power/vibration area. When the US power is increased at constant horn surface area, the US intensity increases. The collapse time, the temperature, and the pressure on collapse are dependent on the US intensity. In this study, the temperature and the bubble generation were increased with increasing the US power but the collapse time was decreased. The main primary chemical process in the sonolysis of the aqueous solutions was the thermal dissociation of water to hydrogen atom and hydroxyl radicals. However, the hydrogen peroxide concentration continuously increased during US treatment (Naffrechoux *et al*., 2003). An increase in US intensity would thus lead to greater sonochemical effects in the collapsing bubble. It has been shown that increasing US intensity increases the degradation rate of organic compounds (Katsumata *et al*., 2007). Furthermore, the pulsation and collapse of bubble in the reaction cell occurred more rapidly, number of cavitations bubbles increased and concentrated the $^{\bullet}$OH radicals by increasing the US power. These $^{\bullet}$OH radicals reacted with HA in the solution. Therefore, the degradation of HA increased with increasing the US power because of the radical reaction enhancement. At higher power of irradiation, a large number of gas bubbles or cavities in the solution were produced and the sound waves were scattered to the walls of the vessel or back to the transducer. Thus, a lesser level of energy focusing or concentration occurred although the vessel was exposed to higher and higher intensities. Thus, it was advisable to operate with higher dissipation areas or at lower power of operation. However, it needs a minimum threshold power for dissociating HA. The concept of onset was attributed to the fact that there are always a minimum number of hydroxyl radicals or a minimum temperature (where the mechanism of destruction is pyrolysis) required the destruction reaction to proceed and this can only be achieved with the supply of a certain minimum amount of power depicted as the threshold power. The beneficial effect of power was associated with increased cavitations activity occurring at higher levels of power. As power increased, the number of collapsing cavities also increased and led to enhance HA degradation and higher H_2O_2 formation.

3.1.2 Effect of Ultrasound Time

Experiments were performed with 5 to 30 min of irradiation time and the samples were collected and analyzed. Figure 4 and 5 gives the variation of percentage degradation in NOM and HA removal observed with time at 110 W power and 10 mg.L^{-1} initial concentrations of HA. Degradation of HA was increased with the time of the operation and it appears that the rates of degradation are highest at 20 min.

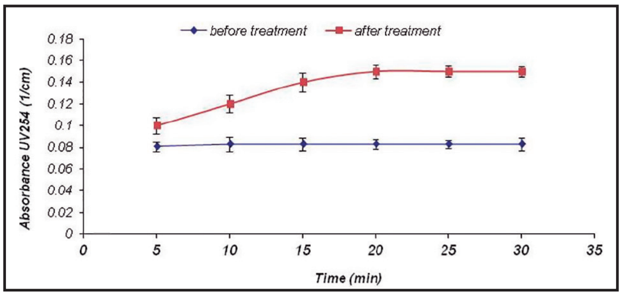

Figure 4 Effect of US time on the UV254 absorbance (HA initial concentration 10 mg.L^{-1}, pH 7, and power 110 W).

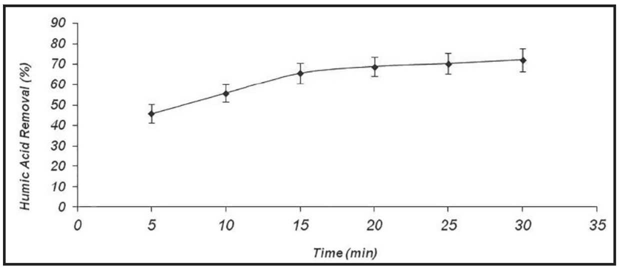

Figure 5 HA removal percent at different US time (HA initial concentration 10 mg.L^{-1}, power 110 W, and pH 7).

Results show that the degradation percentage of HA increased with increasing the time. Since the significant change did not occurred after 20 min, this time was selected as the optimal time. Similar results are also seen in the experiment with Katsumata *et al.* (2007).

This can be explained by the predominant sonochemical action on the dissolution of HA, related to the formation of hydrogen peroxide. Based on Figures 4 and 5, it was possible that HA was not degraded directly to water and carbon dioxide but via a series on intermediate and that needed an optimal time for degradation. Also in 20 min of ultrasound, the presence of dissolved gases in the medium increased and enhanced the extent of cavitations due to possible nucleation. Also, the extent of cavitations might be occurred due to the intensity of cavitations in result of higher total magnitude of pressure pulse. Gogate *et al.* (2003) found similar results with experiments on the decomposition of aqueous fluvic acid solutions in the US setup.

HA was degraded more rapidly than hydrophilic natural organic maters, due to the aliphatic structure of hydrophilic fraction, which was more difficult to degrade by oxidation. HA contained more phenolic and aromatic compounds that easily degraded by US, as noted HA was degraded after 20 min.

3.1.3 Effect of Initial Concentration of HA

Figure 6 depicts the effect of initial concentration of HA (10, 20, and 30 mg.L^{-1}) with degradation of HA in 20 min and 110 W ultrasound. It should be noted that the degradation was not greater in the higher HA concentration since sonochemical processes involved different reactive species. For the initial HA concentration of 10 and 20 mg.L^{-1}, the results indicated an increasing degradation but at higher concentration (30 mg.L^{-1}), HA degradation was decreased. These results indicated the non-isolated nature of the sonochemical reaction with HA and NOM.

Figure 7 shows effects of initial concentration on NOM removal (as UV254 absorbance percent).

Figures 6 and 7 depicts the initial degradation rate versus concentration for each concentration. It should be noted that increasing HA concentration did not enhance the decomposition rate. Percentage degradation was also found to be inversely proportional to the concentration of HA taken initially.

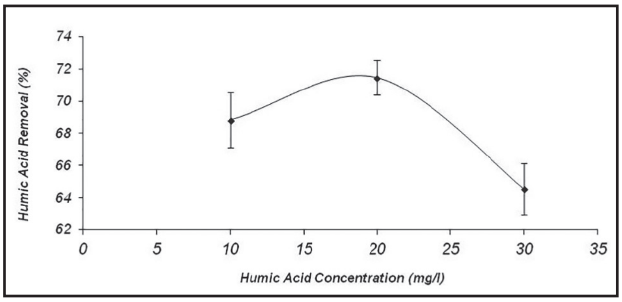

Figure 6 HA removal percent at different initial concentration (110 W, 20 min US, and pH 7).

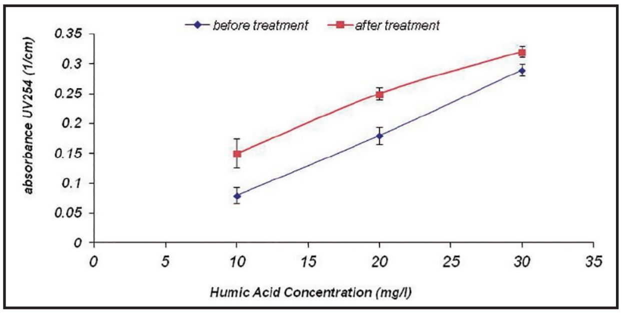

Figure 7 UV254 absorbance percent at different initial concentration (110 W, 20 min US, and pH 7).

3.2 Oxidation of HA by Hydrogen Peroxide Without US

Hydrogen peroxide (oxidation potential 1.77 V) has long been used commercially as an oxidant, bleaching and disinfectant agent. It was an effective oxidant used for destruction of organic species (YazIcI *et al*., 2007). The effect of hydrogen peroxide was tested at three different concentration levels (2.5×10^{-3}, 5.0×10^{-3}, and 10×10^{-3} mol.L^{-1}). Hydrogen peroxide has long been recognized as a free radical producer (Tan *et al*., 2013). Although the H_2O_2 was produced by US irradiation in an aqueous solution, its amount for decomposing the HA in water and wastewater should be investigated. Figure 8 and 9 illustrates the effect of H_2O_2 on HA removal and an increase of UV 254 in the water solution. These figures illustrate that the percent of HA increased by increasing the dose of H_2O_2, over 20% of HA removal and achieved with 10×10^{-3} mol.L^{-1} of H_2O_2 concentration after 120 min of reaction time.

Based on Figure 8, HA degradation increased when hydrogen peroxide concentrations increased. It reached a maximum beyond which it appeared to decline at a high hydrogen peroxide dose. The effect of hydrogen peroxide can be explained by radical reaction mechanisms. The added hydrogen peroxide

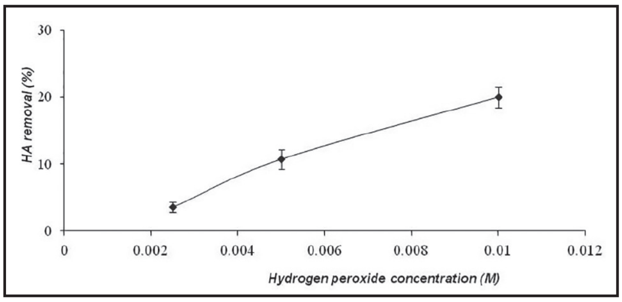

Figure 8 Effect of hydrogen peroxide on HA removal from aqueous solution with 120 min contact time.

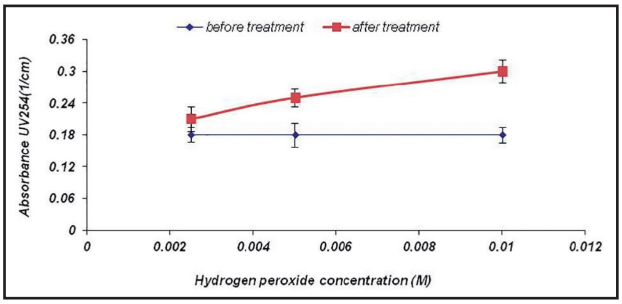

Figure 9 Effect of hydrogen peroxide on UV254 absorbance percent with 120 min contact time.

could accelerate the reaction by the electrons. Hydrogen peroxide may react with hydroxyl radical to form the perhydroxyl radical.

3.3 Effect of US/H_2O_2 on NOM and HA removal

The advantage of H_2O_2 over other methods of chemical oxidation was its rapid decomposition and yield of hydroxyl in the solution and its direct reaction to the organic substrates. This oxidant does not change water characteristics.

Taking into account that higher power density was effective for faster HA degradation, we applied a power input of 110 W and the solution volume of 250 mL, giving the power density of 0.37 W.mL^{-1} in the subsequent experiments. Previous studies demonstrated that H_2O_2 was a crucial intermediate produced during US irradiation But, amount of produced H_2O_2 is low for HA degradation (Chen *et al*., 2004; Olson & Barbier, 1994; Kreller *et al*., 2005). It is common practice to add H_2O_2 into the system to improve the efficiency of US treatment. Figure 10 and 11 shows the effect of US irradiation and hydrogen peroxide combination on HA removal and the increase of UV 254 in the water solution.

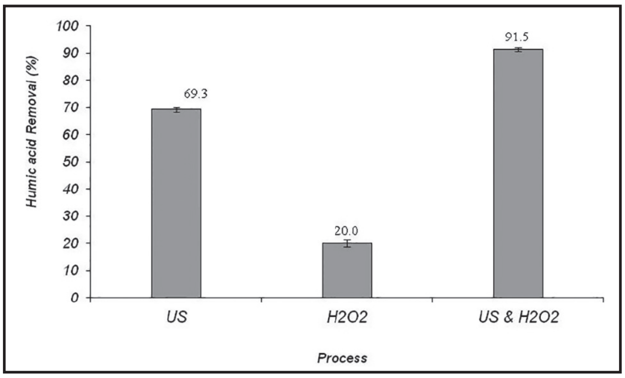

Figure 10 Compare of US and hydrogen peroxide on HA removal form aqueous solution at optimum condition.

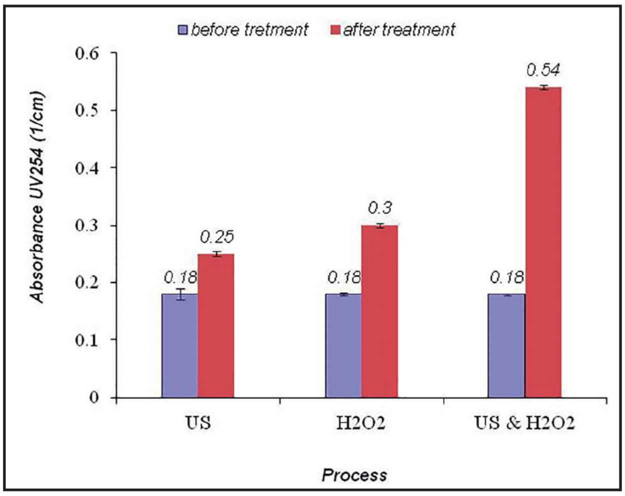

Figure 11 Compare of US and hydrogen peroxide on of UV 254 absorbance in aqueous solution at optimum condition.

The results indicated that the actual efficiency of the US system at optimal power employed for HA removal was 69.3%. Furthermore, it was observed that the removal of HA by the ultrasound irradiation with hydrogen peroxide at optimal conditions (US: 110 W, 25 KHz, 20 min and 20 mg.L^{-1} HA- H_2O_2: 10×10^{-3} mol.L^{-1}, 120 min) was over 91 percent.

The total effect of US/H_2O_2 was more to the superposed affects of individual US and H_2O_2 due to the excess of hydrogen peroxide. The hydrogen peroxide acted as a whole or hydroxyl radical scavenger that was produced by US, and the degradation of HA was enhanced. In addition, hydrogen peroxide might be reacted with OH radical to form the perhydroxyl radical, a much weaker oxidant. Overall, H_2O_2 improved the US efficiency in HA removal. Based on the design of the experimental (DOE) analysis there was a difference between H_2O_2, US, and their combination in HA removal (P-value < 0.05).

The study was performed in optimal conditions for a two series process. First H_2O_2 (10×10^{-3} mol.L^{-1} concentration and 120 min contact time) was added to the solution to produce OH radical and react with HA, after which US at optimum condition (110 W, 25 KHz, and 20 min) could degraded HA. In the Chemat *et al.* (2001) study for uses of H_2O_2 with US simultaneously, was revealed that a 60 min contact time was required to totally reduce organic carbon by half and having a complete degradation of HA. It was recommended that hydrogen peroxide must be kept at optimal levels.

The US irradiation combined with H_2O_2 increased the absorbance of UV 254 in water solution more than US and H_2O_2. Such improvements are consistent with the studies carried out by Zhang *et al*. (2011) reported that the increased rate of BPA removal by US irradiation correlated positively to the increasing dosage of H_2O_2.

The synergetic effect of US/H_2O_2 was inferred when the removal efficiency of the combined process is higher than sum-up of removal efficiencies for individually conducted US or H_2O_2 experiments. The above results showed that the combined process of US and H_2O_2 has a notable synergetic effect. The added H_2O_2 accelerated the reaction by scavenging the electron, producing hydrogen radicals by cavitation (Chemat *et al*., 2001; Verma *et al*., 2013).

For the $^{\bullet}OH$ radical oxidation, $^{\bullet}OH$ should be introduced from a liquid phase to HA molecules surface through the gas- liquid interface. However, a large portion of H_2O_2 is usually consumed in the form of large $^{\bullet}OH$ radicals. In the case of the US/H_2O_2 combination, a myriad of tiny air bubbles are produced by the cavitation effect of US, allowing most $^{\bullet}OH$ radical to enter the liquid phase or react on the gas/liquid interface. The increase of mass transfer and decomposition processes of H_2O_2 coupled with a transient local high temperature and ultra-high pressure caused by the collapse of cavities, enhances the production of free $^{\bullet}OH$ and other radicals for further oxidation of organic pollutants, resulting in a higher reaction rate.

Effects of ultrasound degradation on organic compounds were due to the phenomenon of acoustic cavitations. US irradiation promoted the growth and collapse of gas bubbles (cavitations) with the concomitant release of heat. The pollutant molecules degradated by three different pathways depending on their chemical properties, i.e. hydrophobicity, volatility, and Henry's law constant. These reaction pathways typically occurred in specific regions: pyrolysis reactions inside the vapor regions, oxidation by hydroxyl radical in the bulk medium, supercritical oxidation, and hydrolysis in the hydrophobic interface.

Organic compounds in aqueous solution showed differently behavior in contact with US irradiation according to their physical and chemical properties (Pétrier and Francony, 1997).

The mechanism of the US and H_2O_2 combined process is as follows:

1. When H_2O_2 was added to water during US irradiation, the synergistic increase in the production of hydroxyl radicals was due to an additional pathway that involves the thermal decomposition of H_2O_2.

2. A further advantage of such a combination was the enhanced oxidant transfer in solution, resulting from larger gas diffusion coefficients in the presence of US vibrations than in non-irradiated solutions.

3.4 Effect of US and H_2O_2 on water Characteristics

Table 1 illustrates the effect of US irradiation and hydrogen peroxide on water characteristics.

Table 1 illustrates that US causes an increase in temperature, turbidity, and EC, however, will caused decreasing of ORP and salinity. The pH changing by US is not significant while the results of Qi *et al*.(2004)demonstrated that the pH of the solution increased slightly from 7.3 to 7.4 and then dropped to 7.2 with an increase in the ultrasonication period. H_2O_2 process caused an increase in EC, TDS, and salinity and caused a decrease in ORP. The US/H_2O_2 process also increased temperature and turbidity but decreased the ORP and EC. In Cui *et al*. (2011) study, US, O_3, and US/O_3 process used for HA removal, caused a pH level reduction. However, in this study the use of H_2O_2 did not change the pH levels of water. The changes in the pH can possibly be attributed to the fact that, when the aqueous

Parameter	US process			H_2O_2 process			US and H_2O_2	
	Before US	After US		Before H_2O_2	After H_2O_2		Before US-H_2O_2	After US-H_2O_2
T (°C)	26.3±0.175	54.8±0.668		26.3±0.17	26.3±0.15		26±0.391	54.4±1.75
pH	6.9±0.12	7.3±0.2		6.9±0.12	7.3±0.07		6.8±0.08	7.2±0.1
ORP (mv)	269.7±3.4	255.7±4.2		269.9±2.8	205.8±15.2		271.3±7.1	241.5±7.01
Turbidity (NTU)	4.2±0.53	16.5±0.1		4.2±0.55	4.4±0.64		3.9±0.3	13.1±0.96
EC (μs/cm)	281.8±48	291±2.1		281.8±38	336.7±59		279±31.2	259±22.6
TDS (mg/l)	143.6±18.9	144.5±0.74		145.6±18.3	173.5±17.3		137.7±10.6	139.8±11.4
Salinity (%)	0.14±0.052	0.1±0.00		0.13±0.048	0.17±0.048		0.13±0.05	0.13±0.05

Table 1 Effect of US and H_2O_2 on water characteristics in optimum condition (US: 110 W, 20 min and H_2O_2: 10×10^{-3} mol.L^{-1}, 120 min and HA 20 mg.L^{-1}).

solution is irradiated by ultrasound, water vapors that present in the ultrasound bubble are split to yield $^{\bullet}$H and $^{\bullet}$OH radicals.

Comparing the changes in the UV absorption (Figure 2) with the partial changes in the pH (Table 1), ultrasonication could induce changes in disassociation or protonation of carboxyl and phenolic hydroxyl groups of the HAs.

Changes in the ORP of the aqueous HA solution can for the most part be attributed to electron transfer in the system between the radical species in the US field and the reactive functional groups of the HA (Qi *et al*., 2004).

4 Conclusion

Degradation of the NOM such as acid humic (as index) in aqueous solution by US irradiation and hydrogen peroxide was investigated utilizing solely US and oxidation for removal of organic pollutants in water and wastewater.

However, they were not sufficient to resolve the problems related to the effluent to meet current discharge standards. This study showed that the degradation efficiency was strongly affected by the sonication power and reaction time. In addition, the efficiency of the US treatment was significantly enhanced by the H_2O_2 oxidation. It was established that the synergetic effects observed for the overall degradation of the HA and NOM reflected the potential applicability of the US/H_2O_2 combination for minimizing the survival time of the intermediates. Their effects can be attributed to not only the mechanical effects of cavitations, which increased the mass transfer, but also the enhanced decomposition of H_2O_2. Accordingly, the physico-chemical properties of the US/H_2O_2 combination can enhance both the rate of direct reactions and $^{\bullet}$OH radical's oxidation of intermediate products. The proposed combination may have a great potential in treating polluted water, wastewater, leachate, tannery/dyes dye and wastewater, etc.

The current study highlights the importance of various parameters and additives for the potential development of an effective US treatment method for water and wastewaters. However, since the general application of ultrasound for water treatment can be costly, careful evaluation of the economic feasibility is required prior to large-scale treatment.

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