Degradation efficiency of humic acid in presence of hydrogen peroxide and ultrasonic from aqueous media

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ABSTRACT

Natural organic matters (NOMs) are present in many water resources across the world, particularly surface and groundwater sources. NOMs in water supplies cause several issues, particularly in the conventional water treatment procedure. One of the most important precursors of water disinfection by-products is the existence of contaminants such as acid humic (HA) in water. This study aimed to investigate the simultaneous function of hydrogen peroxide (H_2O_2) and ultrasonic in the removal of HA from aqueous solutions. In the presence of H_2O_2 and ultrasonic, the influence of affective factors such as pH (3–9), contact time (5–30 min), HA concentration (10–50 mg/L), and H_2O_2 (mM) concentration was evaluated discontinuously on HA removal effectiveness. A spectrophotometer set to 254 nm was used to determine the final HA concentration. As a result, H_2O_2 concentration was directly related to HA removal effectiveness, whereas HA concentration was inversely related. Under optimal ultrasonic time of 5 min, the maximum removal effectiveness of HA (50%) was 10 mg/L = HA, H_2O_2 = 0.10 mM. Also, this degradation process followed pseudo-first-order kinetic ($R^2 > 0.9$). The removal rate by ultrasonic and H_2O_2 was acceptable, indicating that the combined use of H_2O_2 and ultrasonic in the generation of hydroxyl radicals is successful. As a consequence, ultrasonic and H_2O_2 pre-treatment of HA-containing water may be a reasonable solution.

Keywords: Humic acid; Hydrogen peroxide; Kinetic; Ultrasonic; Water

1. Introduction

One of the most serious issues in many developing countries is the contamination of surface water by various contaminants and the necessity to access new water resources. Natural organic matter (NOMs) is abundant in many water resources across the world, particularly surface and groundwater sources [1–3]. The humic and non-humic constituents of natural organic matter in water impact the efficacy of treatment processes and, consequently, the disinfection unit and the generation of disinfection by-products (DBPs). These substances are the result of both natural and anthropogenic environmental degradation of biological materials [4,5].

Since changes in human activities and natural ecosystems, the concentration and structure of NOMs vary from

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region to region. Non-humic compounds have a larger potential for halo acetic acid (HAA) generation than humic substances, whereas humic substances have a higher potential for trihalomethane (THM) formation [6]. Both substances, however, are suspected of being carcinogenic in humans. The maximum concentrations of THMs and HAAs in water in the initial standard of the EPA Disinfection Act are about 80 and 60 µg/L, respectively, and in the secondary standard, they are less than the aforementioned limits of about 20 and 30 µg/L, respectively [7,8].

Humic acids (HAs) are components of humic substances that are insoluble in water at acidic pH levels (pH < 2) but soluble at higher pH levels. They dissolve in dilute alkaline solutions and precipitate when exposed to acid [9]. The typical molecular size and molecular weight of these materials range from 5,000 to 100,000 daltons. These compounds have 33%–36% of oxygen and 4% of nitrogen. Humic acid is a polymeric, multifunctional acid with a complicated chemical structure and excellent acidic characteristics. Because of their negative impacts on people, humic compounds should be eliminated from water [8].

In conventional drinking water treatment techniques, NOMs are eliminated to a level of 10%–50%. Many water treatment plants and facilities confront the problem of DBPs due to the presence of NOMs and the requirement for chemical disinfection to preserve public health. As a result, organic substances must be removed from water sources [10]. Humic acid and similar chemicals are removed from water sources using a variety of processes including biodegradation, adsorption, photolysis, oxidation with ozone, Fenton, etc. [11–15]. Many advanced oxidation processes (AOPs) can also decrease humic acid, including gamma-ray radiolysis, O_3/H_2O_2, TiO_2 photocatalyst, photolysis, ultrasonic, UV, Fenton, and photo Fenton [16–20]. Because of the appropriate generation of highly active hydroxyl ($^{\bullet}OH$) radicals in the aqueous phase, the advanced oxidation process is known as a novel approach among all the methods discussed. The major oxidizing species of organic compounds are hydroxyl free radicals [21–26].

Due to the sound cavitation generated by the ultrasonic process, it has a high penetration capability. This phenomenon has the potential to enhance the sonochemical process [27–29]. Previous research found that photocatalytic methods using TiO_2 and Fe_3O_4 nanoparticles coupled with ultrasonic had high effectiveness in removing HA [30–32]. Ultrasonic and H_2O_2 used in AOPs are an efficient approach to removing organic compounds from aqueous solutions and oxidizing organic materials to safe end-products including H_2O and CO_2. The combination of ultrasonic and H_2O_2 appears to be a good alternative for increasing free radical generation. The concentration of H_2O_2 is critical to the hybrid process' development [33].

When ultrasonic waves (US) are emitted into aqueous solutions, gas bubbles can generate and disintegrate. As a result, it generates heat and pressure, which causes the thermal degradation of water and oxygen to produce free radicals [34]. Humic acids need to be removed because of the aforementioned issues they create when present in water. The main goal of this study is to compare how well H_2O_2 and ultrasonic work separately and together to remove humic acids from water.

2. Materials and methods

2.1. Chemicals and instruments

The humic acid (HA) and hydrogen peroxide (H_2O_2) utilized in this investigation were purchased from Sigma-Aldrich USA Company. A pH meter (Wegtech Mi 151 22, UK) was used to determine the pH of the solution. The solutions were stirred using a stirrer (HS 6000, Iran). A UV-Vis spectrophotometry apparatus (Model Optima SP3000 Plus, Japan) was used to measure the concentration of HA at a wavelength of 254 nm. Ultrasound waves with a frequency of 60 Hz were generated using ultrasonic equipment (Elmasonic, Germany).

2.2. Batch experiments

In this investigation, HA concentrations 10, 25, and 50 mg/L, reaction time 5–30 min, pH 3, 7 and 11, and H_2O_2 concentrations 0.02, 0.04, 0.06, 0.10 mM were optimized. The varied HA concentrations were prepared by diluting a HA stock solution with a concentration of 100 mg/L. HCl and NaOH (1 N) were used to adjust the pH of the solution. Finally, Eq. (1) was used to calculate the elimination effectiveness of HA after various reaction times in the presence of hydrogen peroxide and ultrasonic [14].

$$\text{Removal Efficiency} = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

where C_0 and C_t represent the initial and final HA concentrations in mg/L, respectively.

The number of samples was determined using the one factor at a time (OFAT) technique in accordance with the number of variables (initial concentration of humic acid, pH, H_2O_2 concentration, and contact time), and the test of each sample was performed three times to confirm the accuracy of the results. By doing so, it first considers one parameter as a variable and considers the other variables as constants, after which parameters optimize the variable in test before moving on to the other variables [35].

3. Results and discussion

3.1. Effect of H_2O_2 concentration on HA removal

The concentration of H_2O_2 is one of the important factors in the degradation of HA. The effect of varied H_2O_2 concentrations 0.02, 0.04, 0.06, 0.10, and 0.12 mM was investigated in this study. As indicated in Fig. 1, raising H_2O_2 concentration from 0.02 to 0.12 mM enhanced HA removal effectiveness. The elimination efficiency of HA was 12% at a concentration of 0.02 mM of H_2O_2, and 34% at a value of 0.10 mM, and with its further increase, no significant increase in removal efficiency was observed. Radical reaction processes can explain the impact of H_2O_2. Adding H_2O_2 to the process can speed it up by generating active and energetic $^{\bullet}OH$ and $^{\bullet}O_2^-$ radicals, which eventually destroy organic molecules including HA [15,36]. Since H_2O_2 is an oxidant that requires to activator for the production of an active and energetic free radical, there has been no substantial rise in the removal efficiency of HA as its concentration
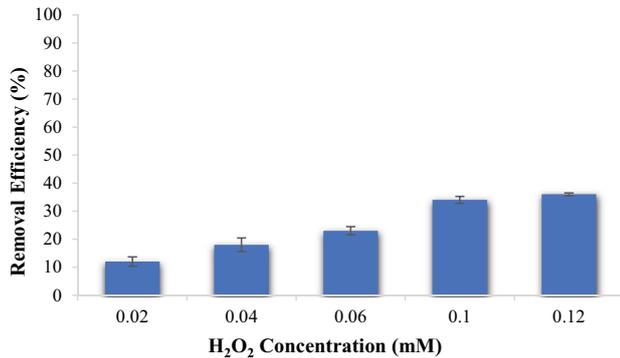
Fig. 1. Effect of H_2O_2 changes on HA removal efficiency (contact time 5 min; HA 25 mg/L; pH 7).

Fig. 2. Effect of pH changes on HA removal efficiency (contact time 5 min; HA 25 mg/L; H_2O_2 0.10 mM).

in the reaction medium increases. However, because the concentration of HA in the reaction medium is low, the interaction between H_2O_2 molecules and radicals with HA molecules is low, and the removal efficiency does not significantly improve [37]. As a consequence, a concentration of 0.1 mM was considered to be the optimal concentration of H_2O_2. The findings of this investigation matched those of Pourzamani et al. [38], Nazmara et al. [39], and Dehghani et al. [40]. The following equations describe when H_2O_2 generates these radicals [41]:

$$O_2 + H_2O \rightarrow 2^{\bullet}OH \tag{2}$$

$$2^{\bullet}O_2^- + 2H^+ \rightarrow H_2O_2 + O_2 \tag{3}$$

$$H_2O_2 + {}^{\bullet}O_2^- \rightarrow O_2 + OH^- + {}^{\bullet}OH \tag{4}$$

3.2. Effect of pH on HA removal

The influence of pH on the removal effectiveness of HA by H_2O_2 and ultrasonic was evaluated at pHs 3, 5, 7, and 9. Fig. 2 shows the obtained results. According to the findings, the maximum removal effectiveness for HA was around 50% at pH = 9. The elimination efficiency improved as the pH increased from 3 to 9. The removal efficiencies rose from 15 to 37% in the presence of H_2O_2, 30% to 35% in the presence of ultrasonic, and 43% to 50% in the presence of both. There was no noticeable increase in efficiency when the pH was raised from 7 to 9. The major explanation for the improvement in efficiency with raising pH might be related to a decrease in H+ ions in the reaction medium since the presence of this ion causes the generated radicals to be consumed and their influence on organic molecules to be reduced. It is prominent in alkaline pHs, such as OH– ions, and can operate as a precursor of hydroxyl radicals, enhancing the synthesis of this radical and, as a result, improving the removal effectiveness of HA. On the other hand, when the pH of the reaction medium rises, HA's solubility rises, increasing its interaction with radicals in the reaction medium and improving removal efficiency [42,43]. However, pH 7 was chosen as the optimum since the removal efficiency did not increase much. Pourzamani et al. [38] obtained similar results on the influence of pH on removal efficiency, which was compatible with the findings of this investigation.
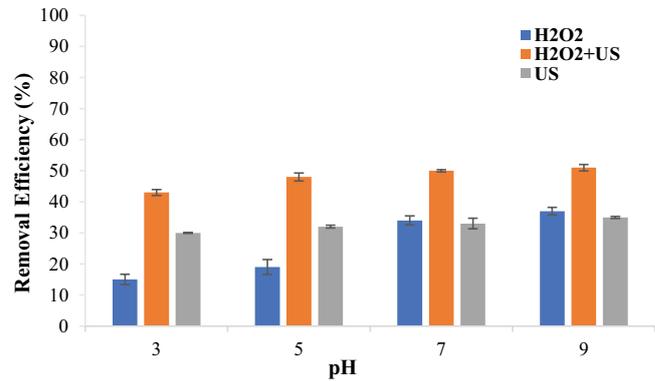
3.3. Effect of HA concertation on removal efficiency

The effects of HA concentrations of 10, 25, and 50 mg/L were studied. As can be observed in Fig. 3, the removal efficiency declined from 38% to 30% for the US, 41% to 20% for H_2O_2, and 58% to 35% for US + H_2O_2 as the HA concentration increased from 10 to 50 mg/L. This was because raising the concentration of HA increased the formation of by-products and intermediates. Due to the strong tendency of by-products and intermediates to react with $^{\bullet}$OH, they inhibited additional decomposition of HA in the reaction medium, lowering its removal effectiveness [9]. Since the quantity of radicals generated in the reaction medium remains constant, the rate of radical consumption increases as the concentration increases, leaving fewer radicals to degrade additional HA molecules, resulting in a loss in removal efficiency at high HA concentrations [15]. As a consequence, a concentration of 10 mg/L was considered to be the optimal concentration. Similar results were achieved by Dehghani et al. [44], who found that removal efficiency declined with increasing concentration.

3.4. Effect of reaction time on HA removal

Under optimal operating conditions, 5, 10, 20, and 30 min of reaction time were investigated to determine the influence of reaction time. The maximum removal effectiveness was found at a reaction time of 30 min, which was 40.5%, 39.3%, and 53%, respectively, in the presence of H_2O_2 and ultrasonic separately, in the presence of H_2O_2 and ultrasonic combined. In addition, in the presence of H_2O_2 alone, the lowest elimination efficiency was found throughout the 5 min reaction time. However, because the removal efficiency did not significantly improve with the increased contact time, the optimal process time was determined to be 5 min. Long-term retention may be the cause of increased efficiency as contact time increases. Long-term exposure of HA molecules to free radicals in the reaction media might be the explanation for the improvement in efficiency as contact time increases [11,16]. However, because the number of these molecules in the reaction media was not particularly large, there was not a considerable improvement in removal efficiency. Pourzamani et al. [38] found that in the presence of both ultrasonic and hydrogen peroxide, the
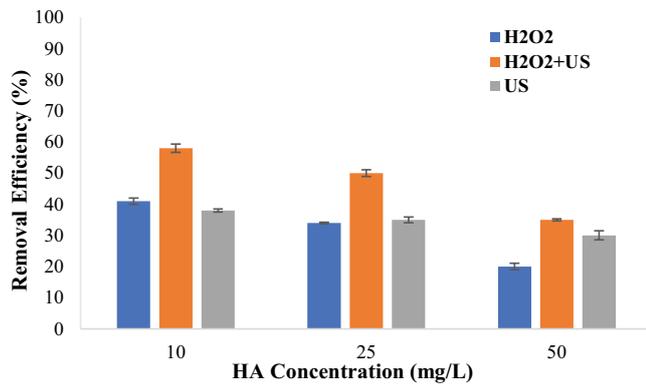
Fig. 3. Effect of HA concentration changes on HA removal efficiency (contact time 5 min; pH 7; H_2O_2 0.10 mM).
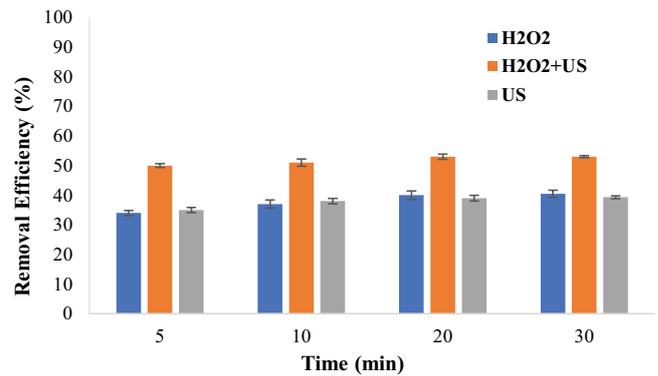

Fig. 4. Effect of contact time changes on HA removal efficiency (HA concentration 10 mg/L; pH 7; H_2O_2 0.10 mM).

Table 1
Pseudo-first-order kinetic parameters of HA degradation

C_0 (mg/L)	R^2	K_{obs}	Line equation
10	0.938	277.778	$y = -0.0036x - 0.8555$
25	0.945	232.558	$y = -0.0043x - 0.6755$
50	0.980	384.615	$y = -0.0026x - 0.4214$

best removal efficiency of HA was 20 min, which is consistent with the findings of this investigation.

3.5. HA degradation process kinetic

The pseudo-first-order kinetic [Eq. (7)] model was used to determine HA degradation kinetic [40].

$$\ln \frac{C_t}{C_0} = -K_{obs}t \tag{5}$$

where C_0 and C_t (mg/L) are the initial and final HA concentrations, respectively, and K_{obs} is the rate of the reaction constant (min⁻¹). The amount of K_{obs} was calculated for the various concentrations listed in Table 1 by graphing $\ln(C_t/C_0)$ vs time.

The data in Table 1 shows that the HA degradation process follows pseudo-first-order kinetics. This study's findings are congruent with those of Dehghani et al. [40].

3.6. Effect of H_2O_2 + US process on real water

To assess the process's effectiveness on a real water sample, a sample of drinking water with specifications NO_3 29.5 mg/L, total hardness 462 mg/L, SO_4 164 mg/L, chloride 81 mg/L, pH 7.8, total dissolved solids (TDS) 665 mg/L, and Na 54 mg/L was obtained from Shiraz University of Medical Sciences and the optimal conditions were applied to it; the removal effectiveness was 41%. The presence of cations, anions, and other interfering components in the process may influence the degradation of humic acid molecules and function as scavengers of generated radicals, which may explain

why the removal efficiency of humic acid in real water samples has decreased [15].

4. Conclusion

The elimination of HA from aqueous solutions using ultrasonic waves and hydrogen peroxide was studied in this work utilizing only US and hydrogen peroxide. Initial HA concentration, pH, reaction time, and hydrogen peroxide concentration in HA removal were all evaluated as factors impacting process performance. The findings revealed that just adding varied amounts of H_2O_2 enhanced HA removal effectiveness. The removal efficiency rose as the pH increased from 3 to 7, but there was no significant difference in the removal efficiency when the pH increased from 7 to 9. In addition, when the initial concentration was increased, the removal effectiveness of HA decreased, with the maximum removal efficiency observed during a 5-min reaction time in the presence of ultrasonic and hydrogen peroxide under optimal conditions (HA concentration 10 mg/L, pH 7, and H_2O_2 0.10 mM).

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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