

Use of ultraviolet and ultraviolet /peroxide hydrogen processes for degradation of humic substances from aqueous solutions

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ABSTRACT

In this study, the degradation of humic acid was studied using advanced photochemical oxidation by exposing humic acid aqueous solution with low-pressure mercury vapor lamp as a UV light source after the addition of hydrogen peroxide. The effect of different parameters such as H₂O₂ dosage, pH, and initial concentration of humic acid on the removal efficiency of UV/H₂O₂ was evaluated and investigated in detail. Increase of initial H₂O₂ dosage (up to optimum dosage) and also increase of humic acid concentration resulted in the decrease of humic acid degradation. The residual concentrations of humic acid were measured for assessing the process performance and understanding the process reaction behavior. The results showed that humic acid was degradable in the presence of hydrogen peroxide under UV irradiation. In the absence of H₂O₂, the degradation efficiency was very negligible. The results show 91% humic acid removal in 60 min of reaction time when 30 mmol L⁻¹ of H₂O₂ aqueous solution was added to the solution compared with only 20% of removal in similar conditions and in the absence of H₂O₂. Investigation of the kinetics of the UV/H₂O₂ process demonstrated that the semi-log plot of the humic acid concentration versus time was linear, which suggested a first order reaction.

KEY WORDS: HUMIC ACID, WATER SOLUTIONS, UV, PEROXIDE HYDROGEN

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INTRODUCTION

Humic acid (HA) is one of the major components of humic substances which arise from the microbial degradation of biomolecules. Natural organic matters (NOMs) such as HA enters water from natural and artificial sources. These materials are caused a variety of problems in treatment operations and distribution systems due to having unpleasant smell and taste, yellow to brown color, reaction with chlorine, and formation of disinfection by-products (DBPs). NOMs could also stimulate the growth of the micro-organisms in water distribution pipelines as well as production of biologically unstable water and other unwanted water quality issues such as metal complexes (Vilhunen *et al.* 2010; Alkan *et al.* 2007 Wang *et al.* 2014).

THMs exhibit mutagenic properties during the chlorination step water treatment. The guideline for THMs in drinking water announced by World Health Organization (WHO) states that DBPs should not exceed 100 μgL^{-1} (Zhang and Minear, 2006). Consequently, the removal of HA from surface waters or wastewaters is important because of health and environmental concerns (Jacangelo *et al.* 1995).

HA may account for up to 90% of NOM. Actually, it is not possible to completely remove NOM by conventional methods in water treatment plants. Different treatment technologies have been used in practice to improve NOM removal such as ion exchange, sorption, and membrane processes. But, many of these are not acceptable in terms of economy and efficiency. Advanced oxidation processes (AOPs) are frequently applied for the oxidation of organic and toxic materials. These processes are based on the production of hydroxyl radicals which demonstrate great efficacy in breaking down organic materials (Katsumata *et al.* 1987; Magdaleno & Coichev 2005; Panyapinyopol *et al.* 2007; Golmohammadi *et al.* 2016).

AOPs are defined as the processes that involve highly reactive species, specifically hydroxyl radicals (oxidation potential = 2.8 V) in sufficient quantities to oxidize the majority of complex organic chemicals in water and wastewater. Hydroxyl radicals have a significant role in the treatment of organic materials due to their high reactivity and lack of selectivity toward organic compounds. UV photolysis and UV/H₂O₂ have been successfully used in removing NOMs from water solutions. However, if the UV absorbance of water is considerably high, the efficient treatment might require great reaction time of UV. In such cases, removing the majority of organic materials by other methods prior to oxidation treatment leads to decreased UV absorbance and improved NOM mineralization (Zepp *et al.* 2007; Vilhunen *et al.* 2010; Hui *et al.*, 2011; Bazri *et al.* 2012; Hiroshi *et al.* 2013 and Yazdanbakhsh *et al.* 2014).

The advantage of UV/H₂O₂ including high reactivity, low sludge production, and capability to achieve complete destruction (mineralization) of pollutants to less harmful by-products (Hui *et al.*, 2011; Bazri *et al.* 2012; Hiroshi *et al.* 2013). In UV/ H₂O₂ process, optimum H₂O₂ dosage has been reported for each target compound, because the characteristics and concentration of the organic compounds can directly influence H₂O₂ utilization for degrading organic matters (Kruithof *et al.* 2007; Pereira *et al.* 2007; Kim *et al.* 2009).

Upon the UV irradiation, H₂O₂ absorbs UV energy and results in the production of HO•. The excess H₂O₂ can react with HO• radicals (Sheikhmohammadi *et al.* 2013) and serve as an HO• inhibiting agent in the UV/H₂O₂ process (Vilhunen *et al.* 2010; Lamsal *et al.* 2011; Jung *et al.* 2012; Chandran *et al.* 2014). Many studies have illustrated the effectiveness of the UV/H₂O₂ process in the oxidation and mineralization of various organic pollutants and this process has been widely studied for the remediation of both ground and drinking waters (Lamsal *et al.* 2011; Jung *et al.* 2012). Therefore, the aim of this study was investigate the suitability and efficiency of the UV and UV/H₂O₂ processes for the removal of HA as an important problem in treatment operations and distribution systems

MATERIAL AND METHODS

The chemical materials were of reagent grade. Commercially, available HA was extracted from peat coal. HA was contained 56.2% of C, 3.91% of H, 36.1% of O, and 1.07% of N. It was dried for 1 h at 110°C. A stock solution was prepared by dissolving 1.0 g of HA in 1000 ml deionized water. Then, it was filtered through a 0.45 μm glass-fiber-membrane filter and stored in 4°C conditions. The as-synthetic sample was prepared by adding the measured amount of HA stock solution to the deionized water. 30% hydrogen peroxide (H₂O₂, DUKSAN) was also employed. HA and H₂O₂ solutions were accurately prepared daily to the required diluted concentrations. Ultra-pure water was employed for all the dilutions.

All the photochemical experiments were carried out in a batch photo-reactor, which is schematically shown in Fig. (1) R-52 Mineralight® Lamp which was used a grid design and produces a highly uniform 254 nm UV light with high intensity was used as a light source. A J-225 Black Ray intensity meter was employed to measure the UV irradiation intensity (I). Interior surface of the photo-reactor was made of stainless steel (20 cm diameter and 30 cm depth) for the photo-oxidation of HA in aqueous solutions. UV lamps were fixed parallel at the center of the reactor and covered with a quartz sleeve. The UV lamps were turned on 10 min before performing every

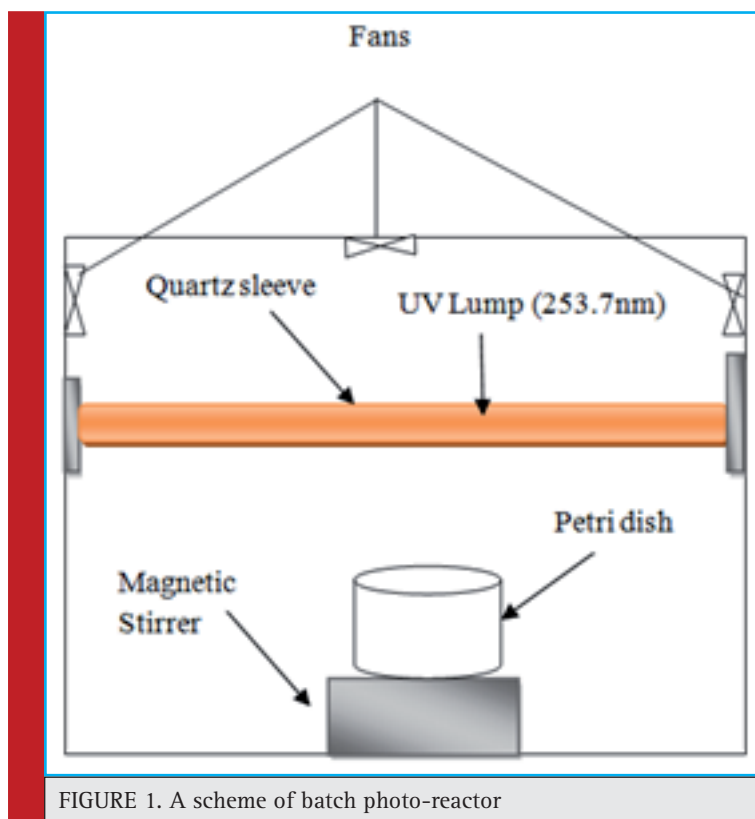


FIGURE 1. A scheme of batch photo-reactor

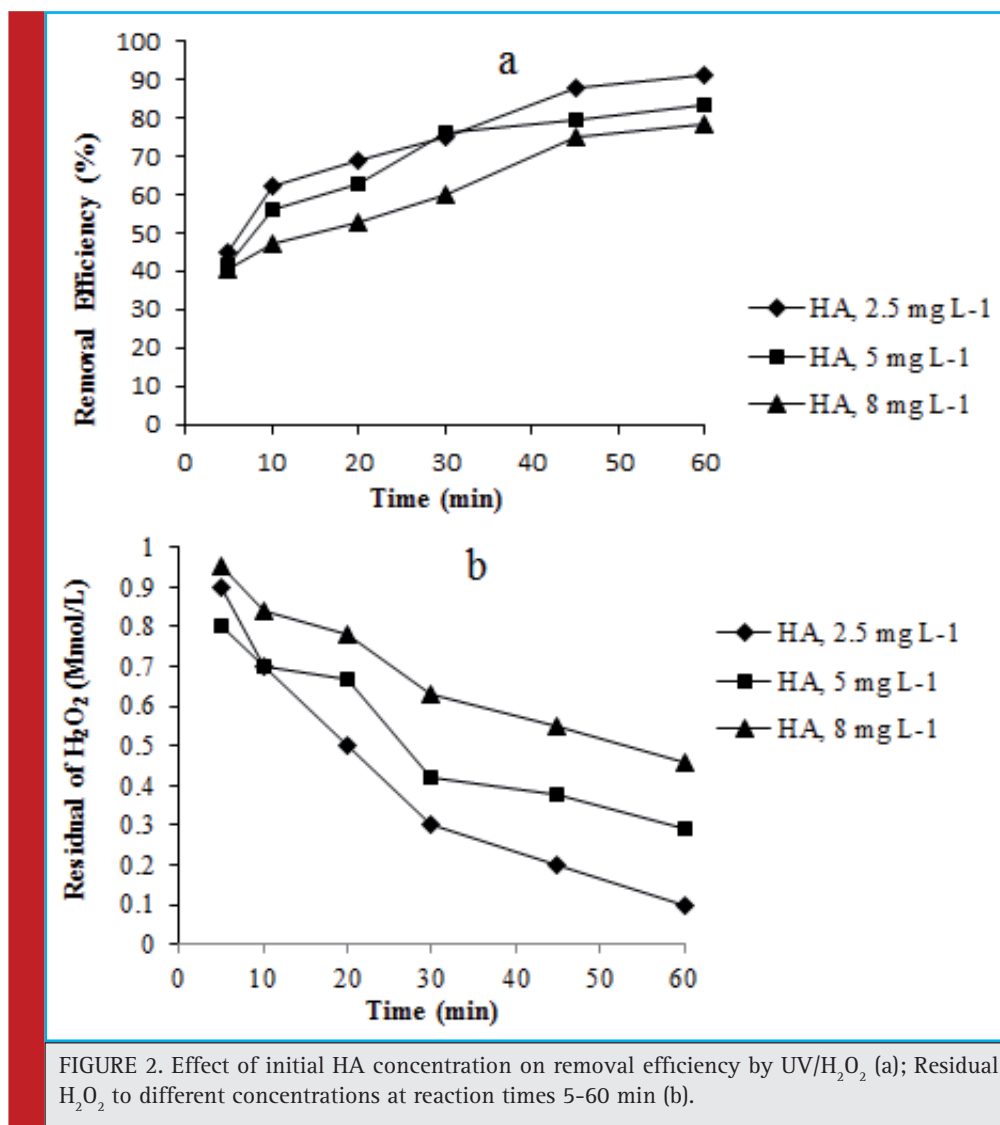
experiment. The total UV intensity was controlled by turning on different numbers of UV lamps. Air cooling system, with electrical fans, was used to prevent the lamp from overheating and to maintain the temperature at 25°C.

The UV/H₂O₂ experiments were carried out in a photo-reactor batch type made of a Pyrex-based material with 2 L volume capacity and a UV-C lamp from LIGHTTECH ($\lambda_{\text{max}} = 254 \text{ nm}$ with the light intensity of approximately 0.05 W cm^{-2}) attached to the center of the reactor. An aqueous HA solution was prepared and subjected to the UV/H₂O₂ process. The selected levels to run the experiments were: H₂O₂ (10–100) Mmol L⁻¹, pH (3–11), reaction time (5–60 min), and initial HA concentrations (2.5–8 mg L⁻¹), set at the beginning of the reactions. The removal efficiency of HA by the UV/H₂O₂ process was determined at the optimum values of pH, H₂O₂ dosage, and reaction time. Reactions were quenched by removing the excess of H₂O₂ by catalase or NaHSO₃ according to the analysis. A Perkin-Elmer (Lambda-II) double beam spectrophotometer was used for the absorption measurements at 254 nm using the 10 mm quartz cell (Rosenfeldt *et al.* 2006).

RESULTS AND DISCUSSION

Fig. (2) presents the HA residual fraction at three different concentrations with initial HA of 2.5, 5, and 8 mg

L⁻¹. At first, H₂O₂ concentration was set fixed in the reaction mixture as 30 Mmol L⁻¹. pH was adjusted at 7.0. As shown in Fig. (2a), it seems that the removal efficiency was less for all the concentrations within the initial reaction for the 5 min period. With increasing reaction time, it was observed that the low concentrations of HA had higher removal efficiency than high concentrations. Removal efficiency for the concentrations of 2.5 and 8 mg L⁻¹ was 78 and 91% after 60 min, respectively. As in Fig. (2b), the residual fraction of H₂O₂ was higher for HA 8 mg L⁻¹ than HA 2.5 mg L⁻¹; therefore, the solution with higher HA concentration was content of higher the residual H₂O₂. Reduction of HA was related to the existence of HO• radicals in the solution; therefore, considering the dual roles of humic substances at UV light photon absorption and HO• scavenging, higher removal of HA at lower concentrations was expected. Also, at high humic concentration, HA competed with H₂O₂ for UV absorption and resulted in the reduced light absorption by H₂O₂ to a greater degree. However, the high generation of H₂O₂ at high concentration of HA might be due to the formation of H₂O₂ as the by-product of sunlight-induced reactions in natural waters, which would more appear when HA with certain concentration was irradiated by UV light (Matilainen & Sillanpa 2010; Chang *et al.* 2010; Haji *et al.* 2011; Jung *et al.* 2012; Gonzalez *et al.* 2013).



The HA solution with the concentration of 2.5 mg L⁻¹ was exposed to UV radiation in the absence of H₂O₂. Fig. (3) shows relative residual concentrations for HA versus time. The samples of the treated solution withdrawn at different times and the residual concentrations of HA were measured. As shown in Fig. (3a), only 20% HA removal was observed after 60 min of the solution exposure to UV radiation. However, the result of this research was different from that of some studies by other researchers, which can be related to the dissimilarity in the experimental conditions, mainly the UV radiation intensity (Vilhunen *et al.* 2010; Lamsal *et al.* 2011). Because it is deduced that the residual concentration of HA in the presence of UV radiation linearly decreased versus time, the reaction of HA with UV radiation was of first order (Lamsal *et al.* 2011), indicating that the removal of HA was affected by UV may be because of UV energy absorbed by HA. Another reason for the

improvement of HA removal could be explained by •OH radicals generated by UV photolysis of water (water could be dissociated into a hydrogen atom and hydroxyl radical when exposed to UV irradiation with the wavelength of less than 200 nm (Shemer&Linden 2007; Alkan *et al.* 2007; Comninellis *et al.* 2008; Hu *et al.* 2008).

UV (occurring at 185 nm) is more effective than UV (occurring at 254 nm) in the photolysis of water, because more energy is transferred to the aqueous solution via UV (6.72 eV) vs UV (4.89 eV). Since this research was focused on the degradation of HA by UV, as shown in Fig. (3a), HA degradation by UV was very slow. Accordingly, the presence of a UV sensitive agent (an oxidizing reagent, for example H₂O₂) was necessary to enhance the HA degradation rate. Therefore, during the UV treatment, the effect of H₂O₂ addition on HA degradation was investigated. The presence of H₂O₂ is necessary to accelerate the HA decomposition process by UV.

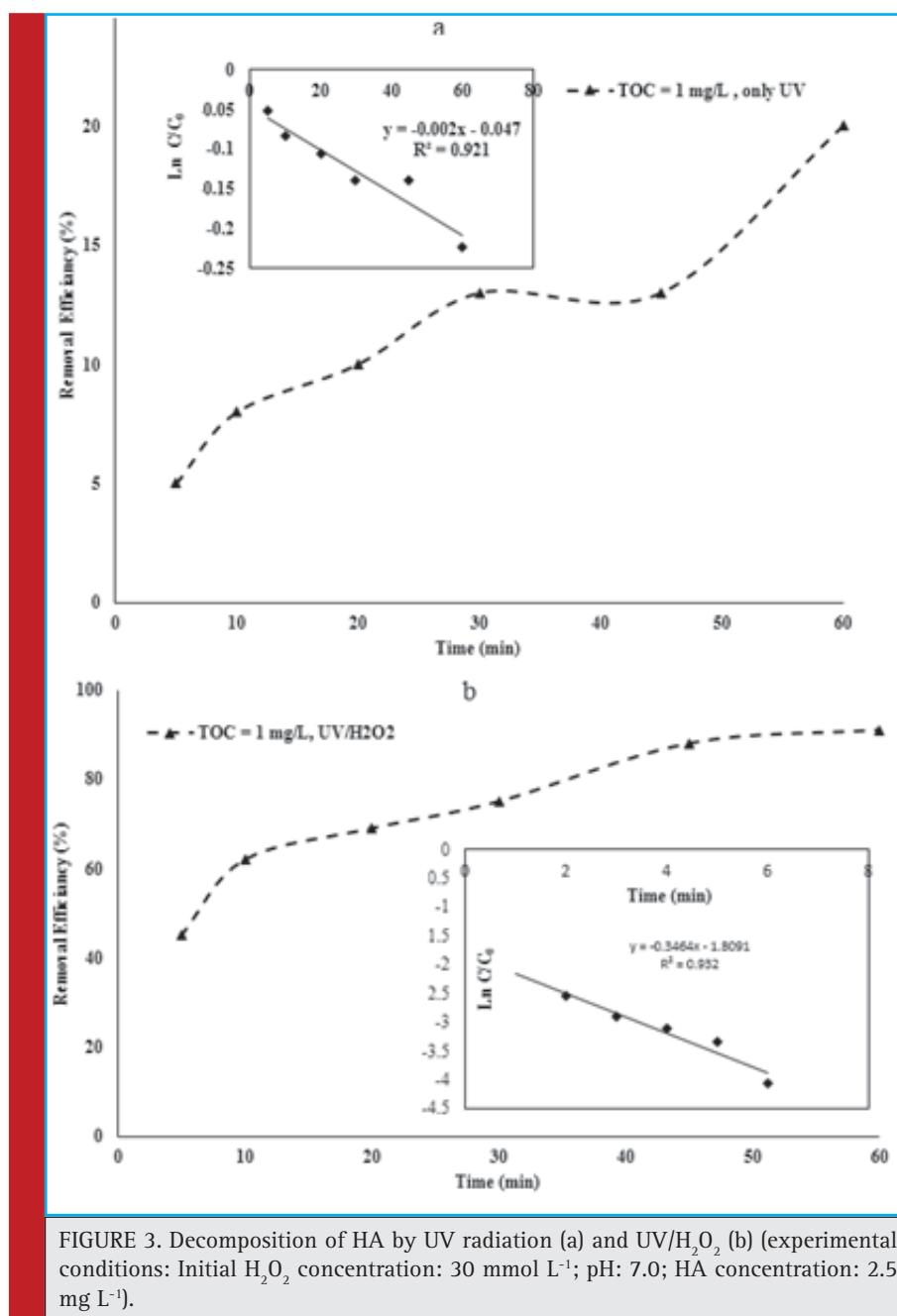
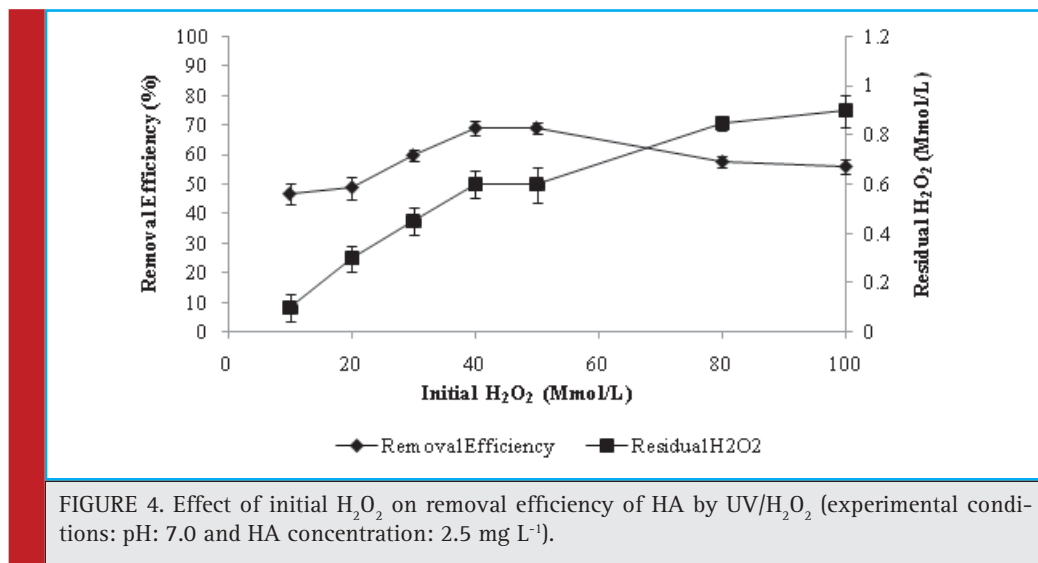


FIGURE 3. Decomposition of HA by UV radiation (a) and UV/H₂O₂ (b) (experimental conditions: Initial H₂O₂ concentration: 30 mmol L⁻¹; pH: 7.0; HA concentration: 2.5 mg L⁻¹).

The solution temperature was maintained at 25°C and pH of the solution was adjusted to 7.0 (Kruithof *et al.* 2007; Li *et al.* 2008). In accordance with Fig. (3b), the highest removal efficiency of HA was 91% in the presence of H₂O₂ and 60 min of exposure to UV radiation which could be compared with the percentage of HA removal by UV radiation in the absence of H₂O₂ due to provoking the generation of •OH by UV with $\lambda_{\max} = 254$ nm in the presence of H₂O₂. Fig. (3b) shows that relative residual concentrations of HA decreased linearly over time. Therefore, it can be concluded that adding H₂O₂

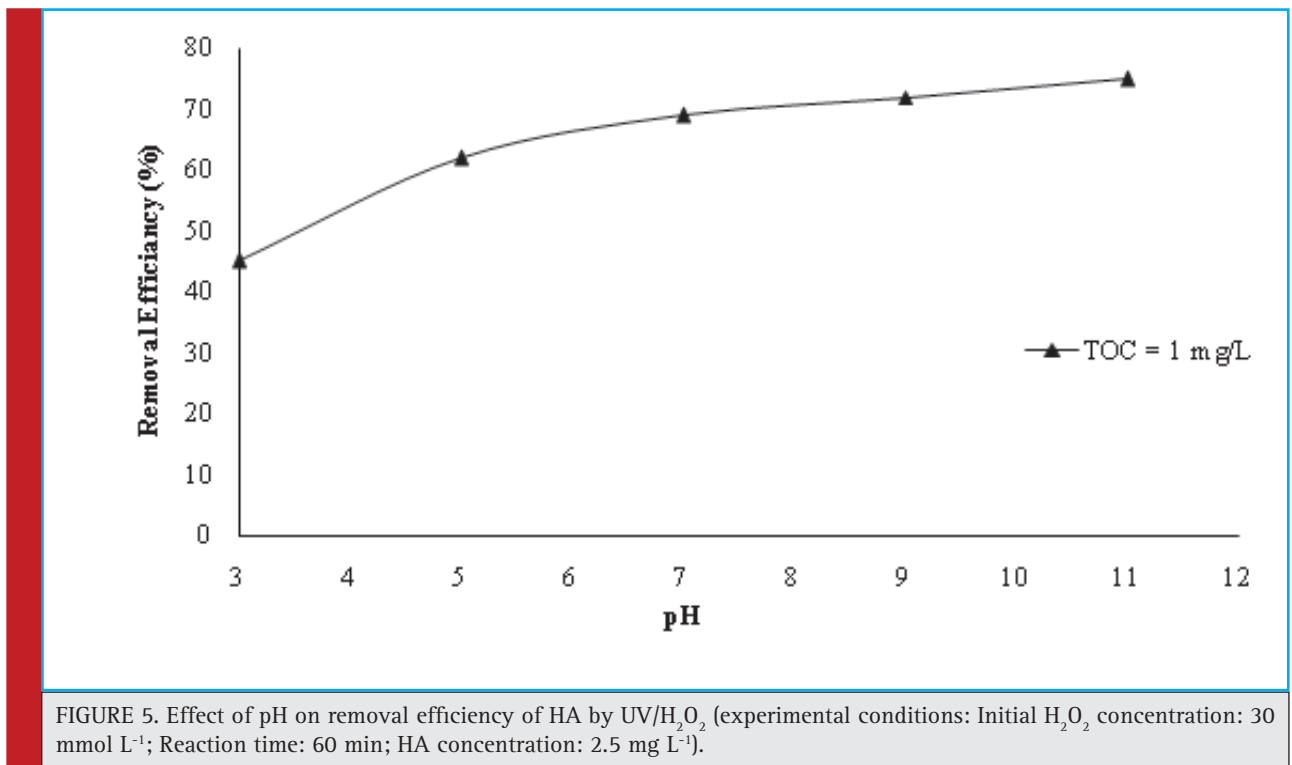
to the solution subjected to UV radiation could result in the generation of •OH radicals by the photolysis of H₂O₂ molecules (Sheikhmohammadi *et al.* 2013; Yazdanbakhsh *et al.* 2014); consequently, these radicals oxidized HA molecules.

The cost of H₂O₂ accounts for most of the cost of AOP processes, so the determination of optimum H₂O₂ amount is quite important in AOP processes. The effect of initial H₂O₂ concentration on the residual fractions of HA and H₂O₂ is presented in Fig. (4). To determine optimum H₂O₂ concentration, the experiments were conducted by



varying the amount of H₂O₂ from 10 to 100 Mmol L⁻¹ (pH was fixed at 7 and HA concentration was 2.5 mg L⁻¹). Fig. (4) shows that the efficiency of HA removal was maximum at 40 Mmol L⁻¹ of H₂O₂. It was observed that HA removal efficiency increased from 47% to 70% as H₂O₂ concentration went up from 10 to 40 Mmol L⁻¹. An increase in the concentration of H₂O₂ up to 40 Mmol L⁻¹ did not significantly affect the removal of HA and there was no significant difference between the dosages of 40 and 50 Mmol L⁻¹ (Chan *et al.* 2010). It is interesting

to find that, with increasing H₂O₂ concentration up to 50 Mmol L⁻¹, the degradation rate of HA was decreased, since with increasing H₂O₂ from 50 to 100 Mmol L⁻¹, removal efficiency decreased from 70% to 56% at 30 min, which might be due to three reasons: 1- At excessive amounts of H₂O₂, it acts as a scavenger of •OH to produce perhydroxyl radical (HO₂•) (Yazdanbakhsh *et al.* 2014), which might be due to three reasons: 1- At excessive amounts of H₂O₂, it acts as a scavenger of •OH to produce perhydroxyl radical (HO₂•) (Yazdanbakhsh *et al.*



2014). According to reaction 4 (HO_2^\bullet has much lower oxidization capacities than $^\bullet\text{OH}$).

2- The second reason might be due to the reaction pathways of HA degradation, mineralizing HA through UV photolysis alone, and $^\bullet\text{OH}$ radical oxidation as follows:

3- As shown in Fig. (3), the residual fraction of H_2O_2 increases with the increasing initial concentration of H_2O_2 that is due to decrease of decomposition H_2O_2 . Reduction of H_2O_2 concentration from 40 to 10 Mmol L^{-1} resulted in a decrease in HA removal efficiency from 70% to 47%, which might be because of partial oxidation at H_2O_2 concentrations of lower than optimum values. At the optimum concentration of H_2O_2 , the generation of hydroxyl radicals increased (Sheikhmohammadi *et al.* 2013; Yazdanbakhsh *et al.* 2014).

Therefore, an H_2O_2 dosage of 40 Mm L^{-1} with the HA removal efficiency of 70% was chosen as the optimum dosage. Reactions were quenched by removing the excess of H_2O_2 by catalase or NaHSO_3 . Masschelein study group used a diluted enzyme catalyst solution made from *Micrococcus lysodeikticus* was used to destroy unreacted H_2O_2 and the amount of residual H_2O_2 was determined via the molybdate-catalyzed iodometric spectrophotometry method (Rosenfeldt & Linden 2007; Elmolla & Chaudhuri. 2010; Nie *et al.* 2010; Ghaderpoori & Dehghani 2015).

To determine the optimum pH for the UV/ H_2O_2 process, pH was varied from 3 to 11. Fig. (5) shows that HA removal by the UV/ H_2O_2 process was affected by pH. As presented in Fig. (5), maximum HA removal was achieved at pH 7-11, 30 Mmol L^{-1} H_2O_2 , and 60 min reaction time. Higher HA removal at pH 7-11 can be compared with pH <9. After the 30 min reaction, 70% of HA was degraded at the pH of 7.0 as compared with less than 45% at the pH of 3.0. At pH < 7.0, a substantial decrease in the efficiency of HA removal was observed (Yuan *et al.* 2009; Nie *et al.* 2010).

These phenomena could be explained by: 1- UV reacts more slowly with H_2O_2 ; therefore, the degradation of H_2O_2 is slow 2- Scavenging effect of $^\bullet\text{OH}$ by H^+ becomes significant in very low pH ranges (the ions of H^+ may have inhibited the generation of hydroxyl radicals necessary to achieve the UV/ H_2O_2 oxidation (Li *et al.* 2008; Yuan *et al.* 2009; Nie *et al.* 2010).

At higher pH values (alkaline), a rapid increase in HA removal was observed, because in this pH At higher pH values (alkaline), a rapid increase in HA removal was observed, because in this pH range (alkaline solutions), the UV/ H_2O_2 process was most effective and HA removal increased significantly. Increased removal efficiency at optimum pH might be because of two possible reasons: H_2O_2 stability is less disturbed, which provides further support to earlier work that HA can be totally removed

in the pH range of 7-11 in 30 min by UV/ H_2O_2 system, resulting in an increase in the oxidation potential of $^\bullet\text{OH}$. Also, it might produce intermediate products that cause an increase in OH radicals (Li *et al.* 2008; Yuan *et al.* 2009; Nie *et al.* 2010).

CONCLUSION

In this study, the UV and UV/ H_2O_2 oxidation processes were employed for the degradation of HA in water solutions. The residual concentration of humic acid was measured for assessing the process performance and understanding the process reaction behavior. The results showed that HA was degradable in the presence of hydrogen peroxide under UV irradiation. In the absence of H_2O_2 , the degradation efficiency was very negligible. It was achieved 91% degradation of HA in 60 min when 40 Mmol L^{-1} of H_2O_2 was added to the solution compared with only 20% degradation achieved in 60 min in the absence of H_2O_2 . The effects of H_2O_2 , pH, and initial concentration of HA were investigated in this research. It was concluded that HA degradation was decreased with excess H_2O_2 amounts and higher HA concentrations. On the other hand, not necessarily guarantee the improvement of the HA degradation in excess H_2O_2 values because of scavenging effect of the $^\bullet\text{OH}$ to produce the per-hydroxyl radical and mineralizing of HA through UV photolysis alone (the UV oxidation of humic acids might dominate the removal of HA in the UV/ H_2O_2 process) and $^\bullet\text{OH}$ radical oxidation. Hence, the degradation of HA was retarded when the H_2O_2 concentration increased and when the humic degradation was dominated by UV oxidation. Also, the solution with higher humic concentration is content of the high residual H_2O_2 . Reduced HA at high concentration was due to the presence of $^\bullet\text{OH}$ in the solution and UV light photon absorption; therefore, considering the dual roles of humic substances at UV light photon absorption and $^\bullet\text{OH}$ scavenging, higher removal of HA was expected at lower concentrations. At higher humic concentrations, HA competed with H_2O_2 for UV absorption and resulted in reduced light absorption by H_2O_2 to a greater degree.

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