

PHOTODEGRADATION OF HUMIC ACIDS IN THE PRESENCE OF HYDROGEN PEROXIDE

**Aleksandar Veselinović¹, Aleksandar Bojić^{2*}, Milovan Purenović²,
Danijela Bojić², Tatjana Andjelković²**

¹Faculty of Medicine, Department of Pharmacy, Niš, Serbia

²Faculty of Sciences and Mathematics, Niš, Serbia

Degradation of humic acids (HA) in water by UV/H₂O₂ oxidation was studied. The photolysis experiments were conducted in a batch photoreactor with ten low-pressure mercury vapor lamps ($\lambda = 253.7$ nm), as a UV light source. The residual concentrations of HA were monitored for assessment of process performance and understanding of process behavior. Without H₂O₂ addition, UV radiation has negligible effect on HA in water solutions, so researches were conducted with different H₂O₂ concentrations. Results show exponential decreasing of the HA concentrations, which indicates great degradation capability of the UV/H₂O₂ process. The rate of HA degradation is highest at the beginning of the treatment process and it decreases with time. Increase of HA concentration has negative effect on UV/H₂O₂ oxidation due to the absorption of UV radiation and scavenging of hydroxyl radicals. The addition of H₂O₂ greatly improved efficiency of HA degradation by UV light and 80 – 90% of the HA was removed within 30 min of photolysis. Excessive dosage of H₂O₂ doesn't improve the degradation of HA and the optimum H₂O₂ dose was 0.01 mol dm⁻³ for HA oxidation.

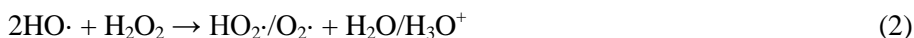
Key words: humic acids, photodegradation, UV light, H₂O₂, photoreactor

INTRODUCTION

The presence of natural organic matter (NOM) in both surface and ground water supplies has received much public attention in recent years because toxic disinfection byproducts (DBPs) can result from chlorination procedures in the water treatment processes. Due to the presence of a wide variety of NOM and the necessity of the

* Adresa autora: Aleksandar Bojić, Prirodno-matematički fakultet, Višegradska 33, 18000 Niš, Srbija
E-mail: bojica@gmail.com

chemical disinfection process to protect the public health, many water utilities have to face the problem of DBPs formation. For the control of DBPs, some alternative treatments have been proposed, including adsorption, reverse osmosis and advanced oxidation processes (AOPs) [1-3]. Among the AOPs, the UV/H₂O₂ has received widespread attention for potential application in drinking water and wastewater treatment [2-5]. The effectiveness of this process was understood due to the formation of hydroxyl radicals (HO·), which show an extraordinarily oxidizing power in the reaction mixture and can thus non-selectively mineralize a different of organic contaminants at a considerable rate. The initiation and the subsequent propagation and termination of radicals are described by following reactions [6,7]:



Hence, the emphasis of this study was placed on the assessment of UV/H₂O₂ process for the removal of humic acids in water [8-10]. Despite the increasing interest in this process for water and wastewater treatment, there is little information available regarding destruction of the NOM by the UV/H₂O₂ process [3]. The aim of this study is to examine the effects of the initial concentration on the photodegradation of humic acid in order to evaluate the applicability of UV/H₂O₂ technology to the remediation of DBP precursors in water. The composition of the NOM was simulated by commercial humic acids.

EXPERIMENTAL

Reagents

All used chemicals were of reagent grade and used without further purification, unless otherwise indicated. Commercially available HA was purchased from Fluka (Germany). Deionized water (< 5 µS_{cm}⁻¹) was used to prepare all aqueous solutions. The stock solution of humic acids was prepared by dissolving a suitable amount of HA in deionized water under alkaline condition and this solution was then filtered through 0.45 µm RC syringe filter (Millipore, USA). The resultant humic concentration of stock solution was 1000 mgdm⁻³ as a dissolved organic carbon (DOC).

Before each experiment, working solutions were prepared by diluting the HA stock solution, and adding known amounts of H₂O₂ and carbonate/bicarbonate. The pH of the solutions was adjusted pH-metrically to the required value by using hydrochloric acid (0.1; 1 M) or sodium hydroxide (0.1; 1 M), without buffering.

Photoreactor

All photochemical experiments were carried out in a batch photoreactor especially made in our laboratory, schematically shown in Fig. 1. Low-pressure mercury vapor lamps, with a maximum emission primarily at 253.7 nm (28W TUV, Philips, Holland), were used as a light source. Ten UV lamps were fixed parallel in a reflector at the top

of the photoreactor. Air cooling system, with electrical fans, was used to vent the heat outside of the reactor and to prevent the lamps of overheating. Interior surface of the photoreactor was made of stainless steel, because of light reflection.

The UV lamps were turned on 10 min before performing the every experiment. Intensity of UV radiation was measured by UV-meter Solarmeter model 8.0 UVC (Solartech, USA). The total UV intensity was controlled by turning on different number of UV lamps and the maximum intensity was $1950 \mu\text{Wcm}^{-2}$ (with all ten UV lamps on) at the distance of 220 mm, from working solution surface.

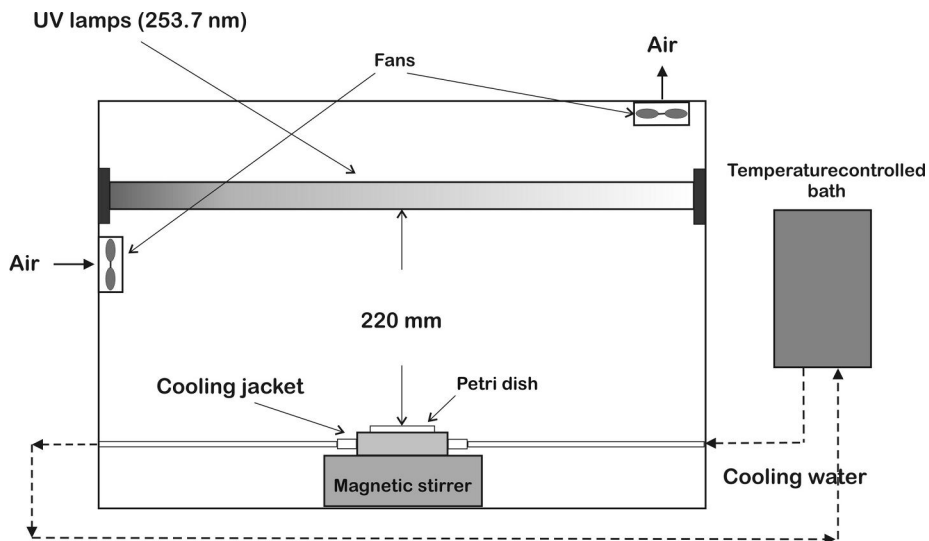


Figure 1. Schematic diagram of photoreactor

Experimental procedure and analysis

The irradiation of water solutions was carried out in an open glass Petri dish, with 400 ml working volume (\varnothing 30 cm), put on magnetic stirrer at the bottom of the photoreactor. Petri dish was immersed in a waterbath to maintain a constant temperature. Aliquot of 20 ml was taken to measure the initial humic acid concentration. Samples of 20 ml were withdrawn from Petri dish for analysis of DOC at different time interval. All of the experiments were conducted at pH 7. All the samples taken from the reactor were filtered through $0.45 \mu\text{m}$ syringe filter and acidified with few drops of diluted HCl, prior to DOC analysis. The humic acids concentration in solution, represented as DOC, was measured by using a total organic carbon analyzer TOC 5000A (Shimadzu, Japan).

RESULTS AND DISCUSSION

Fig. 2. presents the residual profiles of HA at three different initial concentrations of humic acids: 2.0, 4.0 and 8.0 mgdm^{-3} , during UV photolysis in presence of H_2O_2 . The H_2O_2 concentration in the reaction mixture was 0.01 moldm^{-3} , initial pH was 7.0 and

intensity of UV radiation was $1950 \mu\text{Wcm}^{-2}$. The addition of peroxide was necessary since UV radiation on humic acid alone, has negligible effect (results not shown). To compare the effect of different HA concentrations directly, in Fig. 2. concentration change during treatment is given as c/c_0 . Results show exponential decreasing of the HA concentrations, which indicate great degradation capability of the UV/H₂O₂ process. Fig. 2 shows that the degradation curves for all initial HA concentrations have the similar profiles. A rapid decrease of HA concentration was observed at the beginning of the treatment, with partly slower concentration drop during subsequent period. After 5 minutes of treatment, the reduction of HA concentration was from 35 to 20%, for initial concentration from 2.0 to 8.0. After 60 minutes of treatment residual of HA was about 5% in samples with initial HA concentrations of 2.0 and 4.0 mgdm⁻³, but in the case of initial concentration 8.0 mgdm⁻³ it was about 17%. At the end of the treatment (90 min) model solutions had 1.2, 2 and 7.5% of HA residue, respectively. As can be seen from the trend of residual profiles, the HA degradation is not expected to improve much if reaction carries on beyond 90 min.

The results also show differences in degradation rates (k_{obs}) vs. initial HA concentration (Fig. 3). Samples with initial concentrations 2.0 and 4.0 mgdm⁻³ have very similar degradation rates, 0.047 and 0.043 min⁻¹, respectively, and curves of their concentration change are nearly overlapping (Fig. 2.). With initial HA concentration of 8.0 mgdm⁻³ photo degradation process is significantly less efficient and residual concentrations are much higher during entire process (Fig. 2.). Corresponding k_{obs} is 0.028 min⁻¹, rather less than in the case of initial HA concentrations 2.0 and 4.0 mg dm⁻³ (Fig. 3.), which indicates the significant impact of HA concentration on its photodegradation in water.

One of the causes for this occurrence is absorption of UV radiation (254 nm) by HA, which leads to competition with H₂O₂ in absorption process. Aromatic compounds are generally UV absorbers, which should lead to a decrease in the UV transparency of the solution and thus to a decrease in UV treatment efficiency. The absorption is mainly due to conjugated bonds as well as to the presence of free electron pairs on heteroatoms. With increase of HA concentration, the amount of adsorbed UV radiation by HA grows, which leads to the reduction of OH· radicals concentration.

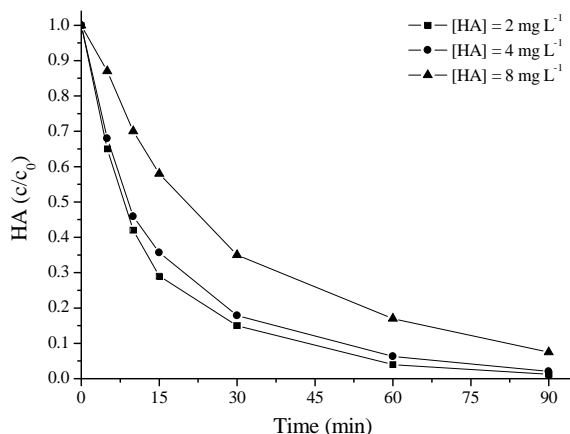


Figure 2. Residual HA concentration versus time at different initial HA concentrations. Initial H_2O_2 concentration was 0.01 mol dm^{-3} , initial pH was 7.0, temperature was kept at $25 \pm 0.5^\circ\text{C}$ and intensity of UV radiation was $1950 \mu\text{Wcm}^{-2}$.

On the other hand, HA acting as $\text{OH}\cdot$ radical scavenger. It inactivates active advanced oxidation processes intermediate, by making relatively stable $\text{HA}\cdot$ radical [11].

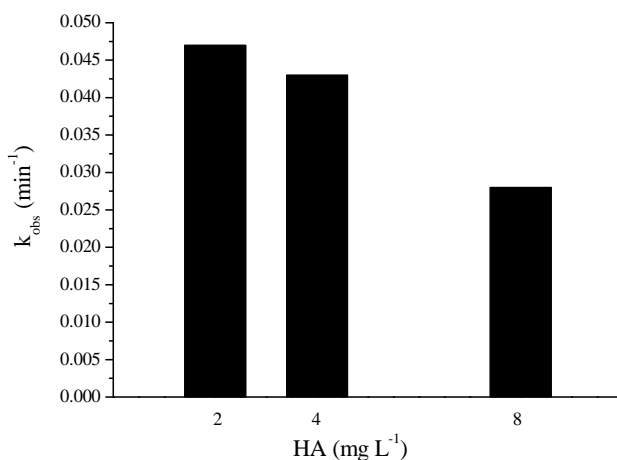


Figure 3. Observed rate constant for humic acid degradation vs. initial HA concentration.

CONCLUSION

This study show that the UV/ H_2O_2 oxidation is promisable treatment for degradation of humic acids in water. The addition of a small amount of H_2O_2 in the UV irradiation

system promotes greatly the degradation rate of aqueous humic acids related to UV radiance alone. Increase of HA concentration has negative effects at UV/H₂O₂ process, due to the absorption of UV radiation and scavenging of hydroxyl radicals.

REFERENCES

- [1] D.M Owen, G.L Amy, Z.K. Chowdhury, R. Paode, G. McCoy and K. Viscosi. Journal of the American Water Works Association 87(1) (1995) 46.
- [2] D.W. Hand, D.L. Perram and J.C. Crittenden. J. Am. Water Works Ass. 87 (6) (1995) 84.
- [3] J.M. Symons and K.L. Worley. J. Am. Water Works Ass. 87(11) (1996) 66.
- [4] D.W. Sundstrom, H.E. Klei, T.A. Nalette, D.J. Reidy and B.A. Weir. Hazard. Waste Hazard. Mater. 3(1) (1986) 101.
- [5] F.J. Beltrán, M. González, F.J. Rivas and P. Alvarez. Environ. Toxic. & Chem. 15 (1996) 868.
- [6] J.H. Baxendale and J.A. Wilson. Trans. Faraday Soc. 53 (1956) 344.
- [7] D.H. Volman and J.C. Chen. J. Am. Chem. Soc. 81 (1959) 4141.
- [8] C.H. Liao AND M.D. Gurol. Environ. Sci. Technol. 29(12) (1995) 3007.
- [9] G.S. Wang, S.T. Hsieh and K.Y. Chiou. In Proceedings: AWWA Water Quality Technology Conference. AWWA, Denver, CO. (1997)
- [10] G.S. Wang and S.T. Hsieh, C.S. Hong. Water Res. 34 (15) (2000) 3882.
- [11] P.L. Brezonik and J. Fulkerson-Brekken. Environ. Sci. Technol. 32 (1998) 3004.

IZVOD

FOTODEGRADACIJA HUMINSKIH KISELINA U PRISUSTVU VODONIK-PEROKSIDA

(Naučni rad)

Aleksandar Veselinović¹, Aleksandar Bojić², Milovan Purenović², Danijela Bojić², Tatjana Andjelković²

¹Medicinski fakultet, Odsek za farmaciju, Niš, Srbija

²Prirodno-matematički fakultet, Niš, Srbija

Proučavana je degradacija huminskih kiselina (HA) u vodi UV/H₂O₂ oksidacijom. Eksperimenti fotolize su vršeni u fotoreaktoru sa 10 živinih lampi niskog pritiska ($\lambda = 253.7$ nm), kao izvorom UV zračenja. Rezidualna koncentracija HA je praćena radi procene efikasnosti i prirode procesa. Bez primene H₂O₂, UV zračenje ima zanemarljiv efekat na vodene rastvore HA, zbog čega su istraživanja vršena sa različitim koncentracijama H₂O₂. Rezultati pokazuju eksponencijalno opadanje rezidualne

koncentracije HA, što ukazuje na veliku efikasnost UV/H₂O₂ procesa. Na početku tretmana brzina degradacije HA je najveća i smanjuje se sa vremenom. Povećanje koncentracije HA ima negativan efekat na UV/H₂O₂ oksidaciju, zbog apsorpcije UV zračenja i skavendžing efekta prema hidroksil radikalima. Dodavanje H₂O₂ značajno povećava efikasnost degradacije HA UV zračenjem i 80-90% HA je uklonjeno nakon 30 minuta fotolize. Povećanje koncentracije H₂O₂ nije povećalo degradaciju HA i optimalna doza H₂O₂ je oko 0.01 mol dm⁻³.

Ključne reči: huminska kiselina, fotodegradacija, UV zračenje, H₂O₂, fotoreaktor

Received / Priljen: 29. maj 2009. godine

Accepted / Pihvaćen: 10. septembar 2009. godine