

## Original Article

# Photocatalytic Degradation of Humic Acid by Ag/ZnO Nanoparticles under UV<sub>C</sub> Irradiation from Aqueous Solutions

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Received: 12/10/2013

Accepted: 3/2/2014

### Abstract

**Introduction:** Humic acid (HA) is the original disinfection byproduct produced in processors in water treatment. So, removing it is necessary before water chlorination. In the present study, photodegradation of humic acid in water using Ag/ZnO nano particle under UV<sub>C</sub> irradiation in batch system was investigated.

**Material and Methods:** Photocatalytic study was carried out to evaluate the effect of UV<sub>C</sub> (15w), irradiation time of (10 - 40min), pH (5 - 9), initial humic acid concentration of (10-50 mg/L) and Ag/ZnO dosage of (0.2 – 0.8 g/L) on humic acid removal. HA concentration was monitored spectrophotometrically by measuring the HA absorbance at 254 nm.

**Results:** HA removal efficiency was obtained 88% at pH 7, Ag/ZnO dosage 0.6 g/L, initial humic acid concentration 25 mg/L and irradiation time of 40 min. The removal of HA from aqueous solution increased by increasing irradiation time and decreasing initial HA concentration. Also, the kinetic study was consistent with pseudo-first order reaction.

**Conclusion:** The results showed that photocatalytic degradation process using Ag/ZnO nanoparticles can be used efficiently for HA removal from aqueous solutions.

**Keywords:** Humic acid, water treatment, Ag/ZnO nanoparticle, photocatalytic oxidation

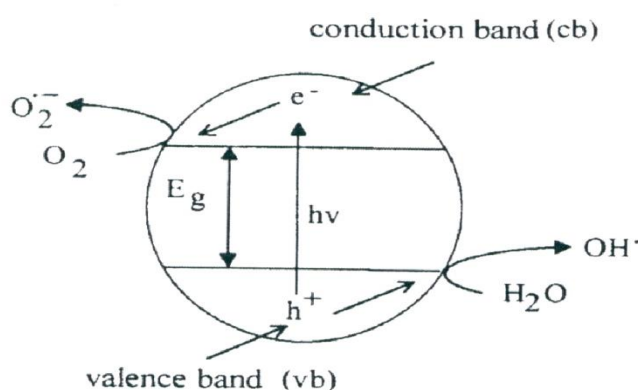
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## Introduction

Humic acid is one of the natural organic matters (NOMs) and a precursor of disinfection byproduct in drinking water treatment. Also, reaction between chlorine and humic acid in water treatment causes generating carcinogenic substances, such as, trihalomethanes (THMs) and haloacetic acid (HAAs), hence, the removal of humic acid is necessary before water chlorination <sup>[1, 2]</sup>. For the removal of humic acid-containing water, various biological, physical and chemical methods such as microbial biodegradation, coagulation, filtration, ozonation, adsorption and heterogeneous photocatalysis have been used <sup>[3-6]</sup>.

Advanced oxidation process (AOP) is an alternative method for the complete degradation of many organic pollutants <sup>[7-10]</sup>.

Photocatalytic oxidation is one of the AOPs processes. When a photocatalyst absorbs radiation, in which  $h\nu > E_g$  (gap energy), an  $e^-$  from its filled valence band (VB) is promoted to its conduction band (CB) and valence band holes ( $h^+$ ) are formed (figure 1). Electrons reduce any available species, including  $O_2$ , converting water and hydroxide ion to hydroxyl radicals. The  $OH^\bullet$  radicals are very strong oxidizing agents and can easily attack the organic molecules. This finally leads to their complete mineralization. Among various semiconductors employed as photocatalyst,  $TiO_2$  and  $ZnO$  are the most preferable materials due to their non-toxic, insoluble, stability and high photo-activity properties <sup>[11-13]</sup>.



**Figure 1:** The photocatalyst interface under UV- illumination

$Ag/ZnO$  is one of the heterostructure photocatalyst with high catalytic activity <sup>[14-16]</sup> that has attracted many researchers' attention. The aim of this study was evaluation of HA

photocatalytic degradation in water using  $Ag/ZnO$  nanoparticles under  $UV_C$  irradiation.

## Material and methods

### Reagents

All purchased chemicals were reagent grade and used without further purification. Humic Acid (Sigma- Aldrich, USA) was commercial product used without further purification.

### Apparatus

A UV-vis spectrophotometer (Optima SP-3000 Plus model, Japan) with 10 mm quartz cells was used to make absorbance measurements. A Wegtech pH meter (Mi 151 22, England) was used for pH controlling, and a Magnetic stirrer and Heater (HS 6000, Iran) was used for stirring the solutions.

### Photocatalytic degradation

Stock solution of the HA ( $50 \text{ mgL}^{-1}$ ) was prepared by dissolving 50 mg of humic acid in appropriate amount of NaOH 0.1 N and diluting to 1000 mL. Working solutions were prepared daily by diluting the stock solution with distilled water. Ag/ZnO was prepared according to procedures used in litterateur <sup>[17]</sup>.

In all cases, during the experiments, 50 mL of humic acid solution ( $25 \text{ mgL}^{-1}$ ) containing

### Results

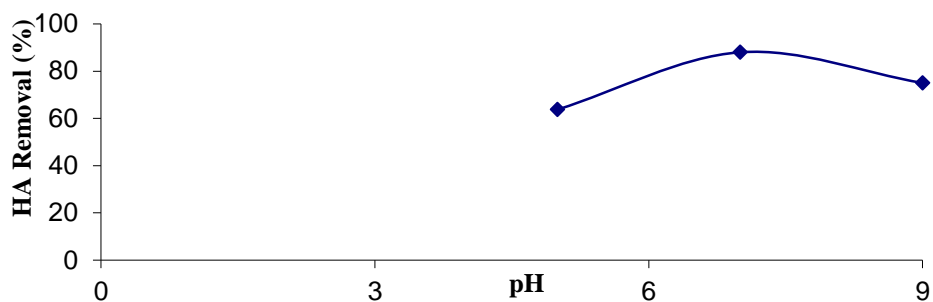
The applied humic acid is receipted in acidic solution; therefore, the effect of pH on the degradation of HA was investigated by using Ag/ZnO over the pH range of 5–9. The

the appropriate quantity of photocatalyst magnetically was stirred. In order to achieve the maximum adsorption of the sample onto the heterogonous photocatalyst, the cell was left for 20 min in the dark condition. The  $UV_C$  irradiation was carried out using Philips lamp (15 W). After photodegradation, photocatalyst particles were separated by centrifuge. Concentration of humic acid was determined spectrophotometrically by measuring the absorbance of HA at  $254 \text{ nm}$  <sup>[18]</sup>. The pH of solution was adjusted by 0.1 N sodium hydroxide or 0.1 N hydrochloric acid. The degree of photodegradation (X) as a function of time is given by:

$$X = \frac{C_0 - C}{C_0}$$

where  $C_0$  is the initial HA concentration, and C is the HA concentration at time  $t$ . The light source emitted light right above the sample. The intensity level of light was controlled by fixing the distance between the light source and the sample.

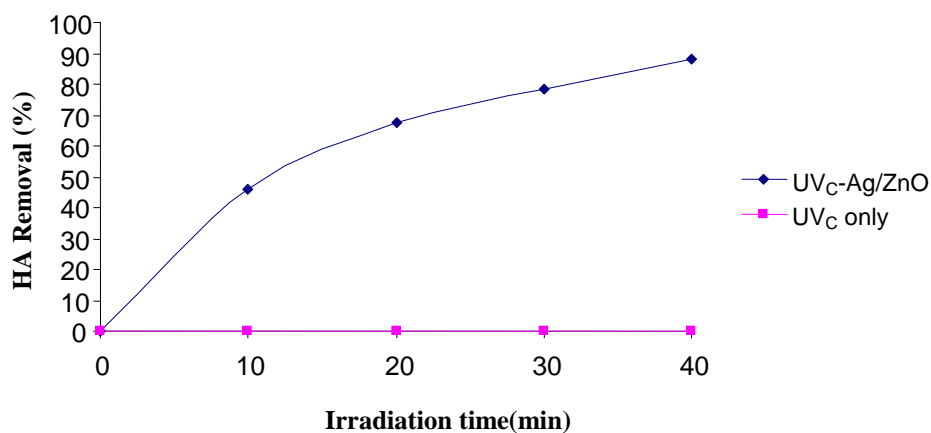
influence of pH on the photo-oxidation of humic acid was studied. Results show that faster degradation of HA was achieved at pH = 7 (Figure 2).



**Figure 2:** The effect of pH on the removal of HA on Ag/ZnO; (HA = 25 mg/L, Ag/ZnO = 0.6 g/L)

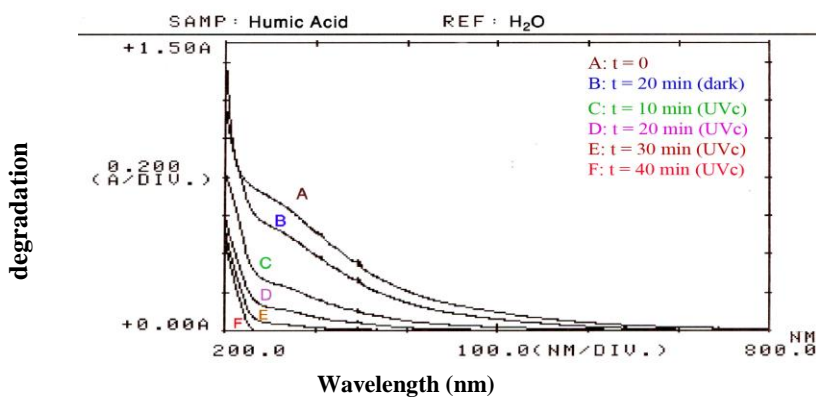
In order to determine the effect of irradiation time, decomposition experiments of HA (25 mgL<sup>-1</sup>) were conducted, in the presence of mixed Ag/ZnO semiconductor, UV<sub>C</sub> and a blank experiment in the absence of semiconductor. Results of these experiments (Figure 3) showed that the degradation of HA

in presence of the photocatalyst and UV<sub>C</sub> irradiation leads to disappearance of approximately 88% of HA after 40 min. A blank experiment under UV irradiation and in the absence of Ag/ZnO demonstrated no changes in the solution absorbance during stirring the sample.



**Figure3:** Removal of HA by UV<sub>C</sub> and UV<sub>C</sub>-Ag/ZnO (pH 7, Ag/ZnO=0.6g/L, HA=25 mg/L)

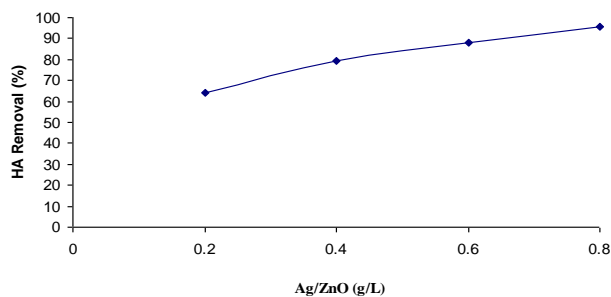
The changes in absorption spectra of humic acid during UV<sub>C</sub>-Ag/ZnO process at different irradiation time intervals are shown in figure 4. The decrease of the absorption band of HA at λ = 254 nm indicates a rapid degradation of sample. Complete degradation of HA was observed after 60 minutes in the optimized conditions.



**Figure 4:** UV-Vis spectral changes of humic acid recorded during the UVc – Ag/ZnO photodegradation at different UVc irradiation times (Ag/ZnO= 0.6 g/L; pH 7, HA=25 mg/L)

In order to determine the effect of catalyst dose, the experiments were conducted by changing catalyst's concentration from 0.2 to 0.8 g/L for HA solution of 25 mg/L at pH = 7. The effect of the level of Ag/ZnO on the photodegradation efficiency is shown in Figure

5. Experiments run with different concentrations of synthesized Ag/ZnO reveal that initial slopes of the curves increase greatly by increasing catalyst loading from 0.2 to 0.8 g/L and there after the rate of degradation remains almost constant.

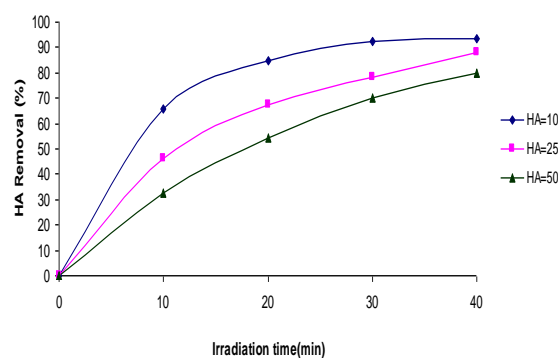


**Figure 5:** Photodegradation of HA vs different Ag/ZnO concentration

(HA=25mg/L, pH=7 and irradiation time =40min).

After optimizing the pH condition and catalyst dose (pH 7.0 and catalyst dose of 0.6 g/L) the photocatalytic degradation of HA was carried out by varying the initial HA concentrations from 10 to 50 mg/L. Figure 6 shows the time dependent graphs of degradation of HA at different concentrations of the solutions. As the concentration of the HA increased, the rate of

photodegradation decreased.



**Figure 6:** Effect of the initial HA concentration on

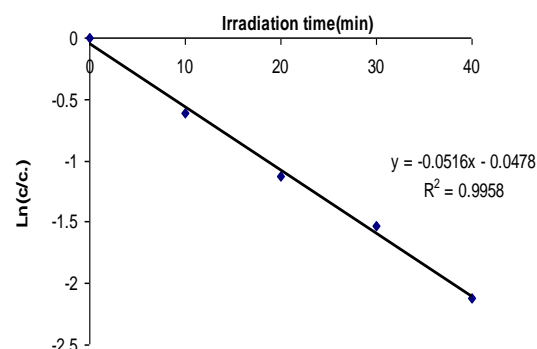
photocatalytic degradation of HA (pH=7, Ag/ZnO = 0.6 g/L)

Kinetic models are used to examine the rate of the photocatalytic process and the potential rate control step. The kinetic data obtained from batch studies have been analyzed using pseudo-first and pseudo-second order models. For this purpose, 0.6 g/L of photocatalyst was used, reaction times were 10, 20, 30, 40 minutes and the pH of the solutions were adjusted to 7. The results are shown in Figure 7. According to the results, the correlation coefficient values ( $R^2$ ) of pseudo-first order and pseudo-second order models were obtained 0.9958 and 0.9116 respectively. So, by comparing those models, the correlation coefficients for the pseudo-first order kinetics

### Discussion

The results indicated that UVc radiation can not be the main factor in removal of humic acid. Still applying UVc coupled to Ag/ZnO nanoparticle increased humic acid removal efficiency. The results of the present study are in accordance with the study by Movahediyani and Rezaei<sup>[19]</sup> on effect of UV radiation in the dye removal and also the study by Dziedzic et al.<sup>[20]</sup> on the photocatalytic degradation of humic acid via TiO<sub>2</sub>/UV and solar UV. Wei et al.<sup>[21]</sup> studied the effects of UV<sub>C</sub> radiation on the removal of humic acid coupled to ozonation and Fenton. Their results agree with the results of the present study. According to the results, photocatalytic degradation efficiency of humic acid increased with increasing the reaction time. PH is one of the

model fits are higher than the correlation coefficients derived from pseudo-second order model fits. This suggests that the photodegradation of HA follows pseudo-first order kinetic.



**Figure 7:** pseudo -first order Kinetic models of photocatalytic degradation of HA,

(humic acid = 25 mg/L, pH=7, Ag/ZnO=0.6 g/L

most important parameters that by influencing the ionization state of pollution and surface characteristics of the applied catalyst could affect the removal of contaminants. According to the results, the maximum efficiency of the humic acid removal was observed at pH=7. The results of the present study is in concordance with Yang et al.<sup>[22]</sup> study on humic acid removal by TiO<sub>2</sub>/UV.

The results showed that by increasing the amount of catalyst from 0.2 to 0.6 g/L and by increasing nanoparticle concentration, removal efficiency of humic acid significantly increased. But at the concentration of 0.8 g/L, partial removal efficiency of humic acid had a little increase. Increasing the removal efficiency in the higher catalyst concentration

can be achieved by exposing the catalyst surface to the most active places, and the possibility of higher effects of UV radiation.

Asgari et al.'s<sup>[23]</sup> study on the performance of catalytic ozonation by activating carbon for the humic acid removal from aqueous solutions indicated that removal efficiency of humic acid increases with increasing catalyst dose. Tabatabaee's<sup>[17]</sup> study on preparation of Ag/ZnO nanoparticles and the catalytic effect on the degradation of reactive dyes indicated that by increasing catalyst concentration up to 160 ppm, photocatalytic degradation increased and then decreased.

The investigation of initial humic acid concentration effect on the photocatalytic removal of humic acid showed that with increasing humic acid, concentration removal efficiency decreases.

### Conclusion

The results of this study showed that mere UV<sub>C</sub> radiation (15w) did not affect the removal of humic acid. However, in the presence of Ag/ZnO nanoparticles, removal efficiency greatly increased. With increasing photocatalyst concentration from 0.2 to 0.6 g/l, increasing the removal efficiency of humic acid was considerable and at higher dosages of Ag/ZnO, removal efficiency of humic acid increased to some extent.

Similar results were obtained by Tabatabaee (2011)<sup>[17]</sup> and khorsandi et al. (2008)<sup>[19]</sup>. Wu et al.<sup>[24]</sup> studied the efficiency of Fenton process in the degradation of humic acid and showed that oxidation rate and removal efficiency of humic acid greatly depends on initial humic acid concentration and with increased initial humic acid, concentration removal efficiency decreased. According to the results, the photocatalytic process of removing humic acid follows pseudo first-order kinetic with  $R^2 = 0.9958$ . Tabatabaee<sup>[17]</sup> investigated the catalytic effect of Ag/ZnO in the degradation of reactive dyes and Asgari et al.<sup>[23]</sup> studied the performance of Catalytic ozonation by activated carbon in the removal of humic acid from aqueous solutions, and obtained similar results. Khorsandi et al.<sup>[18]</sup> also achieved the same results.

The results showed that with increasing PH from 5 to 7, removal efficiency increased and at PH=7, maximum removal efficiency of humic acid was observed. Results showed that by increasing the initial humic acid concentration from 10 to 50 mg/L, the removal efficiency decreased. Reaction kinetic of humic acid by Ag/ZnO photocatalyst in the presence of UV<sub>C</sub> is well described by a pseudo- first- order reaction.

## References

1. Valencia S, Marín J.M, Restrepo G, Frimmel F.H. Evaluations of the TiO<sub>2</sub>/simulated solar UV degradations of XAD fractions of natural organic matter from a bog lake using size-exclusion chromatography. *Water Research*. 2013; 47(14): 5130–5138
2. Xue G, Liu H, Chen Q, Hills C, Tyrer M, Innocenta F. Synergy between surface adsorption and photocatalysis during degradation of humic acid on TiO<sub>2</sub>/activated carbon composites. *Journal of Hazardous Materials*. 2011; 186(1): 765–772.
3. Katsumata H, Sada M, Kaneco S, Suzuki T, Ohta K, Yobiko Y. Humic acid degradation in aqueous solution by the photo-Fenton process. *Chemical Engineering Journal*. 2008; 137(2): 225–230.
4. Alborzfar M, Jonsson G, Gron C. Removal of natural organic matter from two types of humic ground waters by nanofiltration. *Water Research*. 1998; 32(10): 2983–2994.
5. Kati R, Vaisanen P, Metsamuuronen S, Kutovaara M, Nystrom M. Characterization and removal of humic substances in ultra and nanofiltration. *Desalination*. 1998; 118(1-3): 273–283.
6. Wiszniowski J, Robert D, Surmacz-Gorska J, Miksch K, Weber J.V. Photocatalytic decomposition of humic acids on TiO<sub>2</sub>. Part I: Discussion of adsorption and mechanism. *Journal of Photochemistry and Photobiology*. 2002; 152(1-3): 267–273.
7. Fox M, Dulay M.T. Heterogeneous Photocatalysis. *Chem. Rev.* 1993; 93(1): 341-357
8. Ibhaddon A.O, Fitzpatrick P. Heterogeneous Photocatalysis: Recent Advances and Applications. *Catalysts*. 2013; 3(1):189-218.
9. Kansal S.K, Singh M. and Sud D. Studies on photodegradation of two commercial dyes in aqueous phase using different photocatalysts. *Journal of Hazardous Materials*. 2007 ; 141(3): 581-590.
10. Giri R.R, Ozaki H, Taniguchi S, and Takanami R. Photocatalytic ozonation of 2,4-dichlorophenoxyacetic acid in water with a new TiO<sub>2</sub> fiber. *Int. J. Environ. Sci. Tech.* 2008; 5(1): 17-26.
11. Evgenidou E, Konstantinou I, Fytianos K, Poulios I, and Albanis T. Photocatalytic oxidation of methyl parathion over TiO<sub>2</sub> and ZnO suspensions. *Catalysis Today*. 2007; 124(3-4): 156-162.
12. Tabatabaee M, Ghotbifard A, Mozafari AA. Photocatalytic Degradation and Kinetic study of Textile Azo Dyes Direct Blue 71 and Black 19 in ZnO suspended solution. *Fresenius Environ.* 2012; 21(6): 1468-1473.
13. Behnajady M.A, Modirshahla N, and Hamzavi R. Kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst. *Journal of Hazardous Materials*. 2006; 133(1-3): 226-232.
14. Gao Sh, Jia X, Yang Sh, Li Zh, Jiang K. Hierarchical Ag/ZnO micro/nanostructure: Green synthesis and enhanced photocatalytic performance. *Journal of Solid State Chemistry*. 2011; 184(4): 764–769.
15. Zheng Y, Chen C, Zhan Y, Lin X, Zheng Q, Wei K, and Zhu J. Photocatalytic Activity of Ag/ZnO Heterostructure Nanocatalyst: Correlation between Structure and Property. *Journal of Phys. Chem.* 2008; 112(29): 10773-10777.
16. Lu W, Liu G, Gao S, Xing S, Wang J. Tyrosine-assisted preparation of Ag/ZnO nanocomposites with enhanced photocatalytic performance and synergistic antibacterial activities. *Nanotechnology*. 2008; 19(44): 445-711.



17. Tabatabaee M, Mirrahimi SA. Photodegradation of Dye Pollutant on Ag/ZnO Nanocatalyst under UV-irradiation. *Oriental Journal of Chemistry*. 2011; 27(1):65-70.
18. Khorsandi H, Amin MM, Bina B. Removal of Humic Substances from Water by Advanced Oxidation Process Using UV/TiO<sub>2</sub> Photo Catalytic Technology. *Journal of Water & Wastewater*. 2008; 19 (68): 25-32. [Persian]
19. Movahedian Attar H, Rezaei R. Investigating the Efficiency of Advanced Photochemical Oxidation (APO) Technology in Degradation of Direct Azo Dye by UV/H<sub>2</sub>O<sub>2</sub> Process. *Journal of Water & Wastewater*. 2006; 17(59):75-83. [Persian]
20. Dzedzic J, Wodka D, Nowak P, Warszynski P, Simon Ch, Kumakiri I. Photocatalytic Degradation Of The Humic Species As A Method Of Their Removal From Water – Comparison Of UV And Artificial Sunlight Irradiation. *Physicochem. Probl. Miner. Process*. 2010; 45:15-28.
21. Wei MC, Wang Ks, Hsiao TE, et al. Effects of UV irradiation on humic acid removal by ozonation, Fenton and Fe<sub>0</sub>/air treatment: THMFP and biotoxicity evaluation. *Journal of Hazardous Materials*. 2011; 195: 324-331.
22. Yang JK, Lee SM. Removal of Cr (VI) and humic acid by using TiO<sub>2</sub> photocatalysis. *Chemosphere*. 2006;63(10):1677-1684.
23. Asgari Gh, Hashemian SJ, Mosavi Gh. Evaluation of Performance Catalytic Ozonation Process with Activated Carbon in the Removal of Humic Acids from Aqueous Solutions. *Sci J Hamdan Uni Med Sci* 2010; 17(4): 25-33.[Persian]
24. Wu Y, Zhou S, Qin F, Zheng k, Ye x. Modeling the oxidation kinetics of Fenton's process on the degradation of humic acid. *Journal of Hazardous Materials*. 2010; 179(1-3):533-539.