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Original Article

Photocatalytic Degradation of Humic Acid by Ag/ZnO Nanoparticles under UV_C Irradiation from Aqueous Solutions

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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, photodegredation of humic acid in water using Ag/ZnO nano particle under UVc irradiation in batch system was investigated.

Material and Methods: Photocatalytic study was carried out to evaluate the effect of UVc (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 degredation 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 [1, 2]. 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 [3-6].

Advanced oxidation process (AOP) is an alternative method for the complete degradation of many organic pollutants [7-10]. Photocatalytic oxidation is one of the AOPs processes. When a photocatalyst absorbs radiation, in which hν>Eg (gap energy), an ē from its filled valance band (VB) is promoted to its conduction band (CB) and valance band holes (h^+) are formed (figure 1). Electrons reduce any available species, including O_2, converting water and hydroxide ion to hydroxyl radicals. The $OH^•$ 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 [11-13].

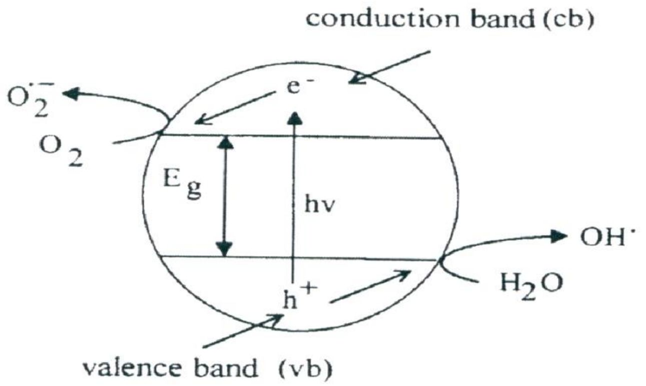

Figure 1: The photocatalyst interface under UV- illumination

Ag/ZnO is one of the heterostructure photocatalyst with high catalytic activity [14-16] 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 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 [17].

In all cases, during the experiments, 50 mL of humic acid solution (25 mgL^{-1}) containing 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 nm [18]. 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.

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 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).

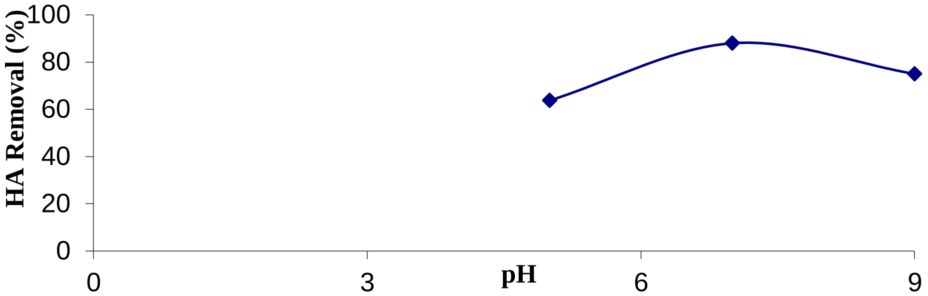

Figure 2: The effect of pH on the removal of HA on Ag/ZnO; (HA = 25 m/gL, Ag/ZnO = 0.6 g/L)

In order to determine the effect of irradiation time, decomposition experiments of HA (25 mgL^{-1}) were conducted, in the presence of mixed Ag/ZnO semiconductor, UV_C 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_C irradiation leads to disappearance of approximately 88% of HA after 40 min. A blank experiment under UV irration and in the absence of Ag/ZnO demonstrated no changes in the solution absorbance during stirring the sample.

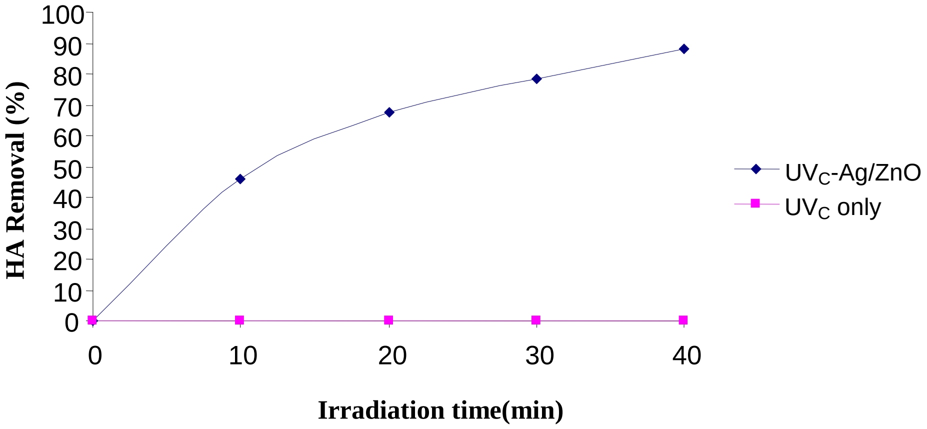

Figure3: Removal of HA by UV_c and UV_c-Ag/ZnO (pH 7, Ag/ZnO=0.6g/L, HA=25 mg/L)

The changes in absorption spectra of humic acid during UVc-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.

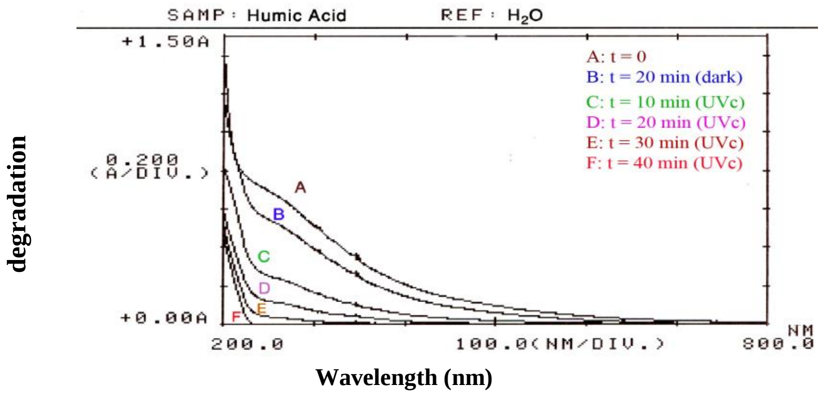

Figure 4: UV-Vis spectral changes of humic acid recorded during the UVc – Ag/ZnO photodegredation at different UVc irradiation times (Ag/ZnO= 0.6 g/L; pH 7, HA=25 mg/L)

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.

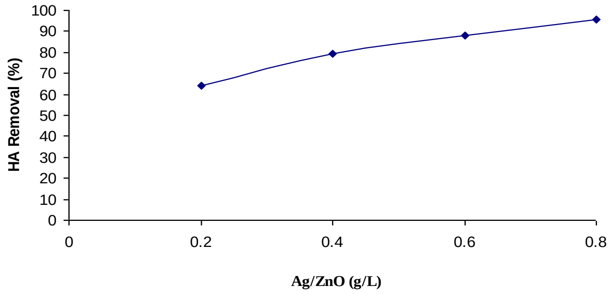

Figure 5: Photodegradation of HA vs different Ag/ZnO concentration

(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.

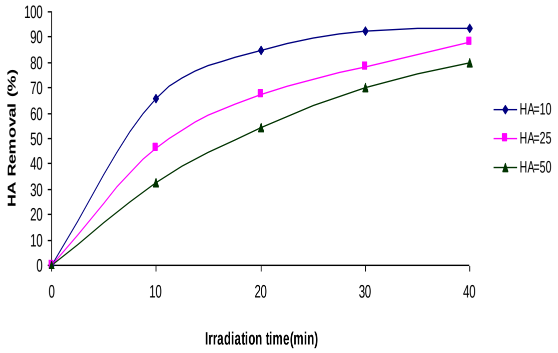

Figure 6: Effect of the initial HA concentration on

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 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.

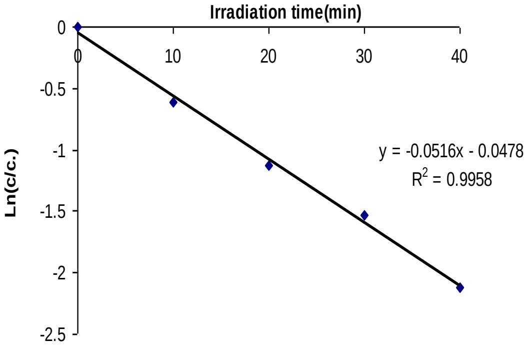

Figure 7: pseudo -first order Kinetic models of photocatalytic degradation of HA,

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

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 occordance with the study by Movahediyan and Rezaei [19] on effect of UV radiation in the dye removal and also the study by Dziedzic et al. [20] on the photocatalytic degrdation of humic acid via TiO_2/UV and solar UV. Wei et al. [21] studied the effects of UV_C radiation on the removal of humic acid coupled to ozonetion 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 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. [22] study on humic acid removal by TiO_2/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 [23] 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 [17] 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.

Similar results were obtained by Tabatabaee (2011)[17] and khorsandi et al. (2008)[19]. Wu et al. [24] 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 followes pseudo first-order kinetic with $R^2 = 0.9958$. Tabatabaee [17] investigated the catalytic effect of Ag/ZnO in the degradation of reactive dyes and Asgari et al. [23] 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. [18] also achived the same results.

Conclusion

The results of this study showed that mere UVc 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.

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_C is well described by a pseudo- first- order reaction.

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