

Humic Acid Degradation by ZnO Photocatalyst

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Abstract. Humic acid (HA) is universally present in soils and natural water resources in a yellow-brown form. HA can react with chlorine during drinking water treatment and produce disinfection byproducts (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs), which are harmful for health. Therefore, HA has to be eliminated from water environment. The photocatalysis is an effective alternative solution for the degradation of HA in a water environment. This research aims to degrade HA from water environment. The rapid degradation of HA, using zinc oxide nanoparticles, irradiated by ultraviolet light (ZnO/UV), is investigated. The optimum conditions of pertinent factors, which include the light wavelength (UV-A and UV-C), and light intensity, HA concentration, ZnO dose, and contact time are investigated at neutral pH conditions, considered for drinking water treatment. HA degradation efficiency reached more than 80% after 60 min for both types of irradiation in optimum conditions of 0.3 g/L ZnO dose in 180 min of contact time. Comparisons for degradation efficiency under UV-A and UV-C irradiation indicate that UV-C has higher efficiency, up to 150 min of contact time. The reusability of catalyst is performed for three reuses and still revealed effective for beneficial commercial applications.

1 Introduction

Humic acid (HA) commonly exist in surface and ground water. Chemical structure is complex and contributes to natural organic matter (NOM). HA sources are from animal and plant materials break down. This can affect drinking water quality. HA can react with chlorine during drinking water treatment and produce disinfection byproducts (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs), which can cause potential health impacts [1], [2]. Hepplewhite et al reported that HA is present in drinking water at concentration levels of between 2 and 15 mg/l [3].

Recently, ZnO is used as an effective photocatalyst for organic pollutants degradation, due to its high photochemical reactivity, low cost and nontoxic [4]. ZnO showed a good performance in promoting generation of reactive oxygen species (ROS) under irradiation with energy [5]. Oskoei et al. studied HA degradation at lower initial concentrations under UV mercury lamp up to 60 minutes of contact time using ZnO [6]. Kim et al. analysed for higher initial concentrations of HA, using UV-C/NZLC [7]. However, behavior of HA degradation under higher range of contact time and under different intensities of UV-A and UV-C lamps are not comparatively investigated.

Thus, in this study, the potential of applying ZnO as catalyst in photocatalytic process to degrade HA from water environment under UV-A and UV-C is evaluated. Effect of pertinent factors affecting degradation are also evaluated.

2 Materials and methods

2.1 Preparation of synthetic HA solution

HA was obtained from Sigma-Aldrich. A stock solution of HA was prepared by using laboratory-grade humic acid-sodium salt solution. HA concentration of 5, 8, 11 and 14 mg/L were prepared from stock solution using serial dilution with deionized water. A calibration curve was plotted using standardized HA solutions.

2.2 ZnO as catalyst

Zinc Oxide nanoparticle with a size of 6-12 nm, hexagonal crystal structure, 99.8% purity, was used. Since ZnO nanoparticles are more difficult to disperse in organic solvent, ultrasonication for 5-10 min is required for dispersion in solution.

2.3 Experimental set up

Experimental setup is shown in Fig. 1. Photocatalytic degradations were performed in sealed conditions. The whole system was covered by aluminium foil. One lamp was installed at the top of the reactor and two lamps on each side of the container. Two reactors each for UV-A (315-400 nm) and UV-C (100-280 nm) lamps, were used. During the experiment, the HA solution was mixed by using a magnetic stirrer.

2.4 Methodology

Photocatalytic experiment was done in a Pyrex beaker placed on the top of magnetic stirrer containing 100 ml of

HA solution at the concentration of 5, 8, 11 and 14 mg/L. The ZnO doses were added at range 0.1 – 1 g/L. The suspensions were irradiated for various contact time ranging from 30 – 180 min in interval of 30 min. After irradiation, the suspensions were filtered using 0.45 μm syringe filters. HA concentrations was analyzed by using UV-visible spectrophotometer Thermo Scientific, Genesys at 276 nm wavelength. Effect of light intensity was investigated by varying the number of 8W UV-A lamps i.e. 0.131 mw/cm^2 , 0.167 mw/cm^2 and 0.236 mw/cm^2 , respectively, and 8W UV-C lamps 0.196 mw/cm^2 , 0.233 mw/cm^2 and 0.284 mw/cm^2 , respectively. Light intensity was measured at liquid surface. All experiments were performed at room temperature ($25 \pm 3^\circ\text{C}$) and at neutral pH conditions. The reusability experiment of ZnO as a catalyst was done by centrifuging the sample for 20 min at 5000 rpm. It is followed by drying the catalyst at 60°C for at least 12 h.

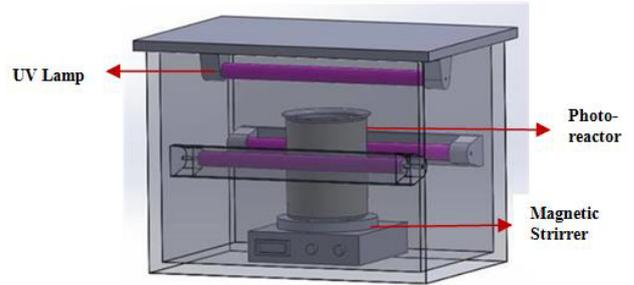


Figure 1. Schematic of the photocatalytic reactor

This experiment was done for UV-A and UV-C at light intensity 0.236 mw/cm^2 and 0.284 mw/cm^2 , respectively, at optimum condition (14 mg/L of HA, ZnO dose 0.3 g/L, contact time 180 min).

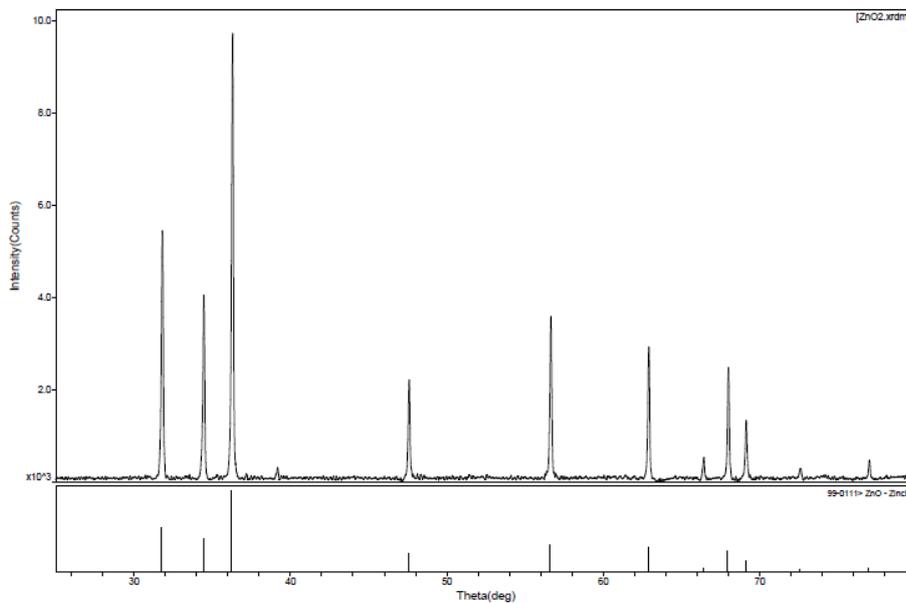


Figure 2. X-ray diffraction pattern of ZnO

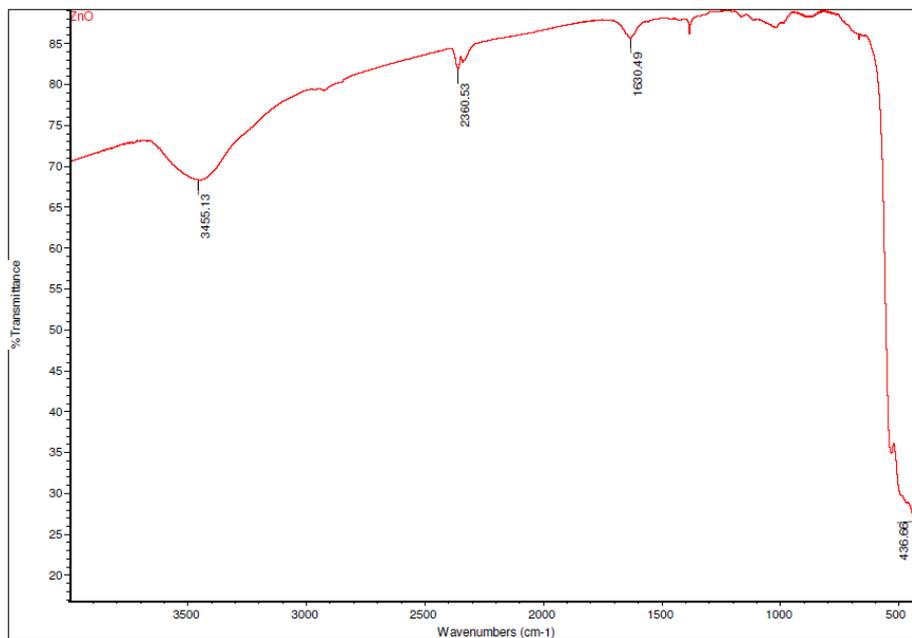


Figure 3. FT-IR spectra of ZnO

3 Results and discussions

3.1 ZnO characterization

From XRD pattern of ZnO in Fig. 2, the facets (2 θ value) at 31.7, 34.3, 36.3, 47.6 and 56.7 were assigned to (100), (002), (101), (102) and (110) reflection lines of hexagonal ZnO, respectively. It indicates that the characteristic peaks represent the ZnO with hexagonal phase [8].

FT-IR spectra of the ZnO nanoparticles in Fig. 3 showed the fundamental mode of vibration at 3000-3600 m^{-1} which corresponds to the O-H stretching vibration, 2360.53 m^{-1} which corresponds to C-H stretching vibration and 1365 m^{-1} corresponds to C=O asymmetric C=O stretching vibration, 1630.49 m^{-1} corresponds to C=O symmetric stretching vibration. O-H bending of the hydroxyl group at 436.66 m^{-1} is observed [8].

3.2 Effect of HA concentration

The effect of HA concentration of was carried out at 0.1 g/L ZnO dose, for 60 min. HA concentrations was varied from 5 to 14 mg/L. From Fig. 4, it can be seen that increasing the initial concentration of HA decreases the degradation efficiency. The efficiency of HA degradation varied from 95% to 51% for UV-A and 97% to 47% for UV-C, respectively.

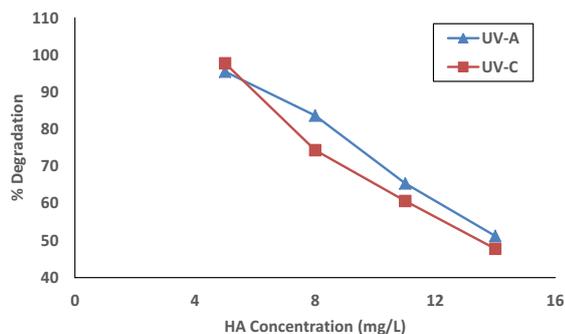


Figure 4. Effect of HA concentration on degradation by ZnO photocatalyst (ZnO dose 0.1 g/L, contact time 60min)

HA degradation decreased as the initial concentration increases and repulsive forces between molecules occurred, which effected in reduction in the number of hydroxyl radicals generated on the surface of catalyst by UV irradiations. Futhermore, a solution with a low concentration of HA with the same amount of hydroxyl radicals will have a higher degradation rate than a solution with a high concentration [9-11]. Previous studies on trichloroethylene (TCE) reported that the reaction by-products generated during the photocatalytic reaction can also decrease the degradation rate [11].

3.3 Effect of ZnO dose

In order to avoid the use of excess catalyst, it is necessary to find out the optimum loading for efficient removal of pollutant. Fig. 5 shows that increasing the ZnO dose from

0.1 to 1 g/L increased degradation of HA from 51% to 94% for UV-A and 48% to 94% for UV-C, respectively, with a contact time of 60 min. This is due to an increase in the active sites available for absorption of UV irradiations and adsorption of pollutant molecules which effects in producing large amounts of hydroxyl radicals. The result showed that rapid increase of HA degradation up to 0.5 g/L ZnO dose. The increase subsequent to 0.5 g/L seemed gradual.

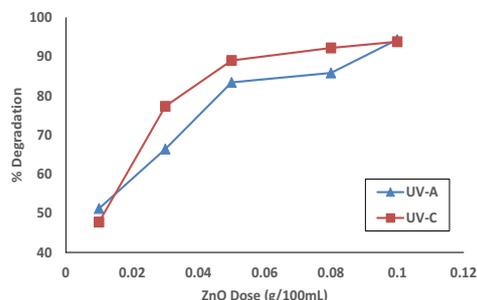


Figure 5. Effect of ZnO dose on degradation of HA (HA conc. 5 mg/L, contact time 60 min)

3.4 Effect of contact time

From the ZnO dose results, 0.5 g/L seemed to be the optimum dose. However, experiments were done for both 0.3 g/L and 0.5 g/L. It was observed that significant results for 60 min of contact time, could be obtained from 0.3 g/L. Therefore, 0.3 g/L was selected as the optimum of ZnO dose. For experiments conducted here onwards.

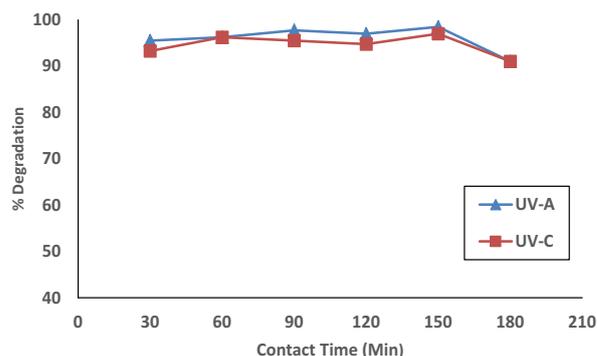


Figure 6(a). Effect of contact time on degradation of HA by ZnO photocatalyst (HA conc. 5 mg/L, ZnO dose 0.3 g/L)

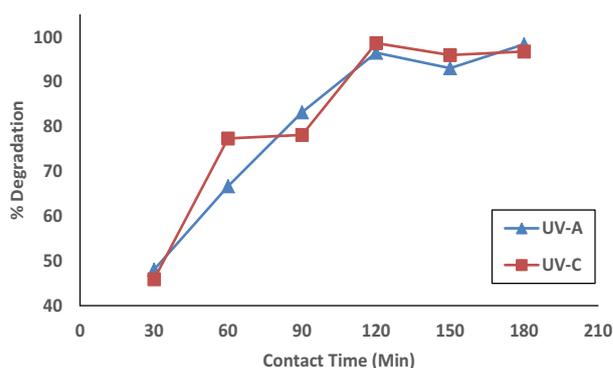


Figure 6(b). Effect of contact time on degradation of HA by ZnO photocatalyst (HA conc. 14 mg/L, ZnO dose 0.3 g/L)

Fig. 6(a) and (b) show the effect of contact time for HA concentration of 5 mg/L and 14 mg/L, respectively. It shows that increasing the contact time from 30 min to 180 min increased degradation efficiency. The result has shown insignificant variation of degradation efficiency for lower concentration at 5 mg/L, with time. The ZnO dissolution might have occurred due to this condition. The results show rapid increase of degradation efficiency for higher concentration at 14 mg/L, especially at low contact time. After 120 min of contact time, degradation efficiency remained nearly constant in this condition. The degradation efficiency was rapid at the beginning because there were a large number of active sites available on the surface of the adsorbent. The number of sites decreased over time with the gradual occupation of sites by HA. This results in increasing repulsive forces between the adsorbed molecules leading to decreased degradation [6].

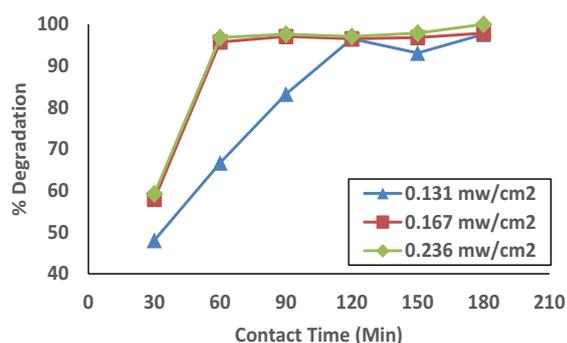


Figure 7(a). Effect of light intensity (UV-A) on degradation of HA by ZnO photocatalyst (HA conc. 14 mg/L, ZnO dose 0.3 g/L, contact time from 30 – 180 min)

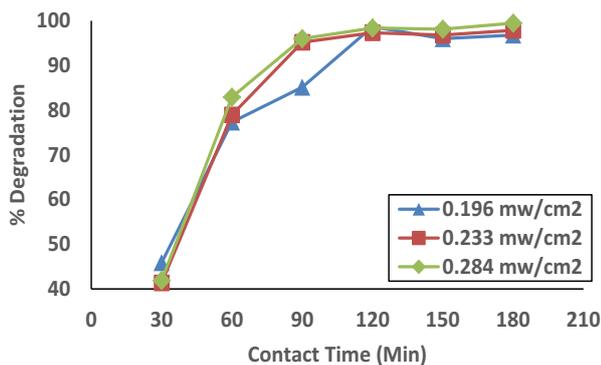


Figure 7(b). Effect of light intensity (UV-C) on degradation of HA by ZnO photocatalyst (HA conc. 14 mg/L, ZnO dose 0.3 g/L, contact time from 30 – 180 min)

3.5 Effect of light intensity

Fig. 7(a) and Fig. 7(b) show the effects of light intensity of 14 mg/L HA concentration for UV-A and UV-C, respectively, with time. In this study, contact time is varied from 30-180 min when finding the effect of light intensity. Fig. 7(a) shows that under UV-A irradiation, different behaviours are observed in different light intensities. The lower intensity required 120 min of contact time to reach more than 90% of HA degradation. On the other hand, higher intensities required only 60 min of contact time. Fig 7(b) shows lower intensity of UV-C irradiation required 120 min to reach more than 90% of HA degradation. For higher intensities required 90 min of

contact time. These graphs indicate that in terms of contact time, UV-A required lower contact time than UV-C to reach 90% of HA degradation. However, UV-C seemed to have higher degradation efficiency up to 150 min. Similar observation was obtained in a previous study by Bak et al, in an experiment done for trichloroethylene [11]. Higher intensity conditions will lead to higher electron-hole pair generation rate. Therefore, higher degradation efficiency is obtained, due to higher photocatalytic activity [12].

Fig. 8 indicates that more than 50% of HA degradation is dominated by photodegradation. The activity of ZnO showed better degradation of HA under irradiation condition. Due to that result, the photodegradation using ZnO provides higher concentration of hydroxyl ions to react with holes to form hydroxyl radicals. Hydroxyl radical is considered to be responsible for oxidation decomposition of organic compound. However, agglomeration and accumulation of ZnO might be occurred in the absence of irradiation.

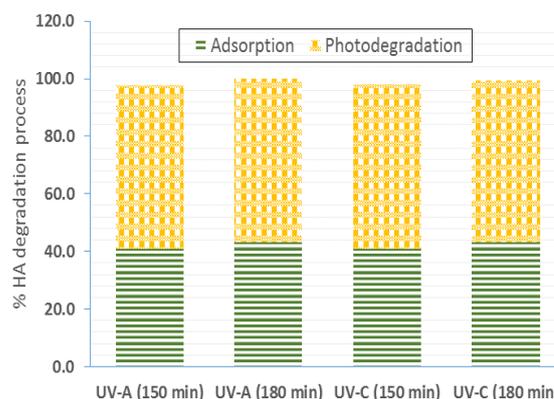


Figure 8. The ratio of adsorption and photodegradation to total of HA degradation percentage.

3.6 Reusability of Catalyst

In order to study the reusability of the catalyst, centrifugation separation method was used. Photocatalytic experiments were performed at 14 mg/L HA and 0.3 g/L ZnO, with 180 min of contact time. The ZnO was reused up to three cycles with consistent activity. Similar studies were done on TiO₂ for five cycles [13]. After three cycles of reusability, the percentages of degradation obtained were 88% for UV-A and 76% for UV-C, respectively. With higher number of cycles, the percentage of catalyst recovery decreased. The decrease of HA degradation might occur from the photocorrosion effect, which affected catalyst to a large extent. L.Huang et al, showed similar result on Cu₂O where the photocorrosion rate was rapid in catalyst as against their micron sized counterparts [14]. Therefore, three cycles of reusability is suggested to be acceptable from the experiments of this study.

4 Conclusions

In this study, HA degradation by ZnO photocatalyst was carried out. The photocatalytic degradation of HA was

studied by varying parameters that can be used to degrade HA in drinking water. Increasing the initial concentration of HA decreases the degradation efficiency due to the reduction of generated hydroxyl radicals. As the ZnO dose increases, degradation efficiency increases. HA degradation under high intensity UV-A irradiation required lower contact time, to reach 90% degradation. HA degradation efficiency under UV-C has higher efficiency, up to 150 min of contact time. The reusability of ZnO was demonstrated with consistent activity, and is still effective at three cycles. The use of catalyst creates a technical problem in retrieving the catalyst from the treated water. The authors suggest an immobilized catalyst for commercial applications for future works. Moreover, using the results of this study, efficiencies of different photocatalysts are to be comparatively investigated to remove HA from drinking water.

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