USING ZNO NANOPARTICLES–PHOTOCATALYSIS FOR HUMIC ACID DEGRADATION AT HIGH CONCENTRATIONS

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ABSTRACT

Humic acid is a natural organic matter that has the ability to react with chlorine forming undesirable disinfection by-products. One attractive alternative for humic acid degradation is photocatalysis because of its ability to remove and destruct the natural organic matter. The purpose of this research is to evaluate the zinc oxide (ZnO) photocatalysis efficiency for humic acid removal at relatively high concentrations up to 25 mg/l at laboratory scale under various operational conditions including catalyst dosage, pH, initial humic acid concentration, light intensity, and contact time. It was found that increasing ZnO dosage from 0.4 to 1.2 g/l increased the removal efficiency from 63.3% to 98.6%. In addition, increasing either of ZnO dosage, contact time, or light intensity increased the removal efficiency, while the opposite was true for increasing initial humic acid concentration or pH level. The kinetics of the photocatalytic degradation of humic acid was analyzed and it showed high correlation with modified Langmuir–Hinshelwood pseudo-first-order model with R^2 = (0.92-0.99). In addition, the apparent first-order constant K_{app} got raised by lowering the humic acid concentration, which confirms the inverse relationship between the humic acid concentration and the removal efficiency.

Keywords: Humic acid, photocatalysis, ZnO, nanoparticles

1 INTRODUCTION

Humic substances represents a high percentage of natural organic matter in natural waters, the exact percentage varies for each source; however, it was reported that humic substances in average makes up around 50% of the natural organic matter in surface waters (Philippe et al., 2010). They are originated from microbial decay of aquatic plants (Liu et al., 2008). They can be subdivided into three categories; humic acid, fulvic acid, and humin (Katsumata et al., 2008). Humic substances are undesirable in treated drinking water because they contribute to the brown color in water, and can absorb organic pollutants (Patsios et al., 2013). In addition, they react with disinfection chlorine producing disinfection by products (DBPs) like trihalomethanes and haloacetic acids, which at high concentration can cause harm to human health (Richardson et al., 2007). That made USEPA regulate them at concentrations of 80 µg/l for trihalomethanes and 60 µg/l for haloacetic acids (U.S. Environmental Protection Agency, 2006).

Many researches were dedicated to humic acid removal including ion exchange (Bolto et al., 2004); conventional and advanced coagulation (Uyak & Toroz, 2007); adsorption using activated carbon (Matilainen et al., 2006); membrane filtration (Schäfer et al., 2001); and advanced oxidation processes such as photo-Fenton (Katsumata et al., 2008), ozone (Siddiqui et al., 1997), and heterogeneous photocatalysis (Eggins et al., 1997; Oskoei et al., 2016).

Photocatalysis rose in the past decades as an efficient alternative for natural organic matter removal because of its ability to remove and destruct the natural organic matter instead of just separate and transfer it to another phase, hence no need for additional treatment or disposal of the residuals (Liu et al., 2008; Patsios et al., 2013). Photocatalysis could be performed using semiconductor catalyst such as titanium dioxide (TiO_2) or ZnO and irradiate it using ultraviolet (UV) light source with energy higher than the band gap of the catalyst to produce hydroxyl radicals ($\cdot$OH), which can capture and oxidize different range of contaminants (Gerrity et al., 2009).

Although TiO_2 is the most widely used catalyst (Patsios et al., 2013), ZnO has the advantage of being less expensive. In addition, Oskoei et al. (2016) achieved high humic acid removal efficiency up to 98.95% using two-stage-ZnO photocatalysis at pH = 4, initial humic acid concentration of 10 mg/l, ZnO = 0.5 g/l, and contact time of 30 minutes. However, they used a maximum humic acid concentration of 10 mg/l that could simulate the natural organic matter in most rivers, although high dissolved organic carbon (DOC) concentrations up to 52 mg/l were recorded at several surface water sources in Florida, USA (McPherson, 2000).

The object of this study is to investigate the efficiency of ZnO-photocatalysis for humic acid removal at higher concentration up to 25 mg/l at laboratory scale, at various operational conditions including ZnO dosage, initial humic acid concentration, pH level, light intensity, and contact time in addition to investigating the degradation kinetics using modified Langmuir–Hinshelwood model.

2   MATERIALS AND METHODS

2.1   Chemicals and materials

Both of humic acid and ZnO nanoparticles were obtained from (Alfa Aesar, Germany), the former in crystalline dark brown powder form and the latter in white powder form with surface area and average particle size of 12 m^2/g and 67 nm, respectively.

2.2   Bench-scale photocatalytic system

The photocatalytic reaction was achieved using ZnO nanoparticles as the catalyst, which were irradiated using a metal halide lamp having power, maximum wave length, and photon flux of 400 W, 510 nm, and 220 µ W/ cm^2, respectively. The lamp was placed 11 centimeters above a 250 ml Pyrex beaker filled with humic acid solution at the required concentration. The ZnO contained solution was kept in motion using magnetic stirrer for homogeneous contact between the water and ZnO particles, as shown in Fig. 1.
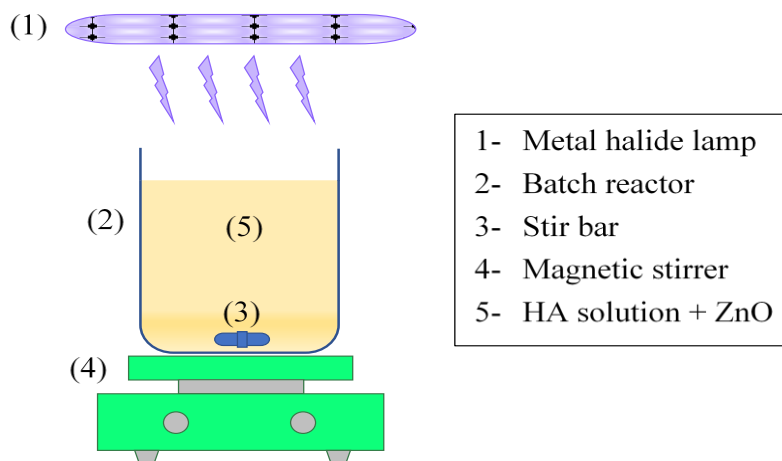

| 1- Metal halide lamp |
| 2- Batch reactor |
| 3- Stir bar |
| 4- Magnetic stirrer |
| 5- HA solution + ZnO |

Figure 1. Schematic of the photocatalytic system setup

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2.3   Experimental conditions

The photocatalytic degradation of humic acid was investigated at initial concentrations of 5, 10, 15, 20, and 25 mg/l; ZnO dosages of 0.4, 0.6, 0.8, 1.0, and 1.2 g/l; and pH of 3.5, 5, 7, 9, and 11. The process was performed at room temperature using 300 ml distilled water contaminated with humic acid at the desired concentration.

The ZnO adsorption capacity was tested at humic acid concentration of 25 mg/l and it reached its maximum adsorption capacity after 15 minutes, so the contact time was assigned at 4.25 hours with the first 15 minutes at darkness for most of the adsorption to happen. The required pH levels were achieved using sodium hydroxide (NaOH) and hydrochloric acid (HCl). The light intensity was measured using (Milwaukee SM700) lux meter and it was found to be 40000 lux at distance of 11 cm between the light source and the beaker. The intensity was changed from 40000 lux to 28000, 2000, and 15000 lux by increasing the distance from 11 cm to 21, 31, and 41 cm, respectively.

2.4   Sampling and analysis

Samples of 10 ml were drawn after the end of the adsorption stage after the first 15 minutes, then every 30 minutes at the photocatalytic stage. The samples were kept motionless for 60 minutes for the majority of the ZnO particles to spontaneously settle, then centrifuged using (MLW-T54, Germany) centrifuge for 30 minutes for the remaining particles to settle.

The remaining humic acid concentrations of the samples were determined using spectrophotometer (AG Lab, N4S, 200-1000 nm, USA) at wavelength UV 254 nm, and the humic acid removal percentage (R%) was calculated using eq. (1).

$$R\% = \frac{C_0 - C}{C_0} \times 100$$

(1)

Where C_0 is the initial humic acid concentration, and C is the humic acid remaining concentration at contact time (t). The ZnO removal capacity (amount of humic acid removed per added ZnO) was also calculated from eq. (2) in milligrams of humic acid removed per gram of added ZnO.

$$HA/ZnO = \frac{R C_0}{Z}$$

(2)

Where R is the humic acid removal efficiency, V is the volume in liters, C_0 is the initial humic acid concentration in mg/l, and Z is the ZnO dose in g/l.

3   RESULTS AND DISCUSSION

3.1   Effect of catalyst dosage

Fig. 2 depicts the effect of different ZnO dosages on the photocatalytic process efficiency at initial humic acid concentration of 25 mg/l and pH = 7. It is clear that increasing the catalyst dosage enhanced the humic acid removal ratio because raising the ZnO dosage resulted in higher active sites, hence increasing the amount of hydroxyl radicals produced (Gar Alalm et al., 2016), which can oxidize and capture the humic acid molecules. However, increasing the ZnO dosage decreased its removal capacity (the amount of humic acid removed per added ZnO), as shown in Fig. 3. The optimum removal efficiency was achieved using ZnO dosage of 1.2 g/l with 98.6% after 255 minutes.
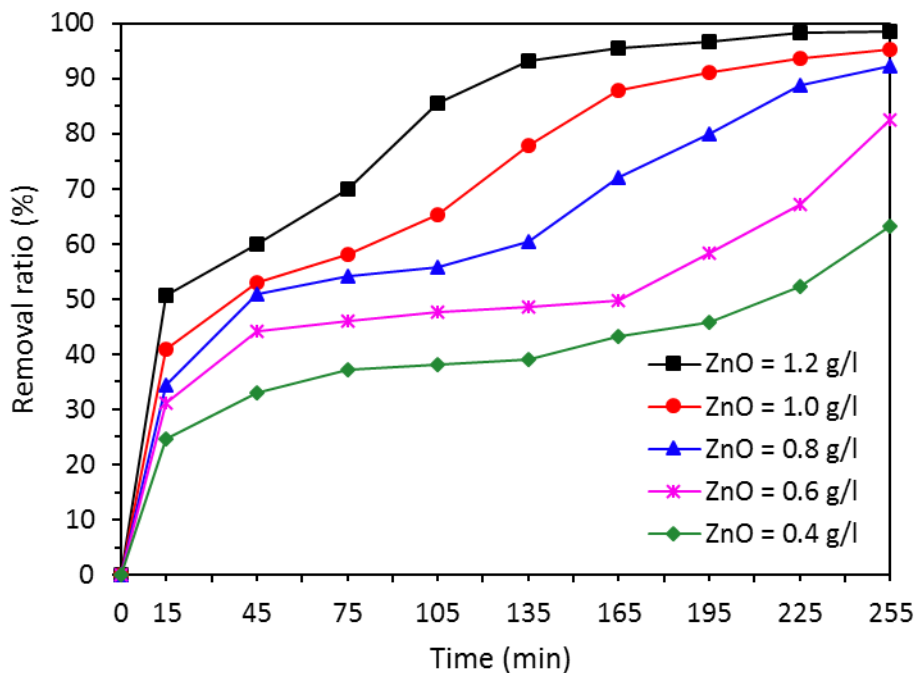
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Figure 2. Effect of ZnO dosage on humic acid removal efficiency (H.A = 25 mg/l, pH = 7)
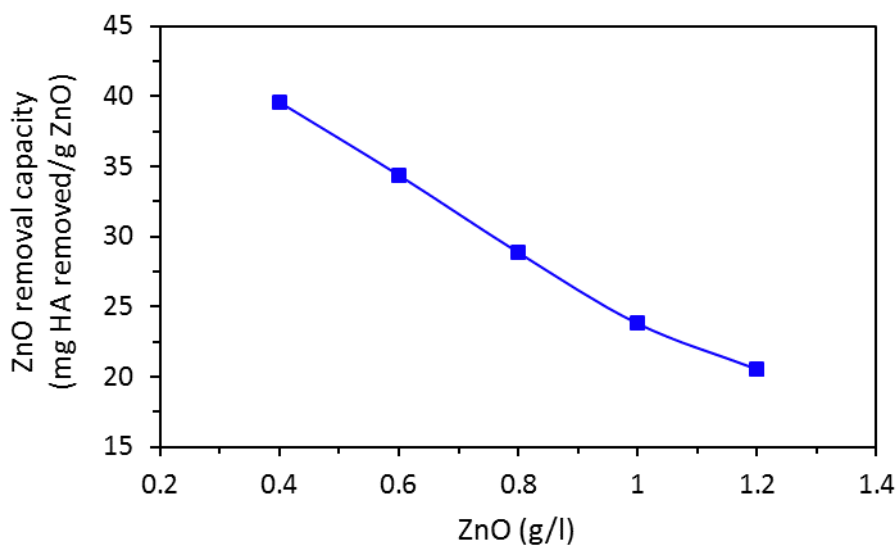

Figure 3. ZnO removal capacity of humic acid after 255 minutes (H.A = 25 mg/l, pH = 7.0)

3.2   Effect of Ph

The relation between changing pH and humic acid removal efficiency is depicted in Fig. 4. It shows that lowering the pH value increased the removal efficiency, and the opposite is true. This could be attributed to two reasons. First, ZnO has been documented to have a positively charged surface in acidic environment that helps it attract the humic acid particles electrostatically, thus may be leading to a higher removal ratio (Bedi & Kaur, 2015; Oskoei et al., 2016). At alkaline environment ZnO tends to have a negative charge, which contribute to creating repulsive forces with humic acid particles, hence lower removal efficiency (Bedi & Kaur, 2015). Secondly, H^+ free ions are formed in lower pH levels, which may helps produce hydroxyl radicals that has the ability to oxidize humic acid, and therefore enhance removal efficiency (Oskoei et al., 2016).
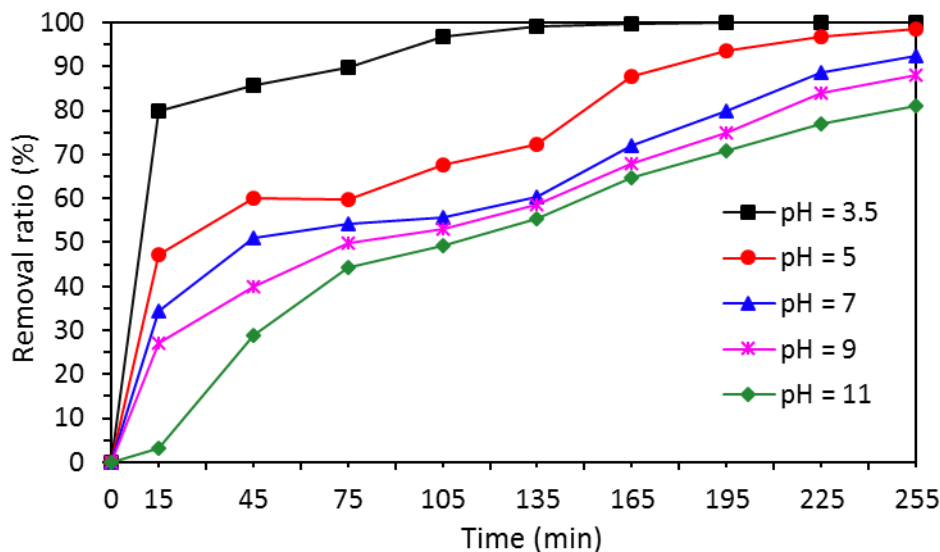
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Figure 4. Effect of pH on the removal efficiency (H.A = 25 mg/l, ZnO = 0.8 g/l)

3.3   Effect of initial humic acid concentration on the removal ratio

Fig. 5 shows that decreasing the initial humic acid concentration increased the removal efficiency and vice versa. This happened because the ZnO dosage was fixed for all experiments, therefore they had the same amount of hydroxyl radicals, and by decreasing the humic acid concentration the number of free active sites per humic acid concentration increased, hence higher removal efficiency. In addition, increasing the humic acid concentration contributed in creating higher repulsive forces between humic acid particles and resulted in lower removal efficiency (Oskoei et al., 2016).
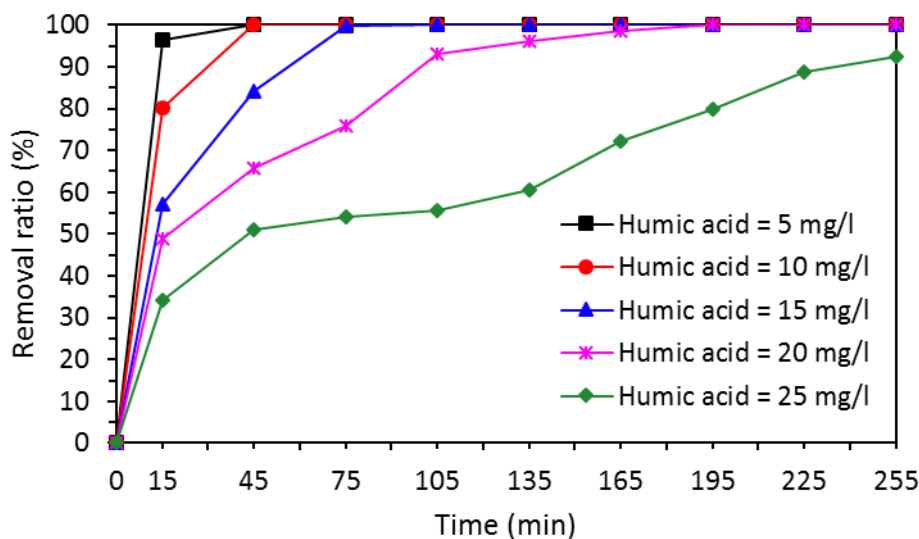

Figure 5. Effect of initial humic acid concentration (ZnO = 0.8 g/l, pH = 7)

3.4   Effect of light intensity

The effect of light illuminance on the humic acid removal efficiency is shown in Fig. 6. It was found that decreasing the light illuminance caused the removal efficiency to drop. The reason behind this is that the number of photons reaching the ZnO catalyst's surface decreased by increasing the

distance between the light and the beaker, causing the number of electrons and holes produced to decline, hence less removal ratio.
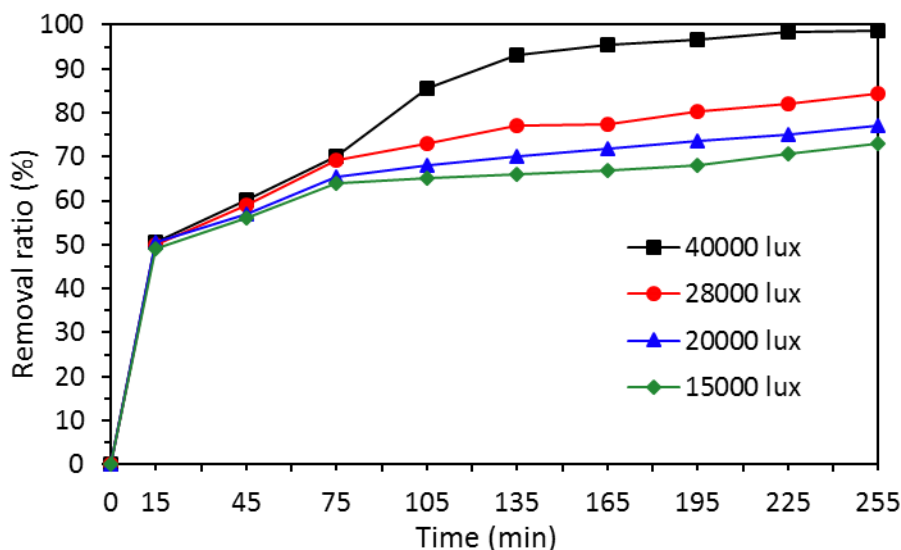

Figure 6. Effect of light intensity on removal efficiency (ZnO = 1.2 g/l, H.A = 25 mg/l, pH = 7)

3.5   Kinetics of humic acid degradation

According to Gar Alalm et al. (2018); Kartal et al. (2001); and Narayana et al. (2011), modified Langmuir–Hinshelwood model—mentioned in eq. (3)—can be used to describe the photocatalytic degradation of organic materials.

$$r = -\frac{dC}{dt} = \frac{k_r \, k_{ad} \, C}{1 + k_{ad} \, C} \tag{3}$$

Where r is the degradation rate, k_r is the reaction rate constant, k_{ad} is the equilibrium constant for adsorption, and C is the concentration of humic acid. When the adsorption is weak compared to photocatalysis and/or humic acid concentration is relatively low, eq. (3) could be simplified into a pseudo-first-order form with an apparent first-order rate constant (k_{app}), as expressed in eq. (4) (Gar Alalm et al., 2018).

$$\ln\left(\frac{C_0}{C}\right) = k_r \, k_{ad} \, t = k_{app} \, t \tag{4}$$

Where C_0 is the initial humic acid concentration, and t is the retention time. The pseudo-first-order relation between $\ln(C_0/C)$ and the contact time time is illustrated in Fig. 7. K_{app} and R^2 were calculated and listed in Table 1. It is obvious that the results had high correlation with Langmuir–Hinshelwood simplified model with $R^2 = 0.92$–0.99, which makes it appropriate to describe the humic acid photocatalytic degradation. In addition, the apparent first-order constant k_{app} increased by decreasing humic acid concentration, which confirms that removal efficiency is increased by lowering humic acid concentration.
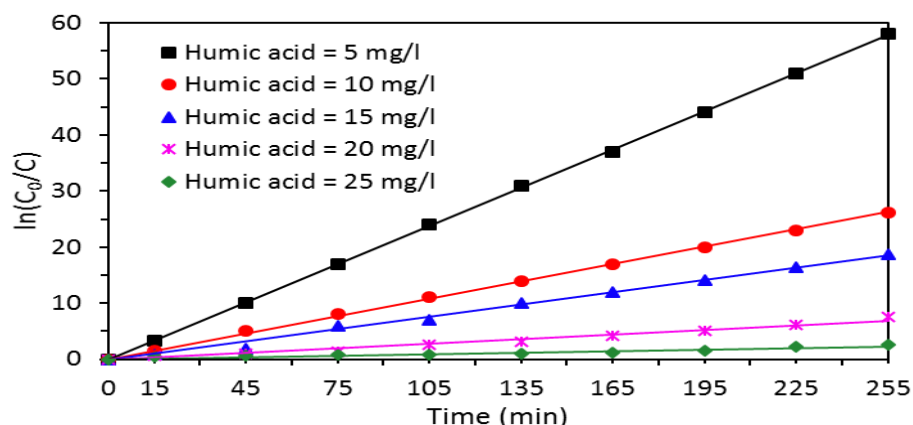
Figure 7. Kinetics of humic acid degradation at different initial humic acid concentrations (ZnO = 0.8 g/l, pH = 7)

Table 1. Analysis of Langmuir-Hinshelwood model (ZnO = 0.8 g/l, pH = 7)

Initial concentration (mg/l)	K_{app}	R^2
5	0.2267	0.999
10	0.103	0.999
15	0.0728	0.993
20	0.0268	0.979
25	0.0091	0.92

4   CONCLUSIONS

Relatively high humic acid concentration degradation using ZnO-photocatalysis was investigated. The optimum removal efficiency was accomplished at ZnO dosage of 1.2 g/l with 98.6% after 255 minutes. Beside ZnO dosage, other operational conditions such as initial humic acid concentration, pH, light intensity, and contact time were found to have direct effect on the removal efficiency. Higher removal ratio was achieved by increasing either of ZnO dosage, light intensity, or contact time; or by decreasing either of initial humic acid concentration or pH level. The degradation kinetics showed high correlation with modified Langmuir–Hinshelwood model with R^2 = (0.92-0.99).

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