Humic Acid Degradation by the Ozonation Process: Parameters Effect and Comparison of Ozonation Method

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Humic Acid Degradation by the Ozonation Process: Parameters Effect and Comparison of Ozonation Method.

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Abstract. Humic acid is one of the constituents that are easily found in the water. Interest of humic acid degradation has been escalating as water is one of the most important source in this world. Though these recent years, extensive research in ozonation has been rising as it a feasible and dynamic process. Thus, this study was aimed to investigate the efficiency of humic acid degradation by ozonation method under different operating conditions, such as initial concentration of humic acid, pH, temperature. Different ozonation method was also studied using catalyst Tin (IV) oxide (SnO_2) and oxidizing agent hydrogen peroxide (H_2O_2). Different methods of ozonation were also applied in order to study the capability of each method for degradation of humic acid. The most efficient method for the degradation of humic acid was ozonation with H_2O_2, gave the higher degradation rates of 98.82 % in 120 min of reaction. The results lead to the conclusion that ozonation process is an efficient method for removing humic acid from aqueous solutions.

1. Introduction

Ozonation is one of chemical water treatment techniques where it is also a type of advanced oxidation process. The process can be explained that it is using the infusion of ozone into water by involve the production of reactive oxygen molecules. The reactive oxygen species have the ability to attack a different range of organic compounds and all microorganisms. Ozone is produced with the use of energy by subjecting oxygen (O_2) to high electric voltage or to UV radiation. Hydroxyl radical are known as a great oxidant where it is generated by ozone for decomposition in water [1].

The treatment of water with ozone has a wide range of applications. This is caused by its efficiencies for disinfection and also in degradation of organic and inorganic pollutants. Hardly biodegradable organic compounds can be cleaved in the reaction. In addition, elimination of odorous, taste-causing and colouring substances can be done by killing bacteria through ozonation.

Most of the natural organic materials are found in natural waters that contain of humic acid around 40–80 %. This is due to the elutriation of the surrounding soils and from microbiological, chemical and photochemical reactions of humification process that occur during the degradation and polymerization of vegetable organic matter in water. Previous study showed that, the ozonation has the ability either eliminate such pollutants completely through mineralization or convert them to the products that are less harmful to human health and the aquatic [2]. Therefore, the degradation of the humic acid through the ozonation process is main focus of this study. The efficiency of humic acid degradation using ozonation

at different parameter condition, ozonation with catalyst and ozonation with oxidizing agent were studied. Other than that, it is to compare the method of ozonation for humic acid degradation.

2. Methodology

Humic acid sodium salt was obtained from Merck, Malaysia. 1 g of Humic acid sodium salt was weighed and then it was inserted into 1000 ml beaker. In the beaker, 1000 ml distilled water was added. After that, the solution was stirred until it fully dissolved. Next, HA solution with concentration of 100 mg/L, 50 mg/L, 20 mg/L, 10 mg/L, 5 mg/L and 2.5 mg/L were prepared by dilution method. The stock was prepared fresh every day in order to lower the possibility of error from degradation of HA. Buffer solution was prepared using 0.1 M monobasic Potassium Phosphate (KH_2PO_4) and 0.1 M Sodium Hydroxide (NaOH) for pH adjustment of HA solution.

2.1. Ozonation experiment

The ozonation process of humic acid was done in batch system. The flow rate of the ozone from ozone generator was kept the same, which was at 600mg/h. Temperature of the process was at room temperature and it was stirred throughout the whole reaction. Humic acid was placed in the conical flask with the presence of rubber stopper on top. The humic acid was continuously stirred during the process of ozonation. Ozone generator was connected to the conical flask as it supplied O_3 gas to the process. There was a sampling port connected to the flask. This was for sample collection every 0 minute, 10 minutes, 20 minutes, 40 minutes, 60 minutes, 80 minutes, 100 minutes and 120 minutes. Other tube connected to the flask was for gas outlet. The temperature of the process was regulated by placing water inside the beaker and the thermometer was observed in order to make sure it was in constant temperature.

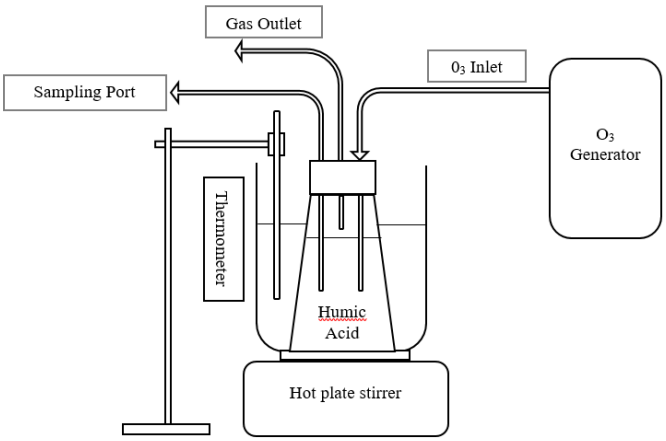

Figure 1. Ozonation set-up.

2.2. Parameter studies in ozonation

Three different parameters studies were conducted for ozonation of humic acid degradation. The parameters are effect of initial concentration, effect of temperature and effect of pH.

Table 1. Parameter study in ozonation

Parameters	Details
Initial concentration (mg/L)	2.5, 5, 10, 20, 40, 50, and 100.
Effect of temperature (ºC)	26, 30, 34, 38, 40, and 44.
Effect of pH	pH 2, pH 4, pH 7, pH 10 and pH 12.

2.3. Methods of Ozonation

Different methods of ozonation were done in order to compare the efficiency of the degradation of humic acid. Ozonation with hydrogen peroxide (H_2O_2) and tin(IV) oxide (SnO_2) were done respectively.

Table 2. Methods of ozonation

Method	Dosage
Ozonation with catalyst tin(IV) oxide (SnO_2) (g/L)	0.25, 0.5 and 1.0
Ozonation with oxidizing agent hydrogen peroxide (H_2O_2) (mg/L)	100, 200 and 400

2.4. Analytical method

HA concentration was analysed using UV-Vis Spectrometer Spectroquant Pharo 300 by reading the absorbance at the wavelength of 254 nm.

2.5. Degradation efficiency

Degradation efficiency was calculated using equation below:

$$\% = \frac{C_0 - C}{C_0} \times 100 \quad [1]$$

where Co is the initial concentration of humic acid, C is the final concentration of humic acid after ozonation.

2.6. Arrhenius Expression

The Arrhenius equation is a formula for the temperature dependence of reaction rates. Arrhenius equation used to define the value of activation energy (Ea) is given by the following equation:

$$\ln k = \ln A - \frac{E_a}{R}\frac{1}{T} \quad [2]$$

where k, A, E_a, R and T, are reaction rate constant, preexponential factor, activation energy (J mol^{-1}), ideal gas constant (8.314 J mol^{-1} K^{-1}) and temperature (K), respectively.

3. Results and Discussion

3.1. Effect of Initial concentration

As observed in Figure 2 lowest concentration of humic acid, 2.5mg/L had achieved the most efficient degradation of humic acid which is 95.29%. It shown that increasing concentration of humic acid, the degradation percentage is slowly decreased. In previous study, it was stated that capacity of adsorption decreased with increasing humic acid concentration [3]. This is because humic acid contains a wide variety of functional groups including phenolic hydroxyls and carboxylates. Therefore, as the concentration of humic acid increase, the amount of composition as for the functional groups increase too and it influences the degradation percentage. Thus, these results comprehend that the humic acid concentration is correlated with the percentage degradation of humic acid.

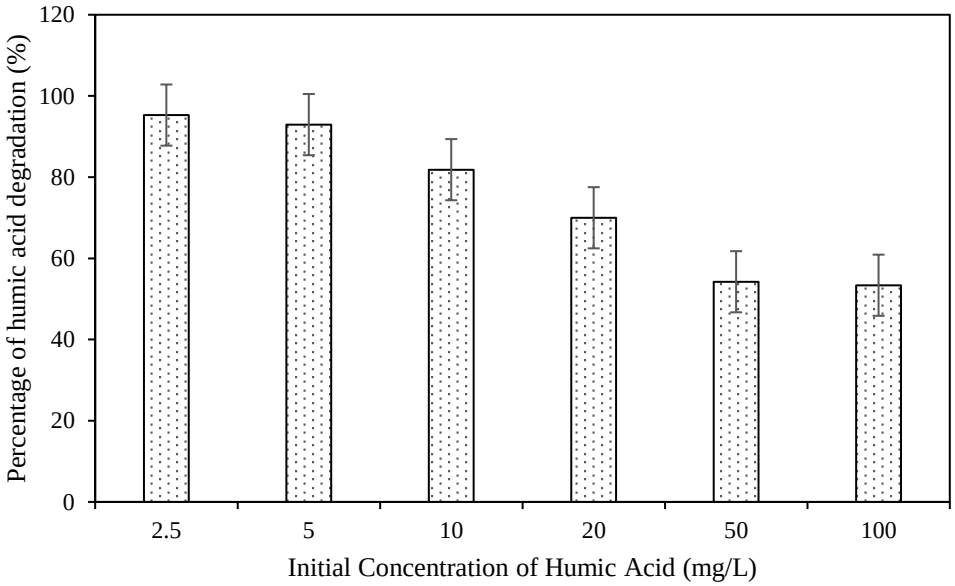

Figure 2. Percentage degradation of humic acid for intial concentration of HA

3.2. Effect of Temperature

The degradation percentage of humic acid was assessed by varying the temperature from 26 ºC until 44 ºC. Temperature of 34 ºC has achieved the highest degradation of humic acid and the decreasing trend of degradation percentage observed starting 38 ºC. This phenomenon can be explained by the fact that when temperatures used are above 40 °C, ozone dissolved in water is low. It is because at high temperature the half-life of ozone is very short causing solubility of ozone decreases less stable [4].

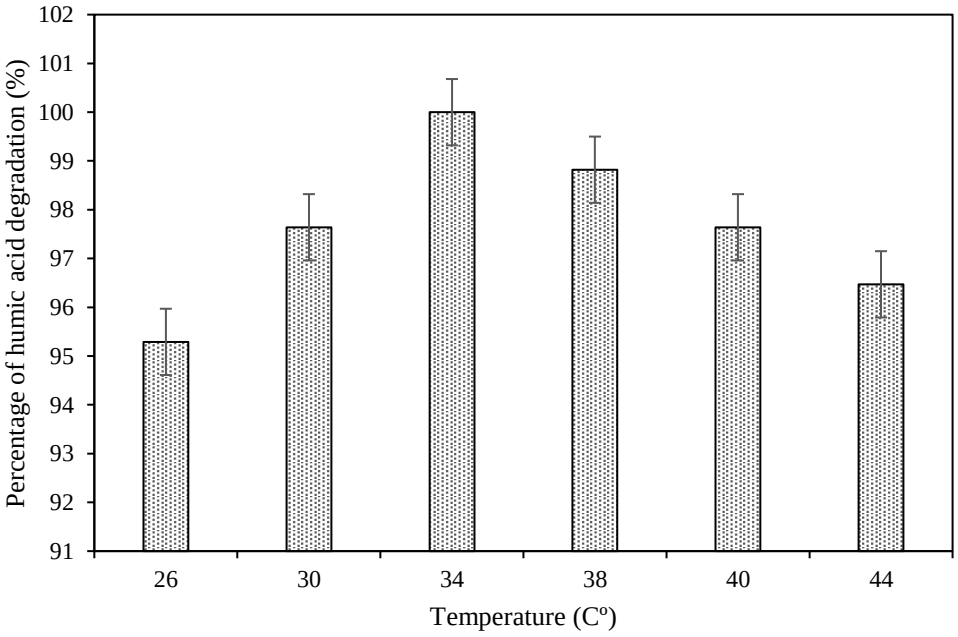

Figure 3. Percentage degradation of humic acid for temperature

3.2.1 Arrhenius Expression

The highest data was -2.938, ln k for 0.0033 1/T meanwhile the lowest rate of constant was -4.4546, ln k of 0.0032 1/T as refers to Table 3.

Table 3. Arrhenius expression data for HA

(1/T)	ln k
0.0033	-2.9375
0.0033	-3.2189
0.0033	-3.4738
0.0032	-3.8632
0.0032	-4.1414
0.0032	-4.4546

This show decreasing trend where it opposed the Arrhenius expression principle. Reaction rate supposed to increase with increase in temperature. However, the proper reaction temperature region could accelerate the reaction rate and increase the collision of molecules. Higher temperature also significantly influences the stability and result in lower solubility of ozone in aqueous solution, resulting in a further negative effect on the reaction rate [5]. Hence, this explained the Ea obtained which is -67.640 kJ/mol.

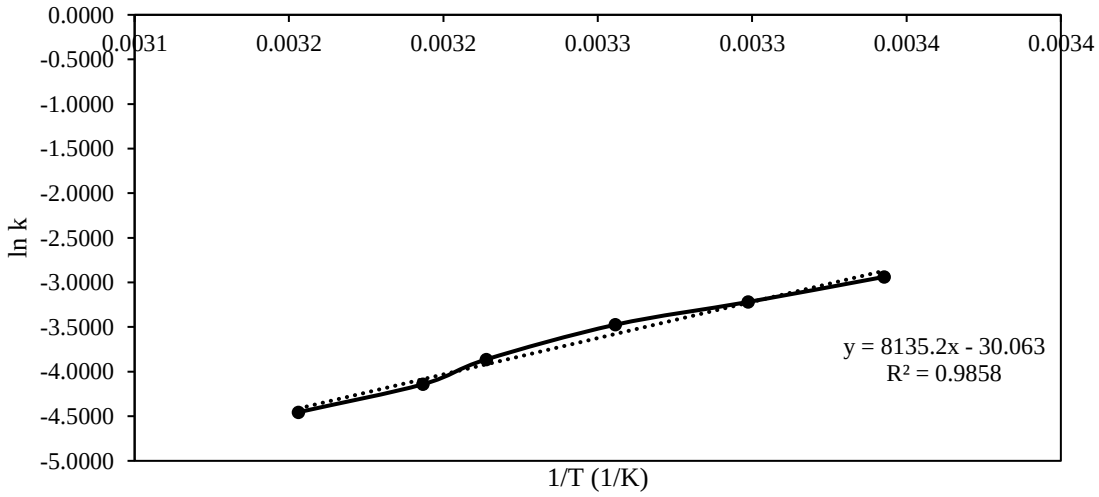

Figure 4. Arrhenius expression of HA

3.3. Effect of pH

Degradation efficiencies of humic acid in the acidic pH region are higher where at pH 2 of ozonation reaction, it resulting the highest percentage which was 89.41% of humic acid degradation. Next, pH 10 and pH 12 were assessed too, and showed the decreasing of percentage removal in degradation of humic acid, 49.91% and 41.18% respectively. The difference of the result can be explained by mechanism ozone oxidation pathways. Ozone oxidation pathway has two different mechanisms which are mainly affected by pH of humic acid. In acidic conditions, mechanism is direct oxidation, where it is more selective and predominates. Second mechanism is radical oxidation by hydroxyl radicals. It is less selective and predominates under basic and alkali conditions [6]. Therefore, it can be pointed out that significant increasing of percentage in humic acid degradation was found at pH 2 is caused by direct oxidation of ozonation because of the acidic condition of humic acid.

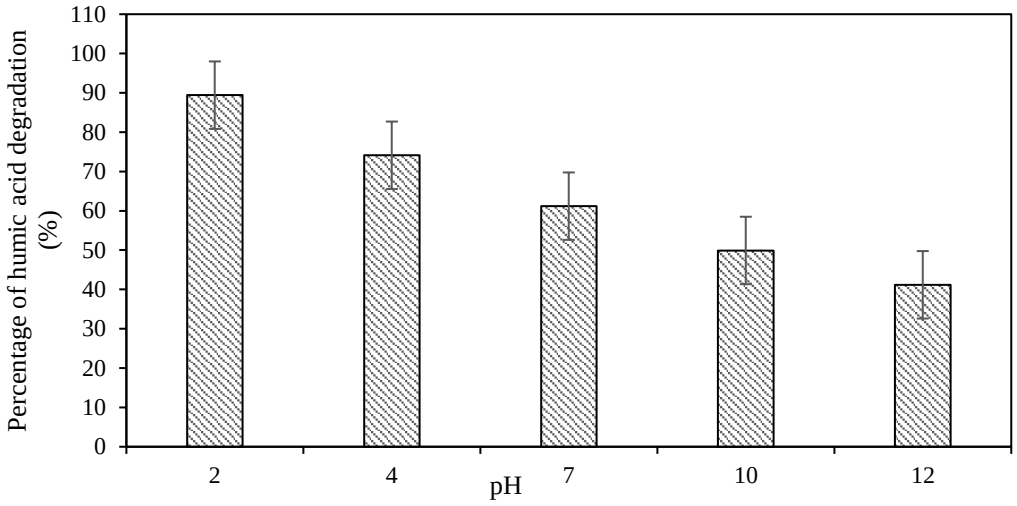

Figure 5. Percentage degradation of humic acid for effect of pH

3.4. Comparison of Different Methods of Ozonation for Humic Acid Degradation

Different methods of ozonation were performed in this study. Both of O_3/H_2O_2 and O_3/SnO_2 have higher percentage degradation of humic acid to be compared with ozonation. Mechanisms of H_2O_2 and SnO_2 as catalyst in ozonation are different. It is because H_2O_2 acts as oxidizer meanwhile SnO_2 acts as heterogeneous catalyst. H_2O_2 is one of the most powerful oxidizers known and through catalysis, H_2O_2 can be converted into hydroxyl radicals where it can improve ozonation [7]. This correlated to the highest degradation percentage, 98.82% achieved by H_2O_2. Comparatively, usage of catalysts in ozonation is an ideal method in improving the degradation of humic acid and the formation of hydroxyl radicals [8]. Therefore, SnO_2 was used and it showed higher degradation percentage than ozonation which is 95.29%. Hence, this explained the different degradation percentage and performance of both methods.

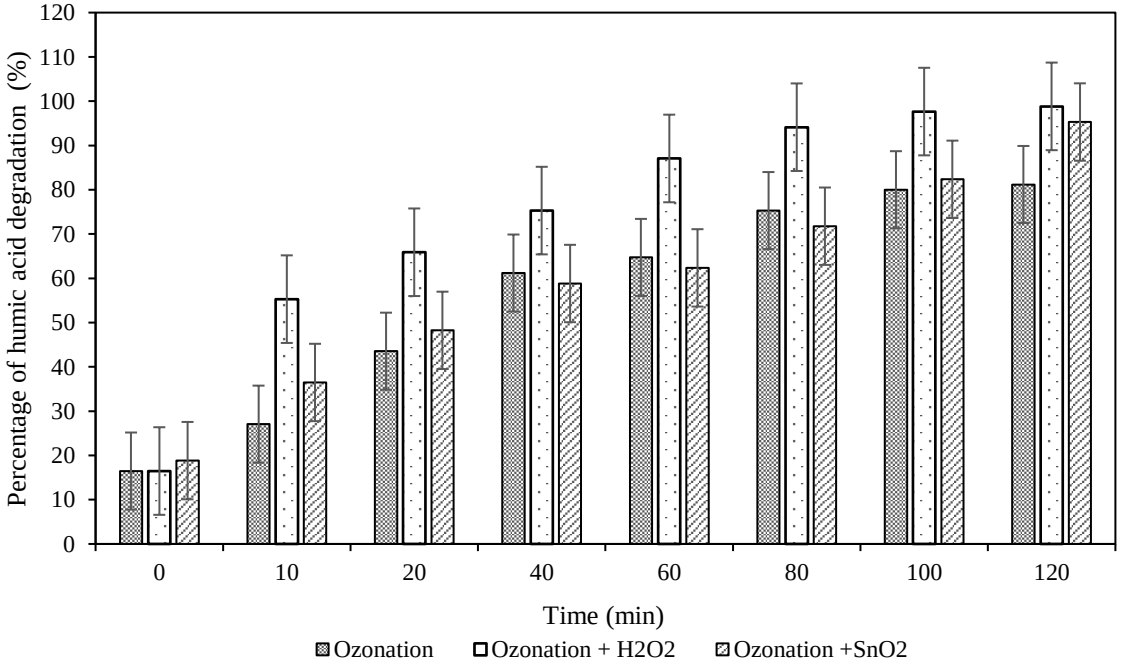

Figure 6. Percentage degradation of humic acid for different method of ozonation

4. Conclusion

Throughout this study, it can be concluded that ozonation is one of the feasible yet effective methods of degrading humic acid. The different parameters used in this study have shown the efficiency in humic acid degradation. Therefore, in initial concentration of humic acid, it was found that 2.5 mg/L obtained the highest degradation percentage of humic acid. It was then followed by the best temperature for degradation of humic acid in ozonation is 34 ºC and pH 2. In order to compare the method of ozonation for humic acid degradation, O_3, O_3/H_2O_2 and O_3/SnO_2 reaction were studied. In was found that O_3/H_2O_2 obtained the highest degradation efficiency followed by O_3/SnO_2 and O_3 respectively for degradation of humic acid at concentration of 10 mg/L in duration of 2 hours. R^2 obtained for Arrhenius expression is 0.9858.

Acknowledgment

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