Degradation Kinetics of Humic acid in Aqueous Solution by Ozonation Treatment under Different Parameter Conditions

View the article online for updates and enhancements.

Degradation Kinetics of Humic acid in Aqueous Solution by Ozonation Treatment under Different Parameter Conditions

Zafirah Mahyun[1], Noor Fazliani Shoparwe[1], Ahmad Zuhairi Abdullah[2], Abdul Latif Ahmad[2], Mardawani Mohamad[1], Abdul Hafidz Yusoff[1]

[1]Faculty of Bioengineering and Technology, Jeli Campus, Universiti Malaysia Kelantan, 17600 Jeli Kelantan, Malaysia.
[2] School of Chemical Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia

Email:fazliani.s@umk.edu.my

Abstract: This study evaluated the kinetics of humic acid (HA) degradation in aqueous solution by ozonation process under different parameter conditions. The effect of initial HA concentration (5 to 100 mg/L), solution pH (2 – 12) and initial ozone doses (1.6– 4.9 mg/L) of HA degradation were evaluated through batch ozonation processes at ambient temperature for 2 hours. The HA degradation followed pseudo-first order kinetics where the rate constant changed based on these parameters effect. Results showed that, the HA degradation by ozonation process was more effective (98% degradation) at 20 mg/L initial HA concentration, initial pH 7 and 4.9 mg/L of ozone dose. These finding suggest that the ozonation process can be effectively used in wastewater treatment for improving the biodegradability of recalcitrant organic compounds.

1. Introduction

Natural organic matter (NOM) is commonly present in natural water sources. The existence of NOM gives negative impact in complicate and decrease the performances of the water treatment process. Besides, NOM mostly causes fouling in membrane process [1]. Humic substances are the important component in the NOM which are high molecule weight in a complex matrix of organic compound [2] Normally, natural water with humic acid (HA) is yellowish-brown that chemically consists of carbohydrates (50-60%), lignins (1-3%), protein (1-3%) and other phenolic compounds [3].

HA which originates from the soil, groundwater or decomposition of organic matter are rich in substance with phenolic structured, aromatic carbon and conjugated double bond [4]. The concentration of HA in surface water might reach up to 50 mg/L. HA in water will give undesired color, odor, and taste which make the water unpleasant to consume. Moreover, HA probably gives the site for heavy metal complexion [4]. The high concentration of humic substances can effect on threaten human health. Thus, they cause negative effects on human health such as damaging neurological, heart malformation, reproductive and ocular functions causing carcinogenic effects in the liver due to high dosage [5].

Advanced oxidation process is one of the methods the degradation of organic pollutants during wastewater treatment. Ozonation is commonly applied in water treatment for oxidation and disinfection [6]. The basic principal of ozonation treatment is to oxidize pollutant substances into small organic molecule and biodegradable organic molecules [7]. However, some drawbacks seriously restricting the availability of ozonation, such as the slow oxidation rate of ammonia, low removal rate of total nitrogen in which the main product is nitrate nitrogen and the demand for alkaline addition [8]. Previous research shows that the application of ozonation can effectively break down straight and

unsaturated bond in molecules. Ozone has potential to oxidize organic, inorganic pollutant, decolorisation and removal of micropollutant [9].

Therefore, the main purpose of this research is to study the kinetic degradation of HA in aqueous solution through ozonation. Pseudo-first-order was performed to identify rate reaction of ozone and HA substances. Parameter factors are initial concentration of HA, pH value, and ozone doses were investigated to determine the degradation of HA.

2. Methodology

The commercial humic acid (HA) was purchased from Sigma-Aldrich company. The HA stock solution was prepared by dissolving 1g of HA in 1000mL of distilled water and mixed vigorously for 24 h to achieve the homogenous solution. pH of HA stock solution was adjusted into pH 7 by using 1M of sodium hydroxide (NaOH).

2.1 Ozonation experiment

The ozonation experiment was carried out in 1L GLS 80 laboratory bottle wide neck (ID 101mm × H 218) operated in a batch mode. Ozone gas was generated from the air discharge ozone generator (Guangzhou Yuejia Environment Protection, China) at a constant flow rate of 15 L/ min and introduced to the bottom of bottle HA samples via a diffuser for 120 min. The dehumidified atmospheric air which was passed through a drying filter within the equipment was used as the feed gas to generate ozone.

The concentration of the HA sample with low (5 mg/L) and high (100 mg/L) were prepared from the stock solution. The samples were mixed eventually by using a magnetic stirrer to ensure the mixing between gas and liquid phases during the ozonation process. Iodometric method titration with sodium thiosulphate was used to determine the concentration of ozone [10]. Residual ozone in the off-gas system was captured in 2% of potassium iodide (KI) solution [11]. The experimental set-up shown in Figure 1.

Different initial pH values were set to study the pH effects. pH adjustment of the HA solution (20 mg/L) from pH 2 to pH 12 was achieved by using 1 M solution of sodium hydroxide (NaOH) and hydrochloric acid (HCl). Different ozone doses were applied in the range from 1.5 mg/L to 4.7 mg/L in order to study the efficiency of HA degradation. The 1.5 ml of HA samples were taken every 10 min for 2 h during the ozonation process. All the experiments were conducted in triplets to obtain as the mean values.

2.2 Parameter studies in ozonation

The ozonation of HA degradation was performed under varying different parameter different parameters as shown in Table 1.

Table 1. Parameter studies in ozonation of HA degradation

Parameter	Details
Initial concentration of HA (mg/L)	5, 10, 20, 50, 100
pH	pH 2, pH 4, pH 7, pH 10, pH 12
Ozone doses (mg/L)	1.6, 3.2, 4.9

2.3 Analytical method

The samples were filtered through 0.45μm of syringe filter before analysis. The UV–Vis Absorbance at wavelength 254 nm was performed by Spectroquant Pharo 300 Merck for spectroscopic measurement of HA concentration. IR spectra was used to observe the functional group and changes before and after the ozonation of HA [12]. FTIR was performed by means of a Thermo Fisher Scientific iZ10 FTIR Spectrometer. The spectrum recorded was in range 400 – 4000 cm^{-1}. The analysis was done automatically by software attached to the system (Spectrum version 5.0.2)
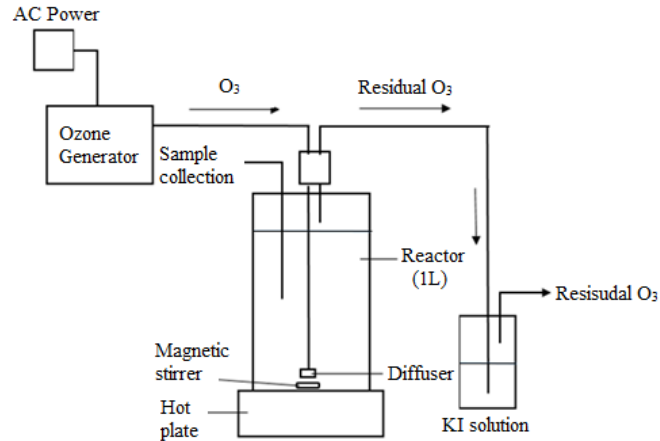
Figure 1. Ozonation set-up

2.4 Kinetic Study
The kinetic degradation of HA by ozonation treatment was determined by using Legergren pseudo first-order kinetic model [13]. It can be written in a differential form as follows:

$$-\frac{dC_{HA}}{dt} = k_1\left(C_{HA_e} - C_{HA_t}\right) \tag{1}$$

In order to predict the parameter based on the experimental results, Eq. (1) was integrated using with the boundary conditions of $C_{HA}(t=0) = C_{HA_o}$ and $C_{HA_e}(t=0) = t_o$. The equations derived and shown in non-linear form is given as:

$$C_{HA} = C_{HA_e} - \left(\exp(-k_1 t)\left(C_{HA_e} - C_{HA_o}\right)\right) \tag{2}$$

where C_{HA_o} is the initial concentration of HA, C_{HA_e} is the final concentration of HA and k_1 is the rate of constant in the reaction of ozonation. The nonlinear model (Equation 2) was simulated using Polymath Software version 6.0. The process parameters obtained were compared with the experimental results.

3. Results and Discussion

3.1 FTIR spectra changes by ozonation
The FTIR spectra of HA solution before and after ozonation are shown in Figure 2. The band of 3417 cm^{-1} shows the O–H vibration of carboxylic and alcoholic groups and it was shifted to 3443 cm^{-1} after ozonation [13]. The peaks of 2843 cm^{-1} and 2913 cm^{-1} show symmetric and asymmetric vibrations of C – H groups which shows the existing of aliphatic chains in HA, and it increased with ozonation time [12]. The band at 1382 cm^{-1} significantly decreased after ozonation. Peak at 1248 cm^{-1} strengthened the ozonation might augmented carboxylic group C–O. The elemental composition of HA solution was changed substantially during ozonation. The peak of 1559 cm^{-1} that is assigned to carboxylic acid salts typically showed a strong, characteristic asymmetric stretching absorption from the CO_2- group. Therefore, ozonation brought about significant change in the structural characteristic of HA solution.
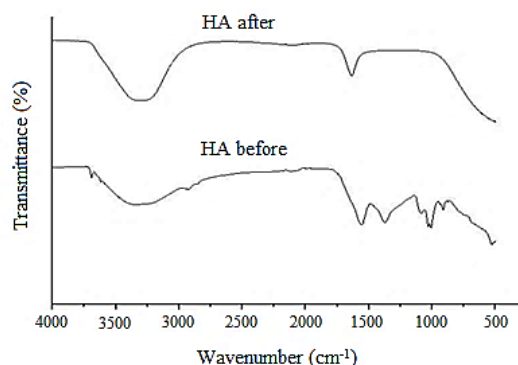
Figure 2. The FTIR spectra of HA solution before and after ozonation

3.2 Kinetic Studies of HA Degradation

3.2.1 Effect of Initial concentration

Figure 3 indicates the kinetics effect of HA degradation on initial concentration via pseudo-first-order kinetic model. This plot shows the nonlinear plots of both experimental and predicted value together. The data tabulated in **Table 2.** Table 2, show the parameters values (C_{HA_e}, C_{HA_o}, k_1) obtained from the simulation of Pseudo-first-order kinetic model for the degradation of HA. The R^2 values are between 0.977 – 0.994 which are close to 1 to indicate that the model fit well for degradation of HA by ozonation. The k_1 value determine the rate reaction for the HA degradation by ozonation process. The highest rate of reaction occurs which is 0.098 min^{-1} at 20 mg/L of initial concentration with a removal efficiency of about 97%.

The lowest rate of degradation was achieved at 100mg/L which is 0.069 min^{-1} with a removal efficiency of 76%. This is because HA could react as scavengers or promoters based on their concentration in the water. Thus, the higher the concentration of HA, the lower the oxidation rate will occur [14]. The reduction color of HA samples changed from brown to light yellow and finally clear water due to the decomposition of aromatic molecules [15]. This result might be explained by the fact that ozone breaks down the carbon double bonds into less complex molecules during the ozone oxidation process [2].
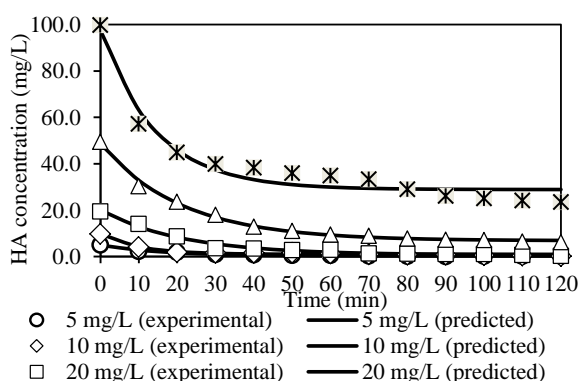
Figure 3. Non-linear plot of Pseudo-first-order kinetic of HA degradation of different initial concentrations.

Table 2. Pseudo-first-order kinetic model of initial concentrations on the degradation of HA

| Initial Concentration of HA (mg/L)	Kinetic Parameter			
	C_{HA_e} (mgL^{-1})	k_1 (min^{-1})	C_{HA_o} (mgL^{-1})	R^2
5	0.157	0.060	5.059	0.977
10	0.196	0.068	9.765	0.976
20	0.235	0.098	19.451	0.993
50	6.196	0.089	49.529	0.994
100	23.49	0.069	99.882	0.987

3.3 Influence of initial pH

The pH of the ozonated water is considered as the essential factor that strongly influences the ozone oxidation pathway. The ozone oxidation pathway involves direct oxidation under acidic medium between molecular ozone and chemical compound, while radical oxidation under basic or alkaline medium by the formation of hydroxyl radical [16]. The direct oxidation pathway is more selective due to the strong nucleophilic sides to oxidized organic compounds [2]. Dipolar structure of ozone

molecule reacts selectively with unsaturated bonds present in a certain organic compound such as electron donor species and aromatic ring [2][17].

　　　　Ozone must persist in the medium for a certain period of time to complete oxidation reaction. This suggests the ozone concentration to mostly remain at values below neutral pH [18]. Figure 4 shows that the experimental values of the pH satisfactorily fit the predicted values. The data plotted show rapid degradation of the HA samples was achieved at the first 20 minutes of the reaction. Based on Table 3, ozonation at pH 7 satisfactorily achieved performance with the highest degradation efficiency (98.79%) at a k_1 value of 0.046 min^{-1}. This result was related to the changes in the HA content during the ozonation process in pH7 [5]. Both direct and indirect oxidation pathways can occur in neutral pH [5][14]. Contrary to expectation, the result from the initial pH 2 was not the highest in terms of HA degradation. However, a previous study showed that the best result of removal efficiency was achieved at an acidic pH value [2].

Table 3. Pseudo-first-order kinetic model of pH on degradation of HA

Initial pH	Kinetic parameter			
	C_{HA_e} (mgL^{-1})	k_1 (min^{-1})	C_{HA_o} (mgL^{-1})	R^2
2	4.392	0.031	19.608	0.964
4	2.118	0.047	19.294	0.967
7	0.235	0.076	19.451	0.983
10	2.745	0.032	21.333	0.939
12	6.118	0.056	20.392	0.960
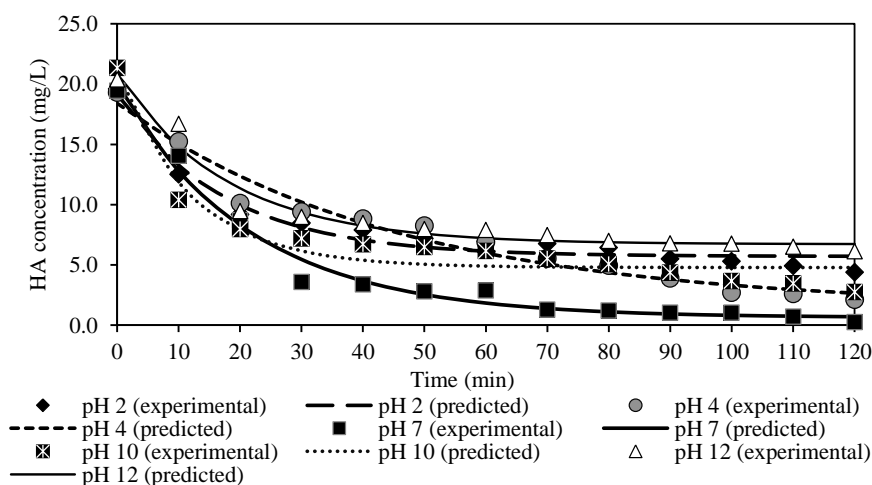
Figure 4. Non-linear plot of Pseudo-first-order kinetic model graph of HA on pH effect

3.4 Influence of initial ozone dosage.

Figure 5 shows a good connection between the experimental and predicted data values. Based on Table 4**,** the R^2 values are near 1 to indicate that the model fit well on the effect of different ozone dosage. The highest rate of reaction occurs at the highest ozone dosage (4.9 mg/L) which 0.046 min^{-1}. The increasing ozone dosages led to increasing at the removal of HA.

　　　　Ozone dosage at 3.2 mg/L with constant flow rate of 15 L/min showed the decreasing HA concentration to obtain the constant line that indicates complete oxidization [3]. The prolonged

exposure to ozone resulted in the cleavage in larger molecule of HA [19]. Due to the complexity of the HS, high ozone dosage (3.0mg O_3/ mg) could be applied according to the raw water ozone demand. Different doses are applied in wastewater treatment due to varying concentrations of components in the water.

Table 4. Pseudo-first-order kinetic model of effect ozone doses on degradation of HA

Ozone dosage (mg/L)	Kinetic parameter			
	C_{HA_e} (mgL^{-1})	k_1 (min^{-1})	C_{HA_o} (mgL^{-1})	R^2
1.6	11.922	0.019	19.529	0.982
3.2	5.373	0.011	19.882	0.956
4.9	0.196	0.046	19.451	0.983
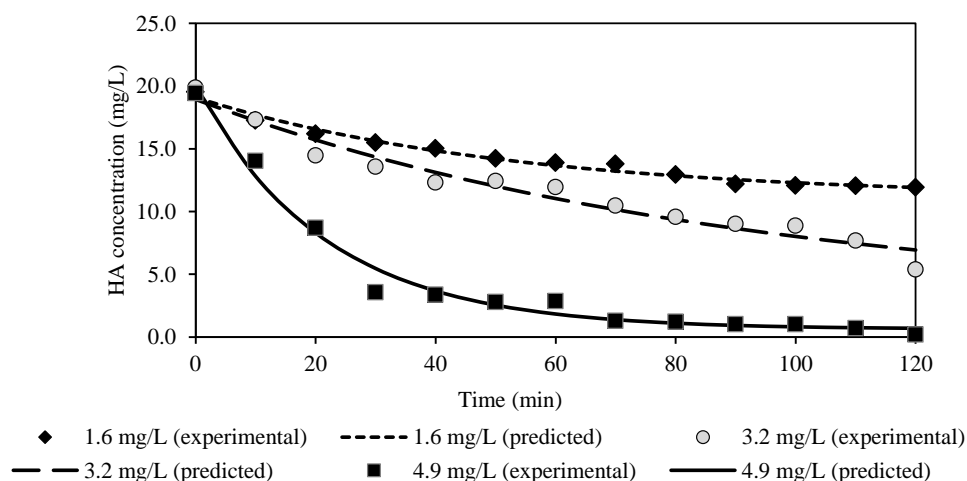
Figure 5. Non-linear plot of Pseudo-first-order kinetic model graph of HA on ozone doses

4. Conclusion

The study was conducted to determine the degradation of humic acid by the ozonation process. The degradation rates of HA fitted well in the pseudo-first-order kinetic reaction. The high concentration of HA has a low degradation rate and difficult to degrade by ozone. It was found that the degradation rate of HA increase as increasing in ozone dosage. The neutral pH had obtained the highest degradation of HA. This study has shown the great degradation of HA in UV_{254} (98%) was at 20 mg/L of Ha concentration, initial pH 7 and 4.9 mg/L of ozone dose at ambient temperature. The higher k_1 value is at pH 7. The ozonation treatment has been confirmed to increase the degradation of HA in water treatment.

Acknowledgment

References

[1]   Khayrullina R, Tizaoui C, Williams P, and Spacie C 2017 *Ozone: Science and Engineering* **39**(5) 310–318

[2]   Turkay O, Inan H and Dimoglo A 2015 *Environmental Science and Pollution Research* **22** 202–210

[3]   Yu M, Kim J, Han Y, and Kim H 2002 *Water Science and Technology* **46** 21–26

[4]   Abdw A A G, Doğan Ş and Pirgalıoğlu S 2018 *Ozone: Science and Engineering* **40** 321–329

[5]   Molnar J, Agbaba J, Dalmacija B, Rončević S, Prica M and Tubić A 2012 *Environmental Science and Pollution Research* **19** 3079–3086

[6]   Spiliotopoulou A, Rojas-Tirado P, Chhetri R, Kaarsholm K, Martin R, Pedersen PB, Pedersen L and Andersen H 2018 *Water Research* **133** 289–298

[7]   Margot J, Kienle C, Magnet A, Weil M, Rossi L, de Alencastro L F, Abegglen C, Thonney D,Chèvre N, Schärer M and Barry D A 2013 *Science of the Total Environment* **461** 480–498

[8]   Liu H, Chen L and Ji L 2019 *Journal of Hazardous Materials* **376** 125–132

[9]   Mishra N, Reddy R, Kuila A, Rani A, Nawaz A and Pichiah S (2017) *Current World Environment* **12** 469–489

[10] APHA, Awwa and Wef 2017 3120 B. *Iductively Coupled Plasma (ICP) Method. Standard Methods for the Examination of Water and Wastewater* **1** 1–5.

[11] Gonçalves A A and Gagnon G A 2011 Ozone: *Science and Engineering* **33** 345–367

[12] Yu M J, Kim Y H, Han I and Kim H C 2002 *Water Science and Technology* **46** 21–26

[13] Miao H, Tao W, Cui F, Xu Z and Ao Z 2008 *Clean - Soil, Air, Water* **36** 893–899

[14] Gottschalk C, Saupe A and Ann Libra J 2010 *Biological Wastewater Treatment Organic Pollutants in the Water Cycle Risk Analysis of Water Pollution Rapid Chemical and Biological Techniques for Water Monitoring Membranes in Clean Technologies : Theory and Practice* **2**.

[15] Yang Y, Li H and Li J 2014 *Frontiers of Environmental Science and Engineering* **8** 854–862.

[16] Tabla-Hernández J, Rodríguez-Espinosa P F, Hernandez-Ramirez A G, Mendoza-Pérez J A, Cano-Aznar E R and Martínez-Tavera E 2018 *Water* **10**

[17] Castro J, Paz S, Mena N, Urresta J and Machuca-Martinez F 2019 *Environmental Science and Pollution Research* **26** 4488–4497

[18] Galdeano M C, Wilhelm A E, Goulart I B, Tonon R V, Freitas-Silva O, Germani R and Chávez D W H 2018 *Brazilian Journal of Food Technology* **21** 1–7

[19] Papageorgiou A, Stylianou S K, Kaffes P, Zouboulis A I and Voutsa D 2017 *Chemosphere* **170** 33–4