



## Sequential ozonation and Fenton process for the removal of refractory organics from semi-aerobic aged refuse biofilter leachate effluent

Xuqin Pan

Faculty of Geosciences and Environmental Engineering, Southwest Jiaotong University, Chengdu 611756, China,  
email: zyluo7335@my.swjtu.edu.cn (X. Pan)

Received 6 January 2020; Accepted 31 July 2020

---

### ABSTRACT

Large amounts of refractory organic matter are present in mature leachate after treatment with a semi-aerobic aged refuse biofilter (SAARB). This study applied a sequential ozonation and Fenton process to the treatment of the refractory organic matter in SAARB leachate. The effects of the operating parameters of the ozonation and Fenton processes were investigated. Under an  $O_3$  flow-rate of 43.68 mg/L, initial pH of 9, and reaction time of 30 min, the ozonation process achieved 66.16% removal of absorbance at a wavelength of 254 nm ( $UV_{254}$ ) and 91.39% color number (CN) removal, and a three-dimensional excitation and emission matrix (3D-EEM) analysis indicated that the ozonation process could effectively degrade refractory humic substances in SAARB leachate. The removal efficiencies of fulvic-like substances in the ultraviolet and visible light regions were 79.12% and 70.32%. The total organic carbon (TOC) removal efficiency in the ozonation process was only 5.88%, and small amounts of organic acids were accumulated after ozonation. The Fenton process was therefore applied after ozonation to achieve a better treatment efficiency of the SAARB leachate. The  $UV_{254}$  and CN removal efficiencies increased to 78.38% and 99.71% under conditions with an initial pH of 3, hydrogen peroxide ( $H_2O_2$ ) dosage of 10 mL/L,  $Fe^{2+}$  dosage of 11 mmol/L, and reaction time of 120 min. The removal efficiencies of fulvic-like substances in the ultraviolet and visible light regions were 87.38% and 81.16%. Some refractory organic matter was degraded and transformed into tyrosine-like and tryptophan-like substances. In addition, the sequential ozonation and Fenton process exhibited a better mineralization capacity (TOC removal of 33.76%). In conclusion, the sequential ozonation and Fenton process could effectively degrade refractory organic matter in SAARB leachate and resulted in a strong mineralization of organic matter.

*Keywords:* Ozonation; Fenton process; Mature leachate; Semi-aerobic aged refuse biofilter

---

### 1. Introduction

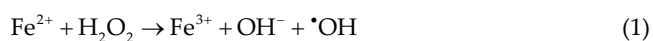
According to the China Statistical Yearbook of China's National Bureau of Statistics, the production of municipal solid waste has reached 200 million tons and sanitary landfill is the main disposal method. In a landfill site, leachate will inevitably be produced. The quality of landfill leachate varies greatly and is significantly affected by landfill age [1–3]. Mature leachate is produced from landfill sites that have been operating for many years and is characterized by

a high content of refractory organic matter, heavy metals, and bacteria. The effective treatment of wastewater with such high concentrations of organic materials is essential.

Previous studies indicated that the use of a semi-aerobic aged refuse biofilter (SAARB) was an effective approach to treat mature landfill leachate, with an excellent removal efficiency for nitrogenous substances [4,5]. A SAARB can be loaded with aged refuse that has been land-filled for many years and acts as a bioreactor bed mainly

utilizing the effects of biodegradation. Most organic matter can be degraded by the various aerobic, anaerobic, and semi-aerobic effects of microorganisms. The effective removal of nitrogenous substances can be achieved by nitrification and denitrification [4,6,7]. However, bio-resistant organic matters in mature leachate are difficult to remove using microorganisms and refractory organic matter will still be present in SAARB leachate, leading to a low biodegradability (indicated by the biochemical oxygen demand/chemical oxygen demand (BOD/COD) ratio). Therefore, SAARB leachate should receive further treatment.

In literature, leachate can be treated by various technologies, including coagulation, biological method, and advanced oxidation processes. Coagulation can be better used as the pre-treatment process [8]. Biological method is suitable for the treatment of leachate with higher biodegradable organics content and also is commonly applied to leachate treatment [9,10]. As for advanced oxidation processes, ozonation, and the Fenton process both have been widely used in refractory organic wastewater treatment due to their strong oxidation capacity for organic matter [11–20]. Ozone ( $O_3$ ) can oxidize organic matters with no secondary pollution formation. Chen et al. [15] combined a SAARB with ozonation to treat young and mature landfill leachate, and reported that refractory organic matter in SAARB leachate can be effectively degraded and biodegradability significantly improved through ozonation. Also, it was found that a combined process of SAARB-Ozonation can significantly remove ammonia nitrogen (almost 100%). Ozonation is effective for organic matter removal and molecules with unsaturated bonds and alcohols can be effectively degraded, but contrasting result have been obtained when degrading saturated alkanes [21]. Additionally,  $O_3$  can degrade macromolecule organic matter into a simpler molecule structure, but  $O_3$  has a low reaction rate with small organic molecules, such as carboxylic acids and aldehydes [21,22]. The Fenton process can degrade organic matter through the action of the hydroxyl radical ( $\cdot OH$ ,  $E^0 = 2.7$  V), which is produced from  $Fe^{2+}$  catalyzing hydrogen peroxide ( $H_2O_2$ ) (Eqs. (1)–(3)) [2,23–29]. Unlike ozonation,  $\cdot OH$  can non-selectively oxidize organic targets [30,31]. In addition, the flocculation and adsorption effects of the Fenton process can also contribute to organic removal. However, the large amounts of iron-based sludge that is produced generates secondary pollution, which also needs to be treated. Applying just one of these methods always has shortcomings, such as poor degradation efficiency and/or secondary pollution; however, previous studies have reported that a combination of ozonation and the Fenton process can be applied to the treatment of organic wastewater. For example, Zhao et al. [19] used a sequential Fenton and ozone-based oxidation process to treat Ni-EDTA containing nickel plating effluents. The combined sequential process had a 99.84%  $Ni^{2+}$  removal and 57.13% TOC removal. However, combining ozonation and the Fenton process to treat SAARB leachate has seldom been reported.



On this basis, sequential ozonation and the Fenton process was applied to treat SAARB leachate. The objectives of this study were to: (1) investigate the effects of the operating parameters of ozonation and the Fenton process on organic matter removal; (2) study the degradation characteristics of humic substances in the SAARB leachate by sequential ozonation and the Fenton process via a three-dimensional excitation and emission matrix (3D-EEM); and (3) compare the mineralization capacity of single ozonation and sequential ozonation and the Fenton process via total organic carbon (TOC) removal. This study provides a technical reference for the treatment of refractory organic matter in biological treatment effluent.

## 2. Materials and methods

### 2.1. SAARB leachate

SAARB leachate was collected from the mature leachate treated by the acclimated SAARB process for 30 d. The mature leachate was collected from a large-scale anaerobic landfill in southwest China with a total design capacity of 3,209  $m^3$  and the treatment capacity of 3,200 metric ton/d. The quality characteristics of SAARB leachate can be found in Table 1.

### 2.2. Reagents and experimental devices

Analytical grade ferrous sulfate ( $FeSO_4$ ),  $H_2O_2$  (30% v/v), and other reagents were purchased from Kelong Chemical Factory (Chengdu, China). Ultrapure water was used throughout the whole experiment. Ozonation was performed in an ozone reactor, which included an oxygen bottle ( $O_2$  purity of 99.99%), ozone generator (CONT KT-OZ-5G, Shanghai, China), stable-flow valve, and ozone absorption device. When the input oxygen flow rate was 0.2, 0.3, 0.4, and 0.5 L/min, the ozone dosage output was 18.92, 32.16, 43.68, and 52.65 mg/min, respectively. The Fenton process was carried out in a thermostatic oscillator.

#### 2.3.1. Ozonation process

The initial pH of 500 mL SAARB leachate was adjusted to the desired value (3–11). Then, each sample was transported to the ozone reactor and the  $O_3$  dosage was

Table 1  
Characteristics of SAARB leachate

Index	Value
pH	7.36
$UV_{254}^a$	0.526
$CN^b$	0.218
$TOC^c$	332 mg/L

<sup>a</sup> $UV_{254}$  refers to the absorbance value at 254 nm.

<sup>b</sup>CN is the color number and is calculated according to Eq. (4).

<sup>c</sup>TOC refers to total organic carbon (mg/L).

precisely controlled to start ozonation (18.92, 32.16, 43.68, and 52.65 mg/min). After a 30 min reaction, SAARB leachate was collected for treatment by the sequential Fenton process. To analyze the water quality of the SAARB leachate after ozonation, each sample was filtered through a 0.45  $\mu\text{m}$  filter. Then the treated samples ( $\text{O}_3$  dosage = 43.68 mg/min and pH = 7) were further treated by Fenton process.

### 2.3.2. Fenton process

The initial pH of 50 mL SAARB leachate after ozonation was adjusted to the desired value (3–11) then transferred to 250 mL conical flask. Fenton reagents of certain dosages were added ( $\text{Fe}^{2+}$  dosage of 0–13 mmol/L,  $\text{H}_2\text{O}_2$  dosage of 0–11 mL/L), then the conical flask was immediately placed into a thermostatic oscillator. After the reaction, the pH value of each sample was immediately determined. Before filtering through a 0.45  $\mu\text{m}$  filter, the pH value of each treated sample was adjusted to 9.0 to stop the Fenton reaction. To prevent the influence of residual  $\text{H}_2\text{O}_2$  on further testing, residual  $\text{H}_2\text{O}_2$  was eliminated by adding catalase (C9322, Sigma-Aldrich, St. Louis, MO, USA).

### 2.4. Analytical method

The pH value of each sample was measured using a pH detector (PHS-25, Fangzhou Co., Chengdu, China). The CN was calculated using Eq. (4), where  $A_{436}$ ,  $A_{525}$ , and  $A_{620}$  represent the absorbance value at wavelengths of 436, 525, and 620 nm, respectively. The relative concentration of aromatic substances in wastewater was determined by measuring the  $\text{UV}_{254}$ . The 3D-EEM was conducted using an Aqualog-UV-800C (Horiba Scientific, Piscataway, NJ, USA) to determine changes in the molecular structure of humic substances in SAARB leachate before and after treatment (scan intervals of 5 nm, scan speed of 500 nm/min, excitation wavelength range of 200–550 nm, and an emission wavelength range of 200–550 nm). A multifunctional 2100 TOC/TN analyzer (Analytik Jena AG, Jena, Germany) was used to determine the TOC of SAARB leachate before and after treatment.

$$\text{CN} = \frac{(A_{436}^2 + A_{525}^2 + A_{620}^2)}{(A_{436} + A_{525} + A_{620})} \quad (4)$$

## 3. Results and discussion

### 3.1. Ozonation process

The ozonation process can effectively degrade aromatic substances. Therefore, we applied ozonation ahead of the Fenton process to treat SAARB leachate. The effects of the  $\text{O}_3$  flowrate and initial pH value on the degradation efficiency of refractory organic matter were investigated.

#### 3.1.1. Effect of $\text{O}_3$ flowrate

As shown in Figs. 1a and b, the  $\text{UV}_{254}$  and CN removal efficiencies increased at higher  $\text{O}_3$  dosages. When the  $\text{O}_3$  flowrate was 18.92 mg/min and the reaction time was 30 min, the  $\text{UV}_{254}$  and CN removal efficiencies were 58.37% and 76.56%, respectively. When the  $\text{O}_3$  dosage was increased to 52.65 mg/min, the  $\text{UV}_{254}$  and CN removal efficiencies increased to 77.76% and 95.67%, respectively. It was concluded that increasing the  $\text{O}_3$  dosage could significantly enhance the removal of humic and aromatic substances, and more effectively destroy the chromophores of organics. It can be seen that the growth of the  $\text{UV}_{254}$  and CN removal slowed down in the latter stage of the reaction, especially at a higher  $\text{O}_3$  dosage. As shown in Fig. 1c, the effluent pH value continuously decreased after 5 min of reaction and a more dramatic trend was observed at a higher  $\text{O}_3$  dosage. The limitation of the reaction substrate concentration led to a less significant degradation efficacy in the latter stage of the reaction. In addition,  $\text{O}_3$  itself can effectively degrade aromatic substances and other macromolecular organics, and oxidize them into smaller molecules with a simpler structure, such as small organic acids, most of which react very slowly with  $\text{O}_3$  [21,32]. Therefore, treatment efficiencies in the latter stage of the reaction increased much more slowly, while the accumulation of small organic acids will lead to a decrease in the pH value of the ozonation effluent.

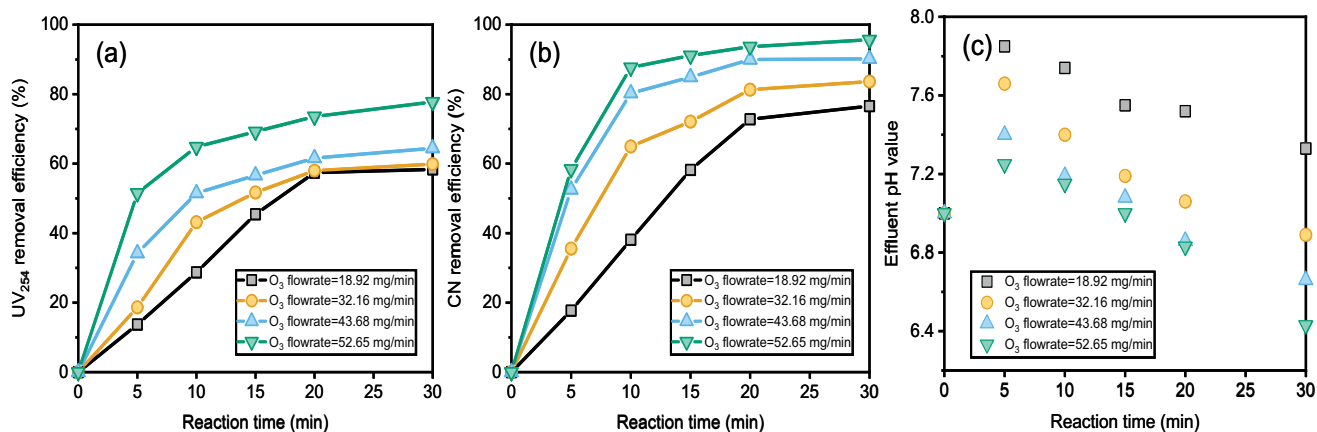


Fig. 1. Effect of the ozone ( $\text{O}_3$ ) dosage on (a)  $\text{UV}_{254}$  absorbance, (b) color number (CN) removal efficiencies, and (c) effluent pH value. Conditions: initial pH value = 7.

### 3.1.2. Effect of initial pH value

As shown in Figs. 2a and b, better treatment efficiencies were obtained under a higher initial pH value. When the initial pH value was 11, the  $UV_{254}$  and CN removal efficiencies were 77.76% and 97.62%, which increased by 22.63% and 22.47%, respectively, when compared to the removal efficiency under the initial pH of 3. The results showed that alkaline ambient conditions improved the oxidation capacity of ozonation, which was in accordance with previous reports [12]. Under acidic ambient conditions, the oxidation of organic matter was mainly due to the effect of  $O_3$ , while under alkaline ambient conditions  $O_3$  will react with  $OH^-$  to produce highly oxidative  $\cdot OH$ , which can significantly enhance the oxidation capacity of the ozonation process. As shown in Fig. 2c, the effluent pH value of each sample gradually decreased with reaction time. The explanation for this was the same as for the  $O_3$  flowrate experiment, which is discussed in section 3.1.1 (effect of  $O_3$  flowrate).

## 3.2. Fenton process

After ozonation, many small organic acids were accumulated in the SAARB leachate. To further treat the residual organic matter, the Fenton process was applied after ozonation. The effects of  $H_2O_2$  dosage,  $Fe^{2+}$  dosage, initial pH value, and reaction time on treatment efficiency were investigated.

### 3.2.1. Effect of $H_2O_2$ dosage

As shown in Fig. 4a, an increase in the  $H_2O_2$  dosage led to a better treatment efficiency of both  $UV_{254}$  and CN. When the  $H_2O_2$  dosage was 11 mL/L, the  $UV_{254}$  and CN removal efficiencies in the sequential ozonation and Fenton process were 71.63% and 97.66%, respectively, which were 5.47% and 6.27% higher than for the single ozonation process. It was found that increasing the  $H_2O_2$  dosage promoted organic degradation; however, an excessive dosage of  $H_2O_2$  did not significantly improve organic removal. Panda et al. [33] reported that  $H_2O_2$  will also compete with organic substrates to react with  $\cdot OH$  (Eq. (5)). Therefore, the supply of too much  $H_2O_2$  would decrease its utilization rate, and thus

treatment efficiency would not significantly increase. Overall, the Fenton process did not produce a significant removal of  $UV_{254}$  and CN. The  $UV_{254}$  represents macromolecular organic matter, while the CN represents certain functional groups, such as C=C and the benzene ring [34,35]. While  $O_3$  can substantially and effectively destroy the molecular structure of macromolecule organics, the Fenton process as a sequential method applied after ozonation, naturally resulted in a slight improvement of  $UV_{254}$  and CN removal. Fig. 3a also indicates that the effluent pH value after the Fenton process was applied for 30 min was stable and close to 3. This was because Fenton reagents have a very low pH value and the Fenton reaction will produce a large amount of  $H^+$ .



### 3.2.2. Effect of $Fe^{2+}$ dosage

As shown in Fig. 3b, the treatment efficiency increased and effluent pH value decreased with increasing  $Fe^{2+}$  dosage. When the  $Fe^{2+}$  dosage increased from 0 to 7 mmol/L, the  $UV_{254}$  and CN removal efficiency increased by 7.74% and 6.49%, respectively. With a further increase in the  $Fe^{2+}$  dosage from 7 to 13 mmol/L, the  $UV_{254}$  and CN removal efficiencies only increased by 2.57% and 0.97%, respectively. The results implied that a high dosage of  $Fe^{2+}$  can better catalyze  $H_2O_2$  to produce  $\cdot OH$ . However, too much  $Fe^{2+}$  will not significantly increase treatment efficiency. This is not only because of the limitation of organic substrates, but also because too much  $Fe^{2+}$  will more rapidly catalyze  $H_2O_2$  to produce large amounts of  $\cdot OH$ , which will generate  $H_2O_2$  (Eq. (6)) and react with  $Fe^{2+}$  (Eq. (7)) [26].



### 3.2.3. Effect of the initial pH value

When the initial pH value increased from 3 to 11, both the  $UV_{254}$  and CN removal efficiencies displayed a

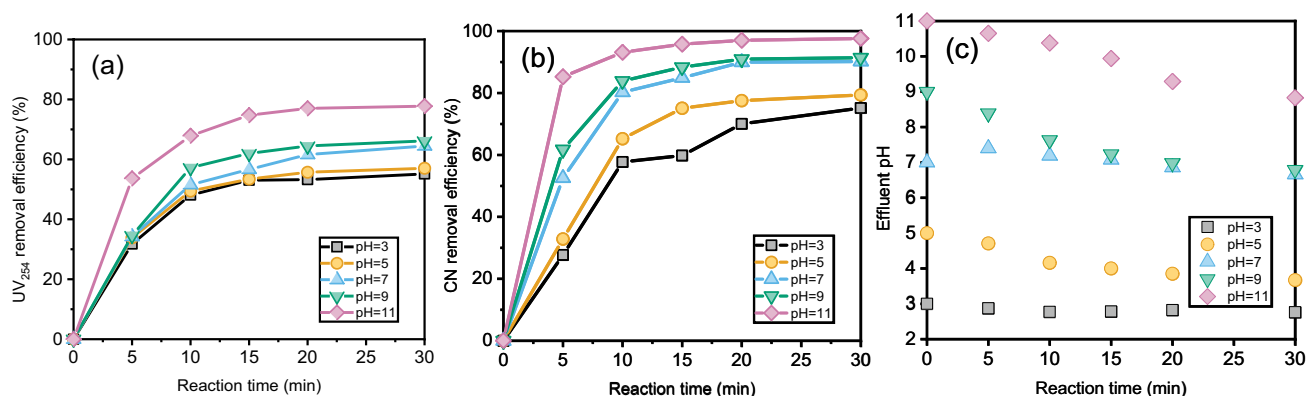


Fig. 2. Effect of the initial pH value on (a)  $UV_{254}$  absorbance, (b) color number (CN) removal efficiencies, and (c) effluent pH value. Conditions:  $O_3$  dosage = 43.68 mg/L.

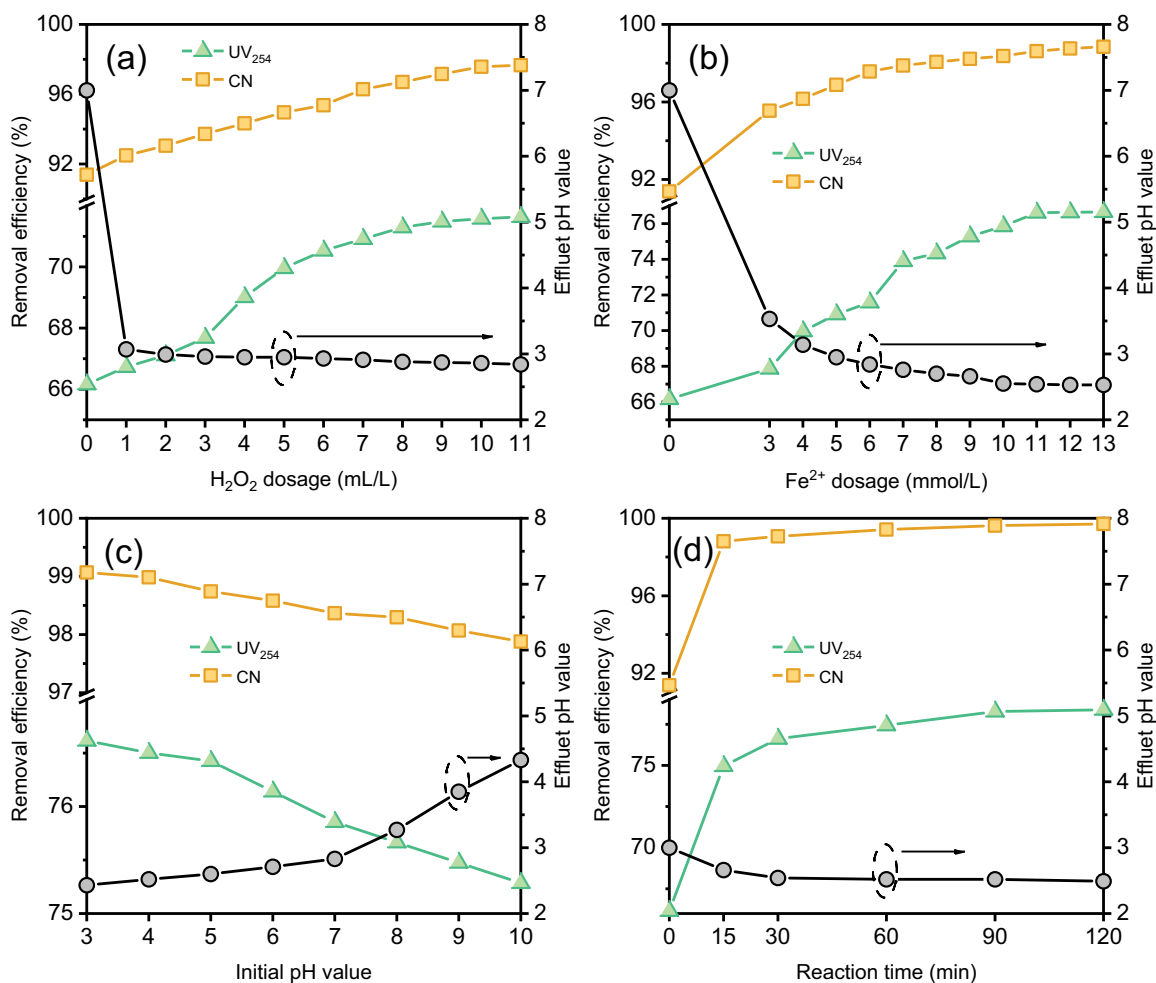


Fig. 3. Effects of (a) hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) dosage, (b)  $\text{Fe}^{2+}$  dosage, (c) initial pH value, and (d) reaction time on the treatment efficiency of the Fenton process. Conditions:  $\text{H}_2\text{O}_2$  dosage = 10 mL/L,  $\text{Fe}^{2+}$  dosage = 11 mmol/L, initial pH = 3, and reaction time = 30 min.

downward trend, as shown in Fig. 3c. This can be attributed to the  $\text{Fe}^{2+}$  that existed in an ionic form under acidic conditions effectively catalyzing  $\text{H}_2\text{O}_2$ . When the initial pH value was too high,  $\text{Fe}(\text{OH})_3$  precipitates will be generated, while  $\text{H}_2\text{O}_2$  will also decompose under alkaline conditions. However, the  $\text{UV}_{254}$  and CN removal efficiencies were 75.10% and 97.47%, respectively, which represented a decline of only 1.52% and 1.60% compared to the conditions with an initial pH of 3. In addition, the effluent pH value dramatically decreased to 5.37 when the initial pH was 11. This indicated that even if the reaction conditions of the Fenton process were strongly basic, the effluent pH value could eventually decline to the acidic range. This could be attributed to: (1) Fenton reagents having a low pH value and their addition consuming the alkalinity of the wastewater; and (2) the reaction of  $\text{Fe}^{3+}$  and  $\text{OH}^-$  also consuming the alkalinity of wastewater and the production of precipitates contributing to the removal of organics to some extent. Hence, the above mechanisms resulted in alkaline conditions having an insignificant inhibitory effect on the treatment efficiency of organics.

### 3.2.3. Effect of reaction time

As shown in Fig. 3d, the  $\text{UV}_{254}$  and CN removal efficiencies gradually increased as the Fenton reaction time increased. After the Fenton process was applied for 30 min, the  $\text{UV}_{254}$  and CN removal efficiencies were 76.62% and 99.07%, respectively, which were 10.46% and 7.68% higher than for a Fenton reaction of 0 min. A continuation of the reaction in the Fenton process thereafter did not result in an obvious increase in treatment efficiency. When the reaction time was 120 min, the  $\text{UV}_{254}$  and CN removal efficiencies only increased by 12.22% and 8.32%, respectively, compared to a reaction time of 0 min. The results indicated that the oxidation reaction of the Fenton process was mostly concentrated in the first 30 min. In the latter stage of reaction, the decrease in the reaction of organic substrates and consumption of oxidation reagents led to an insignificant increase in treatment efficiency. The Fenton process could further degrade residual aromatic substances in the SAARB leachate after ozonation, which improved the treatment efficacy of SAARB leachate.



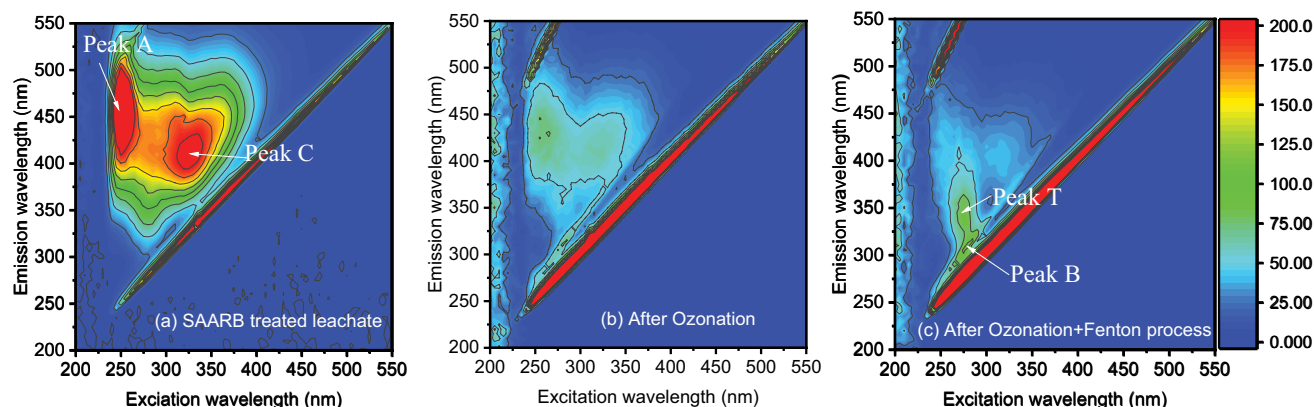


Fig. 4. Three-dimensional excitation and emission matrix (3D-EEM) of (a) semi-aerobic aged refuse biofilter (SAARB) leachate, (b) SAARB leachate after ozonation, and (c) SAARB leachate after the sequential ozonation and Fenton process. Conditions: initial pH = 9 and  $O_3$  dosage = 43.68 mg/L (ozonation process), and initial pH = 3,  $H_2O_2$  dosage = 10 mL/L,  $Fe^{2+}$  dosage = 11 mmol/L, and reaction time = 120 min (Fenton process).

### 3.3. Transformation of organic matter in the different treatment stages

#### 3.3.1. 3D-EEM analysis

To investigate the transformation characteristics of refractory organic matter in SAARB leachate by the sequential ozonation and Fenton process, samples of SAARB leachate, SAARB leachate after ozonation, and SAARB leachate after the sequential ozonation and Fenton process were analyzed by 3D-EEM.

As shown in Fig. 4a, the spectra of SAARB leachate had two fluorescent peaks, which were identified as fulvic-like fluorescent substances in the ultraviolet region ( $E_x/E_m = 235\text{--}255/410\text{--}450$  nm) and fulvic-like fluorescent substances in the visible light region ( $E_x/E_m = 310\text{--}360/370\text{--}450$  nm), respectively [15,36,37]. The fulvic-like fluorescent substances in the ultraviolet region were assigned to fulvic-like substances with a low molecular weight and high fluorescent frequency. The fulvic-like fluorescent substances in the visible light region were assigned to fulvic-like substances that were relatively stable and higher molecular weight.

As shown in Table 2, two peaks were observed in the 3D-EEM spectra [Peak A ( $E_x/E_m = 250/460$  nm) and Peak C ( $E_x/E_m = 330/415$  nm)], with peak intensities of 362.80 and 219.10, respectively. After ozonation, the peak intensities were decreased to 75.76 (Peak 1) and 65.02 (Peak C) and the removal rates were 79.12% and 70.32%, respectively. The results indicated that ozonation could

effectively degrade the humic substances in SAARB leachate. The application of the Fenton process further decreased the fluorescent peak intensity of SAARB leachate. After the sequential ozonation and Fenton process, the intensity of Peak A and Peak C decreased to 45.79 and 41.28, with removal rates of 79.12% and 70.32%, respectively. It is noteworthy that two new fluorescent peaks were found after the Fenton process was applied. They were a tyrosine-like fluorescent substance ( $E_x/E_m = 270\text{--}290/300\text{--}320$  nm) and a tryptophan-like fluorescent substance ( $E_x/E_m = 270\text{--}290/320\text{--}350$  nm). The peak intensities were 115.80 (Peak B) and 92.02 (Peak T). Therefore, the refractory organic matter that remained after ozonation could be effectively degraded by the Fenton process. In addition, some refractory macromolecular organics could be degraded into smaller and simpler structures, and tyrosine-like and tryptophan-like substances were produced in the Fenton process.

#### 3.3.2. TOC removal efficiency

The TOC removal efficiency in the sequential ozonation and Fenton process was investigated to compare the mineralization effect. The TOC concentrations of different samples were determined and are shown in Fig. 5.

As shown in Fig. 5, the TOC concentration of SAABL leachate was 331.50 mg/L. After ozonation, the TOC concentration decreased to 312.00 mg/L, with a TOC removal efficiency of only 5.88%. Similar results were obtained by Cortez et al. [38], with a 7% TOC removal efficiency

Table 2

Fluorescent peak information obtained from the three-dimensional excitation and emission matrix (3D-EEM) of semi-aerobic aged refuse biofilter (SAARB) leachate before and after the sequential ozonation and Fenton process

Peaks	SAARB	Ozonation	Fenton process
Peak A ( $I_A$ )	250/460 nm (362.80)	255/455 nm (75.76)	250/430 nm (45.79)
Peak C ( $I_A$ )	330/415 nm (219.10)	325/405 nm (65.02)	315/400 nm (41.28)
Peak B ( $I_A$ )	/	/	280/310 nm (115.80)
Peak T ( $I_A$ )	/	/	275/340 nm (92.02)

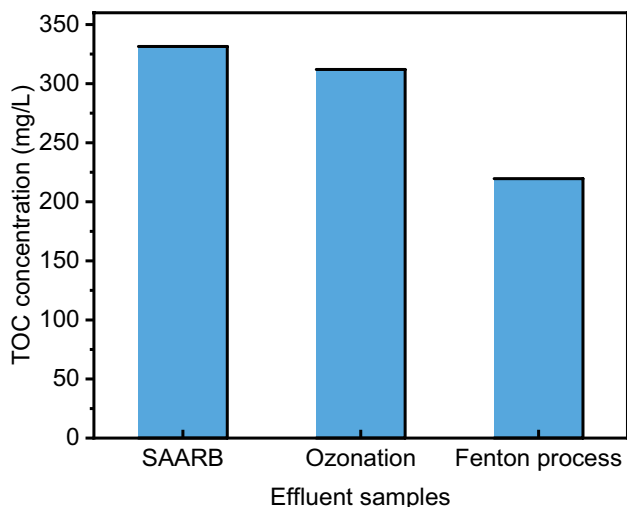


Fig. 5. Total organic carbon (TOC) concentration of semi-aerobic aged refuse biofilter (SAARB) leachate before and after the sequential ozonation and Fenton process. Conditions: initial pH = 9 and  $O_3$  dosage = 43.68 mg/min (ozonation process), and initial pH = 3,  $H_2O_2$  dosage = 10 mL/L,  $Fe^{2+}$  dosage = 11 mmol/L, and reaction time = 120 min (Fenton process).

obtained when the ozonation process was applied to treat mature leachate under conditions with an  $O_3$  dosage of 62 mg/L and reaction time of 60 min. This was because  $O_3$  can effectively degrade aromatic substances and unsaturated organics into carboxylic acids and aldehydes and other intermediates. Therefore, the  $UV_{254}$  and CN removal efficiencies in the ozonation process were high, but the TOC removal efficiency was very low. When applying the Fenton process after ozonation, the TOC concentration of SAARB leachate decreased to 219.60 mg/L and the TOC removal efficiency was 33.76%. This combination significantly enhanced the mineralization effect, indicating that  $\cdot OH$  had a high mineralization capacity in SAARB leachate after ozonation.

#### 4. Conclusions

Increasing the  $O_3$  dosage improved the treatment capacity of the ozonation process for refractory organic matter, with the best  $UV_{254}$  and CN removal efficiencies obtained under alkaline conditions. The  $UV_{254}$  and CN removal efficiencies were 66.16% and 91.39%, respectively, under conditions with an  $O_3$  flowrate of 43.68 mg/L, an initial pH value of 9, and a reaction time of 30 min. In the sequential ozonation and Fenton process, increasing the dosage of Fenton reagents improved the treatment efficiency and better treatment results were obtained under acidic conditions. On the basis of single ozonation, the  $UV_{254}$  and CN removal efficiencies increased by 12.22% and 8.32%, respectively, when the Fenton process was included. In addition, a 3D-EEM analysis showed that ozonation could effectively remove refractory humic substances in SAARB leachate and the application of the Fenton process further enhanced the removal efficiency of humic substances. The final removal efficiencies of fulvic-like substances in the ultraviolet and visible light regions were 87.38% and 81.16%, respectively.

Some refractory organic matter was degraded and transformed into tyrosine-like and tryptophan-like substances. A TOC analysis indicated that ozonation could only achieve 5.88% TOC removal, while the sequential ozonation and Fenton process achieved 33.76% TOC removal. The sequential ozonation and Fenton process resulted in stronger mineralization of organic matter in SAARB leachate.

#### References

- [1] J.L. de Morais, P.P. Zamora, Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates, *J. Hazard. Mater.*, 123 (2005) 181–186.
- [2] N.M. Ghazi, A.A. Lastra, M.J. Watts, Hydroxyl radical ( $\cdot OH$ ) scavenging in young and mature landfill leachates, *Water Res.*, 56 (2014) 148–155.
- [3] Z. Youcai, Chapter 2: Physical and Chemical Treatment Processes for Leachate, Z. Youcai, Ed., *Pollution Control Technology for Leachate from Municipal Solid Waste*, Matthew Deans, Elsevier, 2018, pp. 31–183, <https://doi.org/10.1016/B978-0-12-815813-5.00002-4>.
- [4] Z.-Y. Han, D. Liu, Q.-B. Li, A removal mechanism for organics and nitrogen in treating leachate using a semi-aerobic aged refuse biofilter, *J. Environ. Manage.*, 114 (2013) 336–342.
- [5] Z.-Y. Han, D. Liu, Q.-B. Li, G.-Z. Li, Z.-Y. Yin, X. Chen, J.-N. Chen, A novel technique of semi-aerobic aged refuse biofilter for leachate treatment, *Waste Manage.*, 31 (2011) 1827–1832.
- [6] L. Yang, X.-H. Wang, S. Cui, Y.-X. Ren, J. Yu, N. Chen, Q. Xiao, L.-K. Guo, R.-H. Wang, Simultaneous removal of nitrogen and phosphorous by heterotrophic nitrification-aerobic denitrification of a metal resistant bacterium *Pseudomonas putida* strain NP5, *Bioresour. Technol.*, 285 (2019) 121360, <https://doi.org/10.1016/j.biortech.2019.121360>.
- [7] J. Liu, Z. Tian, P. Zhang, G. Qiu, Y. Wu, H. Zhang, R. Xu, W. Fang, J. Ye, Y. Song, G. Zeng, Influence of reflux ratio on two-stage anoxic/oxic with MBR for leachate treatment: performance and microbial community structure, *Bioresour. Technol.*, 256 (2018) 69–76.
- [8] M.J.K. Bashir, H.A. Aziz, S.S.A. Amr, S.a.p. Sethupathi, C.A. Ng, J.W. Lim, The competency of various applied strategies in treating tropical municipal landfill leachate, *Desal. Water Treat.*, 54 (2015) 2382–2395.
- [9] S.M.A. Abuabdou, W. Ahmad, N.C. Aun, M.J.K. Bashir, A review of anaerobic membrane bioreactors (AnMBR) for the treatment of highly contaminated landfill leachate and biogas production: effectiveness, limitations and future perspectives, *J. Cleaner Prod.*, 255 (2020) 120215, <https://doi.org/10.1016/j.jclepro.2020.120215>.
- [10] Z. Gu, W. Chen, F. Wang, Q. Li, A pilot-scale comparative study of bioreactor landfills for leachate decontamination and municipal solid waste stabilization, *Waste Manage.*, 103 (2020) 113–121.
- [11] L. Bilińska, K. Blus, M. Gmurek, S. Ledakowicz, Coupling of electrocoagulation and ozone treatment for textile wastewater reuse, *Chem. Eng. J.*, 358 (2019) 992–1001.
- [12] N. Amaral-Silva, R.C. Martins, S. Castro-Silva, R.M. Quinta-Ferreira, Ozonation and perozonation on the biodegradability improvement of a landfill leachate, *J. Environ. Chem. Eng.*, 4 (2016) 527–533.
- [13] M. Bourgin, B. Beck, M. Boehler, E. Borowska, J. Fleiner, E. Salhi, R. Teichler, U. von Gunten, H. Siegrist, C.S. McArdell, Evaluation of a full-scale wastewater treatment plant upgraded with ozonation and biological post-treatments: abatement of micropollutants, formation of transformation products and oxidation by-products, *Water Res.*, 129 (2018) 486–498.
- [14] W. Chen, Z. Gu, P. Wen, Q. Li, Degradation of refractory organic contaminants in membrane concentrates from landfill leachate by a combined coagulation-ozonation process, *Chemosphere*, 217 (2019) 411–422.
- [15] W. Chen, A. Zhang, G. Jiang, Q. Li, Transformation and degradation mechanism of landfill leachates in a combined

- process of SAARB and ozonation, *Waste Manage.*, 85 (2019) 283–294.
- [16] Q. Dai, L. Chen, W. Chen, J. Chen, Degradation and kinetics of phenoxyacetic acid in aqueous solution by ozonation, *Sep. Purif. Technol.*, 142 (2015) 287–292.
- [17] A. Zhang, Z. Gu, W. Chen, Q. Li, G. Jiang, Removal of refractory organic pollutants in reverse-osmosis concentrated leachate by microwave–Fenton process, *Environ. Sci. Pollut. Res.*, 25 (2018) 28907–28916.
- [18] G. Zhang, L. Qin, Q. Meng, Z. Fan, D. Wu, Aerobic SBR/reverse osmosis system enhanced by Fenton oxidation for advanced treatment of old municipal landfill leachate, *Bioresour. Technol.*, 142 (2013) 261–268.
- [19] Z. Zhao, Z. Liu, H. Wang, W. Dong, W. Wang, Sequential application of Fenton and ozone-based oxidation process for the abatement of Ni-EDTA containing nickel plating effluents, *Chemosphere*, 202 (2018) 238–245.
- [20] S.S. Abu Amr, H.A. Aziz, M.N. Adlan, M.J.K. Bashir, Optimization of semi-aerobic stabilized leachate treatment using ozone/Fenton's reagent in the advanced oxidation process, *J. Environ. Sci. Health, Part A*, 48 (2013) 720–729.
- [21] C. von Sonntag, U. von Gunten, *Chemistry of Ozone in Water and Wastewater Treatment: From Basic Principles to Applications*, IWA Publishing, London, UK, 2012.
- [22] S. Lim, C.S. McArdell, U. von Gunten, Reactions of aliphatic amines with ozone: kinetics and mechanisms, *Water Res.*, 157 (2019) 514–528.
- [23] A. El-Ghenymy, S. Garcia-Segura, R.M. Rodríguez, E. Brillas, M.S. El Beggani, B.A. Abdelouahid, Optimization of the electro-Fenton and solar photoelectro-Fenton treatments of sulfanilic acid solutions using a pre-pilot flow plant by response surface methodology, *J. Hazard. Mater.*, 221–222 (2012) 288–297.
- [24] M. Verma, A.K. Haritash, Degradation of amoxicillin by Fenton and Fenton-integrated hybrid oxidation processes, *J. Environ. Chem. Eng.*, 7 (2019) 102886, <https://doi.org/10.1016/j.jece.2019.102886>.
- [25] M.-h. Zhang, H. Dong, L. Zhao, D.-x. Wang, D. Meng, A review on Fenton process for organic wastewater treatment based on optimization perspective, *Sci. Total Environ.*, 670 (2019) 110–121.
- [26] T. Sruthi, R. Gandhimathi, S.T. Ramesh, P.V. Nidheesh, Stabilized landfill leachate treatment using heterogeneous Fenton and electro-Fenton processes, *Chemosphere*, 210 (2018) 38–43.
- [27] S.S. Abu Amr, H.A. Aziz, New treatment of stabilized leachate by ozone/Fenton in the advanced oxidation process, *Waste Manage.*, 32 (2012) 1693–1698.
- [28] Z. Wang, J. Li, W. Tan, X. Wu, H. Lin, H. Zhang, Removal of COD from landfill leachate by advanced Fenton process combined with electrolysis, *Sep. Purif. Technol.*, 208 (2019) 3–11.
- [29] P.H. Nakhate, H.G. Patil, K.V. Marathe, Intensification of landfill leachate treatment by advanced Fenton process using classical and statistical approach, *Chem. Eng. Process. Process Intensif.*, 133 (2018) 148–159.
- [30] X. Ruan, Y. Sun, W. Du, Y. Tang, Q. Liu, Z. Zhang, W. Doherty, R.L. Frost, G. Qian, D.C.W. Tsang, Formation, characteristics, and applications of environmentally persistent free radicals in biochars: a review, *Bioresour. Technol.*, 281 (2019) 457–468.
- [31] C. Chen, H. Feng, Y. Deng, Re-evaluation of sulfate radical based-advanced oxidation processes (SR-AOPs) for treatment of raw municipal landfill leachate, *Water Res.*, 153 (2019) 100–107.
- [32] X. Gao, C. Leng, G. Zeng, D. Fu, Y. Zhang, Y. Liu, Ozone initiated heterogeneous oxidation of unsaturated carboxylic acids by ATR-FTIR spectroscopy, *Spectrochim. Acta, Part A*, 214 (2019) 177–183.
- [33] N. Panda, H. Sahoo, S. Mohapatra, Decolourization of Methyl Orange using Fenton-like mesoporous Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> composite, *J. Hazard. Mater.*, 185 (2011) 359–365.
- [34] Y. Deng, C. Jung, R. Zhao, K. Torrens, L. Wu, Adsorption of UV-quenching substances (UVQS) from landfill leachate with activated carbon, *Chem. Eng. J.*, 350 (2018) 739–746.
- [35] A. Gupta, R. Zhao, J.T. Novak, C. Douglas Goldsmith, Application of Fenton's reagent as a polishing step for removal of UV quenching organic constituents in biologically treated landfill leachates, *Chemosphere*, 105 (2014) 82–86.
- [36] W. Chen, A. Zhang, Z. Gu, Q. Li, Enhanced degradation of refractory organics in concentrated landfill leachate by Fe<sup>0</sup>/H<sub>2</sub>O<sub>2</sub> coupled with microwave irradiation, *Chem. Eng. J.*, 354 (2018) 680–691.
- [37] S. Huo, B. Xi, H. Yu, L. He, S. Fan, H. Liu, Characteristics of dissolved organic matter (DOM) in leachate with different landfill ages, *J. Environ. Sci.*, 20 (2008) 492–498.
- [38] S. Cortez, P. Teixeira, R. Oliveira, M. Mota, Ozonation as polishing treatment of mature landfill leachate, *J. Hazard. Mater.*, 182 (2010) 730–734.