Study on Treatment of Landfill Leachate by Electrochemical, Flocculation and Photocatalysis

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Abstract. In this study, the landfill leachate of different seasons in Liaoyang City is as the research object, and COD removal rate is as the main indicator. The electrochemical section’s results show that the optimal treatment conditions for the water of 2016 summer are as follows: voltage is 7.0V, current density is 40.21 A/m², pH is equal to the raw water, electrolysis time is 1h, and the COD removal rate is 80.41%. The optimal treatment conditions for the 2017 fall’s water are: electrolysis voltage is 7.0 V, current density is 45.06 A/m², electrolysis time is 4 hours, and COD removal rate is 28.03%. The flow rate of continuous electrolysis is 6.4 L/h using the water of 2016 fall, and the COD removal rate is 10.28%. The results of the flocculation process show that the optimal treatment conditions are as follows: pH is equal to the raw water; the optimal flocculant species is Fe-Al composite flocculant, wherein the optimal ratio of Fe-Al is n(Fe):n(Al)=0.5:1; the best dosage of flocculant is 2.0 g/L and COD removal rate is of 21.11%. The results of photocatalytic show that the optimal conditions are: pH is 4.5, Al₂(SO₄)₃ is 1.0 g/L, FeSO₄·7H₂O is 700mg/L, H₂O₂(30%) is 4 mL/L, stirring and standing UV lamp light irradiation 3 hours, and adjusting pH to 6.0 or so, COD removal rate is 36.15%.

1. Introduction
So far, sanitary landfill remains the main method of domestic garbage disposal [1-2]. The landfill process will produce a complex and difficult to deal with waste water—the landfill leachate. Landfill leachate has the characteristics of high concentration of organic pollutants, large content of metal ions, large chroma and foul odor, high content of NH₄⁺-N [3-4], wide range of change and complex pollutants. Currently, landfill leachate is mostly treated directly by membrane [5] retention, but it has the problems of high treatment cost and secondary pollution. The paper is intended to response to the above problems, the process can reduce processing costs and is recognized as the “environmentally friendly” green treatment process. Therefore, the use of the process has important theoretical and practical significance [6].
2. Materials and Methods

2.1. Electrochemistry
Water quality: COD average 15990mg/L; pH average 8.00; conductivity average 54.9 mS/cm for the water of 2016 summer and COD average 5850mg/L; pH average 8.30; conductivity average 21.5 mS/cm for the water of 2017 fall.

Experimental methods and procedures: Using the homemade electrolyzer to verify the experiment to determine the optimal current density, electrolysis time, pH, electrolysis voltage and other factors. Based on the verified experiment results, the optimal flow rate was obtained, and then continuous experiments were carried out.

(1) The volume of 0.3 L and 2.4 L electrolyzer were taken, installing the amount of landfill leachate and with DC power supply, meter, controller and other devices connected. According to the conditions obtained in the previous experiment, adjusting the corresponding parameters for verification.

(2) The optimal process conditions were determined.

(3) The volume of 2.4 L electrolyzer were taken to experiment according to the above steps.

(4) 4 cells of 2.4 L were connected in series for continuous experiments, analyzing the experiment results.

2.2. Flocculation
Water quality: The landfill leachate used in the process is the effluent after pretreatment by electrolysis. COD average 3450 mg/L; pH average 8.00.

Experimental methods and procedures: 200 mL landfill leachate were put in 200 mL beaker, under the conditions of pre-configured 10% coagulant 3.2 mL, with a digital display type overhead mechanical stirring at a speed of 280 r/min for 30 s, then adjusting the speed of 120 r/min for 5 min, mixing 0.10 mL pre-configured 0.1% polyacrylamide coagulant. Stop stirring, the water was allowed to settle 0.5, 2, 6, 10, 24 hours, photographed and measured the supernatant pH, measured COD at 6h. After 24 hours, the supernatant was separated, the amount of supernatant was taken, the volume of supernatant was recorded, and the weight of filter cake was weighed. After the supernatant was allowed to stand for 2 hours, the supernatant was separated and tested for COD.

2.3. Photocatalytic
Water quality: The landfill leachate used in this experiment was taken from the effluent after flocculation and pre-electrolysis treatment. COD average 2600 mg/L.

Experimental methods and procedures:
(1) 1L flocculation-electrolytic landfill leachate was taken, adjusting the pH to 4.5;
(2) 1g/L Al2(SO4)3 and a certain amount of FeSO4.7H2O, H2O2 (30%) were added. Stirring and under UV lamp illumination for 3h, then adjusting the pH to 6.0 or so.

3. Results and Discussion

3.1. Electrochemistry

3.1.1. Water of 2016 summer. The results of the orthogonal experiment were: electrolysis voltage was 4.0 V, electrolysis current was 1.15 A, pH was 6, electrolysis time was 2 h; electrolysis voltage was 4.0 V, electrolysis current was 1.15 A, pH was 8, electrolysis time was 1 h; electrolysis voltage was 4.0V, electrolysis current was 1.15 A, pH was 7, electrolysis time was 1.5 h. The experiment results were repeated, and the conclusion was: When the electrolysis time was 2 hours, COD removal rate was the highest, 83.74%. When the electrolysis time was 1 hour, the COD removal rate was 79.11%, although the COD removal rate was worse than the 2h, it was considered that the pH was very close to the raw water, and the subsequent continuous experiment and the process conditions were determined as: electrolysis voltage was 4.0 V, electrolysis current was 1.15A, pH was 8, electrolysis time was
1h. When using the above conditions for experiments, continuous electrolysis for several times, the power consumption had a greater difference. Mainly because of the concentration polarization, so the electrolytic voltage was increased. Under the condition of electrolysis current was 1.15 A, electrolysis time was 1 h, pH was of the raw water and then did the experiment until eliminating polarization. When the electrolysis voltage was 7.0V, the electrolysis continues for several times, the power consumption of the same electrolysis time remained basically unchanged, that was to say, when the electrolysis voltage was 7.0 V, the influence of concentration polarization on the experimental results was basically eliminated.

3.1.2. Water of 2017 fall. 3L sample was put into 2.4L electrolyzer and remaining was put into the 1000 mL beaker, the peristaltic pump inlet and electrolyzer outlet were placed in the beaker, cycling in the beaker. Electrolysis conditions: electrolytic voltage was 7.0 V, electrolysis current was 2.92 A, peristaltic pump speed was 17.6 r/min, electrolysis time was 1, 2, 3, 4, 5, 6 h. Tested COD, pH, conductivity and other datas.

| Electrolysis time/h | COD×10^3 mg/L | COD removal rate/% | Power consumption/W.h | pH  | Conductivity/mS/cm |
|---------------------|----------------|--------------------|-----------------------|-----|--------------------|
| 1                   | 4460           | 23.76              | 8.85                  | 8.79| 26.10              |
| 2                   | 4440           | 24.10              | 17.28                 | 8.68| 22.30              |
| 3                   | 4320           | 26.15              | 26.28                 | 8.61| 25.00              |
| 4                   | 4220           | 27.86              | 34.48                 | 8.49| 23.62              |
| 5                   | 4160           | 28.89              | 43.18                 | 8.46| 23.50              |
| 6                   | 4210           | 28.03              | 51.51                 | 8.39| 24.60              |

Analysis showed that when the time exceeded to 4 hours, the power consumption has been increasing, but the change of COD removal rate became smaller, considering the power consumption and the economic cost. The electrolysis time was determined to be 4 hours.

3.1.3. Continuous experiment. Flow rates were selected as 9.6, 6.4, 4.8, 3.84, 3.2, 2.4 L/h. When the flow rate was adjusted to 6.4L/h, the COD removal rate was 10.28% and it was the optimal flow rate. Under that conditions the power consumption was 53. 39Wh, the pH was 8.17, the conductivity was 17.20 mS/cm, the power consumption per unit volume of water was 2.38 W.h/L and the unit COD consumption was 4670 W.h/kg.

3.2. Flocculation

3.2.1. Determination of pH and the type of flocculant. Adjusting pH to 10 compares with the pH in raw water. According to the method, COD removal rate, the amount of supernatant and economic costs was taken into account. It can be found that the flocculant with iron had good effect, and then the active ingredient of the flocculant was studied under the condition that the pH was equal to the raw water.

3.2.2. Determination of ingredients. FeSO₄, Fe₂(SO₄)₃, MgSO₄, Al₂(SO₄)₃, H₂O₂, 3mol/LH₂SO₄ were taken preparation of the following mass fraction of 10% flocculant.
Table 2. Measurement results.

| Flocculant                     | COD×10^3/mg/L | COD removal rate/% |
|--------------------------------|---------------|--------------------|
| Mg-Al-Fe^{2+}+H_{2}SO_{4}+H_{2}O_{2} | 2.97          | 13.91              |
| Mg-Al-Fe^{3+}+H_{2}SO_{4}       | 2.80          | 18.84              |
| Mg-Al-Fe^{2+}+H_{2}SO_{4}       | 2.73          | 20.87              |
| Mg-Al-Fe^{3+}                   | 2.89          | 16.23              |
| Mg-Al-Fe^{2+}                   | 2.73          | 20.87              |
| Al-Fe^{2+}                      | 2.85          | 17.39              |
| Al-Fe^{3+}                      | 2.77          | 19.71              |

Considering economic cost and COD removal rate, Al-Fe^{3+} composite flocculant were chosen for follow-up study.

3.2.3. Determination of the ratio. 3.2 mL of 10% flocculant was added to 200 mL beaker as described above. The flocculants were: n(Fe):n(Al)=4:1, 2:1, 1:1, 0.5:1, 0.25:1. Trend as shown in Figure 1.

![Figure 1. COD removal rate trend.](image1)

The removal rate increased first and then decreased, reaching the highest value at n(Fe): n(Al)=0.5:1.

3.2.4. Determination of the dosage. 10% n(Fe): n (Al)=0.5:1 flocculant was added. The dosage was as follows: 4.8 mL (2.4 g/L), 4.0 mL (2.0 g/L), 3.2 mL (1.6 g/L), 2.4 mL (1.2 g/L), 1.6 mL (0.8 g/L) and 0.8 mL (0.4 g/L). Trend as shown in Figure 2.

The removal rate increased first and then decreased, and the optimal dosage was 2.0 g/L.

3.3. Photocatalytic

1g Al_{2}(SO_{4})_{3}, a certain amount of H_{2}O_{2} and FeSO_{4}.7H_{2}O were added in per liter sample. The amount of FeSO_{4}.7H_{2}O was 100, 150, 200, 300, 500, 700, 900, 1100 mg/L. The amount of H_{2}O_{2} was 0, 2, 4, 6, 8, 10, 12 mL/L. The results as shown in Figure 3.
Finally, the economic cost and COD removal rate were combined, the dosage of H$_2$O$_2$ was 4mL/L, the dosage of FeSO$_4$.7H$_2$O was 700mg/L, the COD removal rate was 36.15%.

4. Conclusion

(1) The optimal electrolysis conditions for water of 2016 summer were: electrolysis voltage was 7.0 V, electrolysis current was 1.15 A, electrolysis time was 1 h. The optimal electrolysis conditions for water of 2017 fall were: electrolysis voltage was 7.0V, electrolysis current was 2.92A, electrolysis time was 4h. The flow rate of continuous electrolysis was 6.4 L/h. The area of the 2.4L electrolyzer was 648cm$^2$ and the area of the 0.3L electrolyzer was 286cm$^2$.

(2) The optimal flocculant species was Fe-Al composite flocculant, wherein the optimal ratio of Fe-Al was n(Fe): n(Al)=0.5:1; and the optimal dosage of flocculant was 2.0g/L.

(3) The results of photocatalytic showed that the optimal conditions were: pH was 4.5, Al$_2$(SO$_4$)$_3$ was 1.0 g/L, FeSO$_4$.7H$_2$O was 700 mg/L, H$_2$O$_2$(30%) was 4 mL/L, stirring and standing UV lamp light irradiation 3h, and adjusting pH to 6.0 or so.

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