Experimental Study of Micro-electrolytic Technology on Ship Sewage Treatment

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Abstract. Aims to remove oil and anionic surfactants in domestic wastewater on the ship, the micro-electrolysis treatment with fillers was applied in this paper. The effect of the system on the removal efficiency of oil and surfactants was studied, and the optimal operating conditions were determined. The results show that the removal rate of oil and LAS is 81.2% and 77.5% with safe effluent quality under the optimal working conditions.

1. Introduction
Ship wastewater discharge is the nonnegligible contributor to the marine pollution presently. The implementation of International Maritime Organization (IMO) latest emission standard has raised stringent requirements for ship domestic wastewater discharge. The ship domestic wastewater includes black water and graywater. Black water refers to toilet drainage with high pollutant content; gray water refers to domestic sewage from cabins such as shower rooms and kitchens. The graywater contains a large amount of oil pollutants and surfactants. Oil will form oil-water emulsions causing serious harm to aquatic organisms. Surfactants are toxic, it will hinder the growth of microorganisms and even kill microorganisms. Surfactant mainly refers to LAS, LAS is a component that is degraded preferentially, the degradation of other pollutants will be delayed. Dissolved oxygen and minerals in the water will be consumed when degrading LAS, resulting in if the surfactant wastewater contains N and P, it will cause eutrophication of the water. Therefore, the treatment of ship graywater has become an urgent task.

The micro-electrolysis method uses the Fe and C in the micro-electrolytic filler to generate a large electrode potential difference in the solution to form a galvanic cell, through a redox reaction, physical adsorption and auxiliary action removes pollutants in wastewater. The micro-electrolysis method is suitable for the treatment of high-concentration refractory organic wastewater with stable treatment effect and low filler cost. However, there are problems such as passivation and slab bonding of the micro-electrolytic filler during the reaction, which have an adverse effect on the treatment effect. Therefore, this paper focused on the effect of different filler dosage, reaction time and pH value on the removal rate of oil and LAS in ship graywater, and determine the optimal operating conditions.
2. Materials and methods

2.1. Instruments and materials

During the study, selected instruments included box-type muffle furnace, electric blast drying oven, desktop emulsifier, UV spectrophotometer, pH meter and electronic balance; main chemicals were reducing iron powder, activated carbon powder, bentonite, ammonium bicarbonate, LAS and sodium hydroxide.

3. Results and discussion

3.1. Effect of filler dosage

Prepare 200mL of water sample with an oil concentration of 100mg/L and a LAS concentration of 100mg/L. Other conditions are unchanged to adjust the filler dosage according to the solid-liquid ratio of 1:20 (50g/L), 1:10 (100g/L), 1:5 (200g/L), 1:4 (250g/L), 1:2 (500g/L) ratio dosing. Study the effect of filler dosage on the removal rate of oil and LAS in ship graywater, research results are shown in Figure 1.

As can be seen from Figure 1, when the filler dosage is less than 250g/L, the removal rate shows a rapid increase trend with the increase of filler, and when the filler dosage reaches more than 250g/L, the removal rate tends to be horizontal. The reason is that fewer fillers will form fewer galvanic cells formed in the solution, which results in insufficient electrons to participate in the oxidation reaction and lower removal rate of oil and LAS. With the gradual increase of filler, the number of galvanic cells gradually increases and the removal rate increases. When the added filler is excessive, although more galvanic cells will be formed in the solution, the electrode potential does not change in essence. Reduced iron powder in the excess filler will replace H⁺ in the wastewater, causing the pH value of the wastewater to rise and inhibit the micro-electrolysis reaction. Only activated carbon in the filler plays a small adsorption role, but it will not affect the overall removal efficiency. In order to reduce the usage of the filler and save the operation cost, the filler dosage is finally determined to be the solid-liquid ratio of 1:4 (250g/L).

![Figure 1. Effect of filler dosage on removal rate of oil and LAS](image)

3.2. Effect of reaction time

Prepare 200mL of water sample with an oil concentration of 100mg/L and a LAS concentration of 100mg/L. The filler dosage is 250g/L, take a small amount of water sample at intervals of 10 minutes, other conditions remain unchanged. Study the effect of reaction time on the removal rate of oil and LAS in ship graywater, research results are shown in Table 1.
The results indicated that as the reaction time is longer, the removal rate is higher. The removal rate of the reaction increases rapidly before 20 minutes, and the growth of removal rate slows down from 20 minutes to 40 minutes, after 40 minutes the removal rate has stabilized. The reason is that the concentration of pollutants in the wastewater continues to decrease, which reduces the reaction rate.

| Reaction time (min) | The removal rate of oil(%) | The removal rate of LAS(%) |
|---------------------|----------------------------|---------------------------|
| 10                  | 35.1                       | 47.2                      |
| 20                  | 61.5                       | 53.5                      |
| 30                  | 70.7                       | 67.9                      |
| 40                  | 76.8                       | 73.4                      |
| 50                  | 80.3                       | 75.6                      |
| 60                  | 81.2                       | 77.5                      |

When the experimental is running, it can be observed that the color of the solution begins to change from light green to light yellow around 60 minutes, and the yellow color gradually deepens with time increase. Considering comprehensively the stability and efficiency of the experimental, the micro-electrolysis reaction time is set at 60min.

### 3.3. Effect of influent pH

Prepare 200mL of water sample with an oil concentration of 100mg/L and a LAS concentration of 100mg/L. The filler dosage is 250g/L, adjust the influent pH to 1, 2, 3, 4, 5, 6, 7 when other conditions are unchanged. Study the effect of influent pH on the removal rate of oil and LAS in ship graywater, research results are shown in Figure 2.

The results show that the removal rate of oil and LAS tends to increase first and then decrease. At pH=3, the removal effect is best, reaching 80.2% and 77.2%. The reason is that iron-carbon galvanic cell in the filler has a large electrode potential difference when the acidity is large, which can promote the redox reaction, physical adsorption, auxiliary action and other functions in the micro-electrolysis process. The reaction is as follows:

- **Anode(Fe):** \( Fe - 2e \rightarrow Fe^{2+} \) \( E_0 = (Fe^{2+} / Fe) = -0.44V \) (1)
- **Cathode(C):**
  - Under acidic conditions: \( 2H^+ + 2e \rightarrow H_2 \) \( E_0 = (H^+ / H_2) = 0.00V \) (2)
  - Under acidic oxygenation conditions:
    \( O_2 + 4H^+ + 4e \rightarrow 2H_2O \) \( E_0 = (O_2) = 1.23V \) (3)
  - Under neutral and alkaline conditions:
    \( O_2 + 2H_2O + 4e \rightarrow 4OH^- \) \( E_0 = (O_2 / OH^-) = 0.40V \) (4)

![Figure 2](image)

*Figure 2. Effect of influent pH on removal rate of oil and LAS*

![Figure 3](image)

*Figure 3. The change of effluent pH on removal rate of oil and LAS*
3.4. Effluent pH

Prepare 200mL of water sample with an oil concentration of 100mg/L and a LAS concentration of 100mg/L. The filler dosage is 250g/L, adjust the influent pH to 3, other conditions are unchanged. Study the effluent pH value at various times, research results are shown in Figure 3.

The results reveal that the micro-electrolysis treatment will gradually increase the pH value of the solution with the reaction goes. The pH value rises faster when the reaction is 0~20min, and the acidity has tended to equilibrium after 40min, and it remains at about 4.5. The reason is that H⁺ ions will be consumed in the micro-electrolysis process, so that the acidity of the solution drops.

4. Conclusion

In this paper, the micro-electrolysis treatment was applied to remove oil and anionic surfactants in ship graywater, the results show that the micro-electrolysis method has a well performance. The following conclusions can be drawn from the research:

(1) The filler dosage, reaction time and pH value have significant effects on the removal rate of oil and LAS. The optimal working condition is that the filler dosage is 250g/L, the reaction time is 60min, the influent pH is 3, the oil removal rate can reach 81.2%, and the LAS removal rate can reach 77.5%.

(2) At the end of the micro-electrolysis reaction, the effluent pH remains at about 4.5, and produces a large amount of Fe²⁺ ions, which can be combined with the Fenton reaction to improve the potential economic value of the combined technology and the quality of the effluent.

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References

[1] Zuo Xiangyu, Efficiency of Oil Grease and Anionic Surfactants Removal by Coagulation Processing as Ship Greywater Pretreatment[D], Harbin Engineering University, 2018.
[2] Li Xiangwan, Experimental Study on the removal of anionic surfactants in restaurant wastewater[D], Kunming University of Science and Technology, 2015.
[3] Zheng Jixin, Experimental Study of Combined Microelectrolysis and Fenton Process on Oily Wastewater Treatment[D], Harbin Engineering University, 2017.
[4] Coca J, Gutiérrez G, Benito J. Treatment of oily wastewater[J]. Nato Science for Peace & Security, 2011:1-55.
[5] Wu Xiaolei, Micro-electrolysis and combinations experimental study on the integration process of direct dye wastewater[D], Lanzhou University, 2015.
[6] Zhou Peiguo, Fu Dafang. Application and development for microelectrolysis technology[J]. Techniques and Equipment for Environmental Pollution Control. 2001, 2(4): 18~23.
[7] Ghauch A., Gallet C., Charef A., Rima J., Martin-Bouyer M., Reductive degradation of carbaryl in water by zero-valent iron[J]. Chemosphere. 2001, 42: 419~424.
[8] Pendyal B., Johns M.M., Marshall W.E., Ahmedna M., Rao R.M., Removal of sugar colorants by granular activated carbons made from binders and agricultural by products[J]. Bioresource Technology. 1999, 69(1): 45~51.
[9] Wang Minxin, Zhu Shuquan, Li Fasheng. Study of F-C Micro Electrolysis Treatment of Decolorization of Stimulated Dyeing Water[J]. Journal of Heilongjiang Institute of Science & Technology. 2001, 11(1): 6~10.
[10] Han Hongjun, Treatment of Industrial Wastewater by Iron-carbon Method[J]. Environmental protection. 1991, 1:17~18.
[11] Zhang Longlong. Application of the combined Fe-C micro-electrolysis and anaerobic-aerobic bio-filter with novel ceramics for ciprofloxacin wastewater treatment. Shandong University, 2018.
[12] Li Xingzheng. The studies of preparation of enhanced micro-electrolysis material and treatment of lead and zinc smelting wastewater[D]. Kunming University of Science and Technology, 2011.