Discussion on Factors Affecting the Removal of Organic Pollutants in Reverse Osmosis Concentrated Water of Landfill Leachate

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Abstract. Landfill leachate reverse osmosis concentrated water (RO concentrated water) is a kind of wastewater with high organic matter concentration, chemical oxygen demand (COD), turbidity, and chroma. The RO concentrated water is pretreated using coagulation method; then the coagulation effect of FeCl₃, Fe₂(SO₄)₃, Fe(NO₃)₃ and PAC on the leachate RO concentrated water is investigated in the experiment. The result shows that FeCl₃ is the best coagulant. The removal rate of total organic compounds (TOC) reaches the highest (92.23%) under the condition of 8.0 g/L FeCl₃ dosage, pH=6, 3 mg/L PAM, and 150 r/min rotation speed, and the removal rate of COD, NH₃-N, and chroma are 73.91%, 28.3%, and 79%, respectively.

1. Introduction
In China nowadays, incineration power generation and sanitary landfill are the dominant ways of dealing with garbage, but both of them encounter the problem of landfill leachate treatment[1]. Landfill leachate is a complex wastewater with high concentrations of organic matter, heavy metals, and toxic substances. However, traditional leachate treatment technologies such as recharge are not enough for meeting the requirements of Pollution Control Standards for Garbage Treatment[2]. With the development of membrane technology, reverse osmosis (RO) has become an advanced landfill leachate treatment technology. However, one of the main limitations of the RO process is the generation of a large amount of reverse osmosis concentrated water (referred to as RO concentrated water), which is 20%-30% of the initial volume[3]. The RO concentrated water is high in organic matter concentration, poor in biodegradability, making it difficult to handle, thus causing serious environmental pollution. Based on these characteristics, in pre-treatment, it is common to remove a large amount of organic matter, the effect of which will directly affect the subsequent in-depth treatment. Although there is some research on RO concentrated water treatment technology in China, the results are quite different with few studies on the influencing factors of this treatment technology[3]. Therefore, this study studies the main influencing factors of removing a large amount of organic matter in the RO concentrated water treatment process, which can provides technical basis for the related personnel to select and optimize the high-concentration organic wastewater treatment process[4].
2. Experiment

2.1. Wastewater quality
The RO concentrated water used in the experiment was taken from a waste incineration power plant in Chongqing City. The wastewater was brownish black with no obvious foul smell. The volume of the concentrate was 25% that of the leachate. Water quality is: pH=7.8-8.2; conductivity=90 ms/cm; COD=4515 mg/L; ammonia nitrogen concentration = 2290 mg/L; chroma=420 times.

2.2. Equipment and reagents
Equipment: DSX-90 digital display mixer; 5B-3C SOD rapid tester; PHS-3E pH meter; CD-800 TOC analyzer.
Reagents: polyaluminum chloride (PAC), ferrous sulfate, ferric sulfate, ferric chloride, ferric nitrate, sodium hydroxide, sulfuric acid, and polyacrylamide (PAM), which are of analytically pure.

2.3. Experimental methods
Put 300 mL landfill leachate RO concentrated water in a 500 mL beaker, adjust the pH between 3 and 10 using sulfuric acid and sodium hydroxide, and then add different kinds of coagulant. Stir at a speed of 200 r/min for 1 min and 80 r/min for 20 min, and then let stand for 12 h. After that, take the supernatant for water quality index test. After filtering the sample, measure and evaluate TOC in the wastewater using a TOC analyzer.

3. Result and discussion

3.1. Influence of iron coagulant on RO concentrated water treatment
The experiment was divided into three groups. Take 300 mL of RO concentrated water, and respectively added FeCl$_3$, Fe$_2$(SO$_4$)$_3$, and Fe(NO$_3$)$_3$ (ferric ion concentration = 22 mmol/L). After precipitation for a period of time, take the supernatant for testing the corresponding TOC. The coagulation effect was determined based on the TOC removal rate so as to determine a more reasonable flocculant.

It can be seen from Figure 1 that when the pH rose from 3 to 6, the removal rates of organic matter using the three coagulants were all increasing continuously. When the pH reached 6, the removal rate was at its top, about 90%. When the pH exceeded 6, the removal rate of TOC of the three coagulants all started to decrease significantly. That is because when the pH is close to the isoelectric point of the colloid, the electrostatic repulsive force between the colloids is small, make them easy to agglomerate and mix, thus better coagulation effect. It can also be found that the overall organic removal effects of the three coagulants are basically the same. Since iron nitrate may cause secondary water pollution and ferric sulfate may produce a large amount of mud, while ferric chloride has little effect on subsequent in-depth treatment, this paper selected FeCl$_3$ as the coagulant to treat RO concentrated water.

![Figure 1. effect of the same Fe$^{3+}$ concentration and different pH concentration on the removal rate of TOC](image-url)
3.2. Main effects of different anions on the degradation of organic matter
Iron coagulant is a coagulant commonly used in water treatment. Its ferric ion is the main cationic component affecting the effect of water treatment. In order to find out whether different anions will affect the water treatment effect, this experiment set pH=6, and added FeCl₃, Fe₂(SO₄)₃, and Fe(NO₃)₃ (with the same ferric ion content) to 300 mL RO concentrated water respectively, and let them stand for a period of time. Then, take the supernatant and test their corresponding TOC. The TOC removal rate is taken as the index for judging the coagulation in order to select an appropriate flocculant.

![Figure 2. the effect of different Fe³⁺ dosages on the removal rate of TOC with pH = 6](image)

It can be seen from Figure 2 that when the pH is 6, the removal rates of TOC of the three iron coagulants increased with the increase of the content of ferric ion until it reached 22 mmol/L with the TOC removal rate of around 88%. At the same time, it was found that the overall removal effects of the three coagulants on organic matter were similar, which was consistent with the results obtained above, indicating that anions had no significant effect on the whole coagulation process.

3.3. Effect of different cationic coagulants on RO concentrated water removal
Ferric ion and aluminum ion are the cationic components used in conventional coagulants. To find out their effects, the experiment added the same amount of polyaluminum chloride (PAC) and FeCl₃ (7 g/L) to 300 mL RO concentrated water and test their coagulation effect at different pH. The results are shown in Figure 3.

![Figure 3. effect of Cationic species on Coagulation effect](image)

It can be seen that as the pH increased, the removal rate of the two coagulants to TOC as a whole increased first and then decreased. The optimum pH values for PAC and FeCl₃ coagulants were 4 and 6 respectively. When the pH = 6, the corresponding TOC removal rate of FeCl₃ coagulant reached 89.23%, which was better than that of PAC at its optimum pH.

Although both coagulants can cause the colloid aggregation and destabilization, they are different
in the removal effect of organic pollutants in RO concentrated water. At low pH, both coagulants showed good removal performance, which was because low pH increased protonation and reduced the solubility of humic acid in RO concentrate, making it easier to be adsorbed. FeCl₃ has stronger acidification ability than PAC, so it performs better at low pH[5]. Therefore, FeCl₃ is more suitable as a coagulant for RO concentrated water.

3.4. Effect of the dose of a single coagulant on treatment effect

The effect of different dose of FeCl₃ on TOC removal was tested when pH = 6, see Figure 4.

It can be seen from Figure 4 that the TOC removal rate increased first and then decreased with the increase of FeCl₃ dosage. When the dosage increased from 4 g/L to 8 g/L, the removal rate increased from 75.93% to 91.28%. But further increase led to the decrease of TOC removal rate. That is because when the amount of FeCl₃ in the system is small, the removal effect is poor due to its insufficiency; when it is excessive, a large amount of H⁺ produced during Fe³⁺ hydrolyzation will be adsorbed on the surface of the humus colloid. In this way, Fe³⁺ and humic colloid are electrostatically repelled, preventing the generation of the floc, thus deteriorating the flocculation effect. Experiment shows that the optimum amount of FeCl₃ is 0.8 g/L.

![Figure 4. the effect of different FeCl₃ dosages on the TOC removal rate of pH = 6](image)

3.5. Effect of dosage of organic flocculant on TOC removal rate

The dosage and stirring speed of polyacrylamide (PAM) have a certain influence on the coagulation effect. This paper explores the influence of different PAM dosage and stirring speed on the coagulation effect after determining the pH value and the optimum amount of coagulant, as shown in Figure 5.

![Figure 5. effect of PAM addition on coagulation effect](image)
It can be seen that the coagulation effect can be improved by appropriately increasing the dosage of the coagulant PAM. However, excessive PAM will reduce the removal effect. That is because an appropriate amount of PAM can act as a bridge between colloidal particles, but excessive PAM will make the adsorption surface of the colloidal particles to be covered. When colloidal particles are close in distance, they repel each other, which is not conducive to coagulation. Therefore, insufficient PAM is not enough to bridge the colloidal particles, while excessive PAM will deliver a kind of “colloidal protection” effect, reducing the coagulation effect.

3.6. Effect of stirring speed on coagulation effect
During flocculation, the stirring rate has an influence on the flocculation effect to some extent. This paper explores the influence of different stirring rates on the flocculation effect after determining the pH value and the optimum flocculant dosage, as shown in Figure 6.

Experiment shows that the treatment effect is best when the stirring speed is 150 r/min. This is because insufficient stirring speed cannot overcome the repulsive force between the particles, affecting colloidal aggregation while excessive stirring speed will break up the newly gathered flocs, thus affecting the coagulation effect[6]. Therefore, the optimum speed in this experiment is 150 r/min.

4. Treatment effect of RO concentrated water sample
In order to investigate the effect of RO concentrated water treatment, set pH=6, FeCl3 dosage=0.8 g/L, stirring rate=150 r/min, PAM addition=3 mg/L. After coagulation pretreatment, the quality of RO concentrated water was significantly improved. For comparison result of the effluent quality, see Table 1.

| Table 1. quality of Pretreated effluent with FeCl3 Coagulation |
|-------------------|-------------------|-------------------|-------------------|
|                   | COD(mg/L)         | NH3-N(mg/L)       | Chroma (times)    | pH     |
| Concentrated water| 4515              | 2290              | 420               | 7-8    |
| water after treated| 1178              | 1641.93           | 88                | 5-6    |
| Removal rate (%)  | 73.9              | 28.3              | 79                |        |

5. Conclusion
Coagulant FeCl3 is better than PAC in the pretreatment of RO concentrated water using coagulation method. Under the optimal conditions of pH=6, FeCl3 concentration=0.8 g/L, stirring rate=150 r/min, and PAM dosage=3 mg/L, the TOC removal rate reached 92.23%. The test results of the water sample after treatment are as follows: COD=178 mg/L, removal rate=73.91%; NH3-N=1641.93 mg/L, removal rate=28.3%; chroma=88 times, removal rate=79%.
References

[1] Nie F, Li W, Liu Z, et al. (2017) Treatment of landfill leachate by coagulation precipitation-Fenton-NaClO oxidation. J. Chinese Journal of Environmental Engineering, 9(7): 3153-3158.

[2] Gao J, Oloibiri V, Chys M, et al. (2015) The present status of landfill leachate treatment and its development trend from a technological point of view. J. Reviews in Environmental Science & Bio/technology, 14(1): 93-122.

[3] Wang D, Lang X, Lei F. (2007) Research progress of landfill leachate treatment technology. J. Industrial Water Treatment, 27(2): 6-9.

[4] Long Y, Xu J, Shen D, et al. (2017) Effective removal of contaminants in landfill leachate membrane concentrates by coagulation. J. Chemosphere, 167: 512-519.

[5] An Z Y, Xu X J. (2012) Treatment of Concentrated Liquid of Landfill Leachate by Coagulation and Micro-Electrolysis Strengthened by H2O2. J. Advanced Materials Research, 573-574: 492-496.

[6] Baiju A, Gandhimathi R, Ramesh S T, et al. (2018) Combined heterogeneous Electro-Fenton and biological process for the treatment of stabilized landfill leachate. J. Journal of Environmental Management, 210: 328-337.