Treatment of high salinity organic wastewater by membrane electrolysis

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Abstract. The effects of different operating conditions on the treatment of electrolytic wastewater were investigated by analyzing the removal rate of ammonia and COD before and after wastewater treatment by cation exchange membrane. Experiment shows that as the running time increases the electrolysis effect first increases after the smooth. The removal rate of ammonia will increase with the increase of current density, and the removal rate of COD will increase first and then decrease with the increase of current density. The increase of the temperature of the electrolytic solution will slowly increase the COD removal rate to saturation, but does not affect the removal of ammonia nitrogen. When the flow rate is less than 60L / h, the change of influent flow rate will not affect the removal of ammonia nitrogen, but the effect on COD is small, which will increase and decrease slightly. After the experiment, the surface of the cation exchange membrane was analyzed by cold field scanning electron microscopy and X-ray energy dispersive spectrometer. The surface contamination and the pollutant were determined. The experimental results showed that the aggregates were mainly chlorinated Sodium, calcium and magnesium inorganic salts, which will change the morphology of the film to reduce porosity, reduce the mass transfer efficiency, affecting the electrolysis effect.

1. Introduction

High salt organic wastewater refers to the salt content of at least 1%, even the salt content of wastewater will be higher than 20%[1], with strong alkaline, but also contains a lot of organic matter, ammonia nitrogen. High salt containing organic wastewater contains high concentrations of NaCl, has a high economic value, can be used as raw materials for chlor-alkali industry. But the waste water will contain organic matter, ammonia and other substances will affect the existence of raw materials purity, reduce the use of value. Through the previous process of direct processing will result in waste of resources, will have a greater financial burden. Ion membrane electrolysis, also known as membrane electrolysis[2] as a new process for the treatment of such waste water, on the one hand both to deal with wastewater to optimize the quality of wastewater, on the other hand can also contain a large number of wastewater in the full use of NaCl, resulting in economic value. Ion-exchange membrane electrolysis with a simple operation, easy maintenance equipment, good treatment, no phase change, no secondary pollution, can be used with other processes and other advantages[3]. Chloride ion solubility in electrolysis process of waste water[4], the solution pH[5] and so will affect the electrolysis of wastewater treatment effect, while under different operating conditions, such as electrolyte time temperature, current density[6] and so on, the electrolysis effect will be affected differently.

In this experiment, the effects of different operating conditions, such as current density, electrolyte
temperature on the degradation of COD and ammonia nitrogen in electrolytic high salt organic wastewater were investigated. The surface of the membrane before and after used was analyzed the electrolysis by scanning electron microscopy and X-ray energy dispersive spectrometer. The pollution of the cation exchange membrane was investigated. Which provides an effective reference for electrolytic treatment of such waste water.

2. Experimental part

2.1. Experimental water
Experimental water is a high salt organic wastewater. The main pollutant in wastewater is sodium chloride content of 24070 mg/L, COD 1260 mg/L and ammonia nitrogen 370.4 mg/L.

2.2. Analytical methods and apparatus
COD was determined by potassium iodide alkaline potassium permanganate method, ammonia was determined by nessler's reagent spectrophotometry, determination of chloride ion concentration by silver nitrate titration. The surface morphology of the nanofiltration membrane was analyzed by S4800 cold emission scanning electron microscopy (SEM), and the elemental composition analysis was carried out with the matched X-ray spectrometer. The reagents used in the experiments were of analytical grade.

2.3. Experimental apparatus and method
Cation exchange membrane, the anode is covered with PbO2 titanium mesh plate, the cathode is stainless steel stencil. Plate size is 16cm high, 7cm wide, 0.1cm thick. The cell size is 14cm high, 7cm wide and 3cm thick, with a total volume of 300ml.

In the experiment, the self-made electrolytic experimental device was used. The specific process flow was to set the sodium hydroxide solution with certain mass fraction as the cathodic electrolyte (2). The pH of the solution was adjusted to pH 2, and the anode was introduced into the anode (9), the sodium hydroxide produced on the cathode side is refluxed to the cathodic side electrolyte (2), and the electrolytic solution of the dilute brine is discharged into the fresh salt water collecting tank (9), The generated chlorine gas and the hydrogen gas are respectively collected into the hydrogen gas collecting chamber (6) of the chlorine gas collecting chamber (5), and the inlet water flow rate of the both sides is controlled by the regulating valve (8). Control flow rate below 70L/h.

![Figure 1. schematic diagram of the electrolysis device](image)

1. anode inlet tank; 2. cathode inlet tank; 3. cationic membrane electrolysis device; 4. DC power supply; 5. chlorine collection device; 6. hydrogen collection device; 7. flow meter; 8. valve; 9. light salt water collection box
3. Results and discussion

3.1. Influencing factors of electrolytic performance

3.1.1. Effect of electrolysis time on electrolytic properties. The experimental conditions were maintained under the stable conditions of electrolysis temperature of 25 ℃, current of 10.0A and inlet flow rate of 30 L/h. The influence of running time on the electrolysis effect was investigated by analyzing the removal rate of ammonia nitrogen and COD. It can be seen from Figure 2 that the removal rate of ammonia nitrogen and COD increases with the increase of running time, accumulation of electrolysis over time tends to stabilize. The ability of membrane electrolysis to remove the COD and the removal efficiency of ammonia nitrogen from this kind of wastewater will be saturated with the time accumulation.

![Figure 2](image1.png)

Figure 2. The effect of running time on the removal of pollutants

3.1.2. The effect of current intensity on electrolytic performance. The experimental conditions were maintained under the conditions of electrolysis temperature of 26 ℃, inlet flow rate of 30 L/h and electrolysis time of 60 min. Under the conditions of current intensity of 8.0, 10.0, 13.0, 16.0 and 20.0A respectively. It can be seen from Figure 3 that with the increase of current density, the removal of ammonia nitrogen gradually increases, and the removal rate of COD increases first and then decreases. This is mainly due to the initial increase with the current and the accumulation of electrolysis time, electrolytic reaction speed, electrolysis of organic matter and ammonia nitrogen treatment effect is enhanced, but with the current continues to grow, the anode will appear oxygen evolution reaction, it will affect the effect of the oxidation efficiency and the current efficiency. With the current increases, the removal of ammonia nitrogen shows an increasing trend, mainly because, with the current increases, the electron transfer speed, the oxidation of the material increased. So the same electrolysis time, the higher the current density, the higher the removal rate of ammonia nitrogen, but with the current continues to rise, the side reaction will intensify, the degradation rate of COD began to decline.

![Figure 3](image2.png)

Figure 3. Effect of current density on the removal of pollutants
3.1.3. Electrolysis temperature on the electrolytic performance. The experimental conditions were maintained at inlet flow rate of 30L/h, the current density was 10.0A and the electrolysis time was 60min. The electrolysis temperature was controlled at 25, 35, 45, 55 and 65 ℃, respectively. The effects of temperature on the electrolytic properties were investigated by comparing the COD and ammonia removal rates of electrolyzed water. In Figure 4, the removal efficiency of ammonia nitrogen did not change at different electrolysis temperatures, and it was basically steady state. It was found that the change of temperature had no effect on electrolytic removal of ammonia nitrogen in a certain temperature range. The removal efficiency of COD at different temperatures initially increases with temperature increases, then the removal effect tends to be stable. Electrolysis is an endothermic reaction, when the temperature rises, it will promote the reaction, improve the activity of the material and promote the degradation of organic matter. But with the temperature continues to improve, the role of organic matter degradation did not continue to improve.

![Figure 4](image)

**Figure 4.** Effect of temperature on the removal of pollutants

3.2. Characterization of cation exchange membrane pollution

3.2.1. Surface analysis of membrane surface. The surface morphology of the membrane was observed under scanning electron microscope (SEM). The cation exchange membrane used in the experiment was the structure of porous fabric. As can be seen from Figure 5, the surface of the membrane before use is rather rough, the shape is very irregular. Figure 6 used cation exchange membrane, in the scanning electron microscope can be seen, the film surface is relatively flat, the original loose structure becomes tight and smooth. This is mainly due to the progress of the experiment, the membrane surface of the accumulation of membrane contaminants, so that the original rugged membrane surface is filled with aggregates, changing the shape of the membrane, the membrane surface becomes more flat and dense.

![Figure 5](image)

3.2.2. Spectrum Analysis (EDX). The x-ray energy dispersive spectrometer was used to analyze the elemental composition of the membrane surface before and after the use, and the composition of the membrane contaminant was determined. It can be seen in Table 1 that the main elements of the unused membrane are C, O and S, the mass fraction is 45.26%, 38.90% and 8.73% respectively. After running for some time, the main elements of the cation exchange membrane were C, O, Na, Cl, Mg, S and Ca, and their mass fraction were 19.39%, 13.99%, 25.50%, 35.27%, 2.07%, 1.97% and 0.33% respectively. By comparing the changes in the elements before and after the use of the membrane, we can see that the material accumulated on the membrane surface is mainly sodium chloride and a small amount of calcium and magnesium salts. These salts, which accumulate on the membrane surface, change the morphology of the membrane, form membrane fouling, reduce the porosity of the membrane, and affect the mass transfer efficiency, which can have an effect on the efficiency of wastewater treatment and the stability of the device.
Figure 5. before the use of cation exchange membrane

Figure 6. after the use of cation exchange membrane

| Table 1. Results of line energy spectrum analysis |
|------------------------------------------------|
| Unused cationic membrane element | Wt% | At% | Used cationic membrane element | Wt% | At% |
| C      | 45.26 | 55.87 | C      | 19.39 | 33.63 |
| O      | 38.90 | 35.99 | O      | 13.99 | 18.22 |
| Na     | 04.63 | 02.98 | Na     | 25.50 | 23.10 |
| Cl     | 00.00 | 00.00 | Cl     | 35.27 | 20.73 |
| S      | 08.73 | 04.03 | S      | 01.97 | 01.28 |
| Ca     | 01.00 | 00.37 | Ca     | 00.33 | 00.17 |
| Mg     | 00.69 | 00.42 | Mg     | 02.07 | 01.78 |

4. Conclusion

Through the experiment, it can be concluded that the treatment of high salinity organic wastewater by membrane electrolysis is affected by multiple factors.

1. With the accumulation of running time, the removal efficiency of ammonia nitrogen and COD will rise with time, after running for some time, the removal effect is no longer enhanced, until saturation.

2. The effect of current density on the ammonia nitrogen in the electrolytic wastewater is linearly increased in a certain range, and the removal rate of ammonia nitrogen increases with the increase of current density, and the removal rate of COD increases first and then decreases status. The highest removal rate of COD was at a current density of 13.0 A.

3. The change of influent temperature has little effect on the removal of ammonia nitrogen. Under certain temperature range, the change of temperature will not affect the removal efficiency of ammonia nitrogen. The effect of removing COD is increasing first and then steady with increasing temperature.

4. Morphological and elemental analysis of the cation exchange membrane were carried out by cold field scanning electron microscopy and X-ray spectrometer. It was found that the membrane surface after experiment could enrich some salts such as sodium chloride and calcium and magnesium. These inorganic salts will cover the membrane surface, so that the membrane surface becomes flat and dense, reducing the porosity of the film, affecting the efficiency of electrolytic mass transfer and the effect of electrolytic wastewater treatment, and because of the salt in the membrane surface aggregation, will affect the device running stability, so that the voltage increases, affecting the device running results.

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