Experimental Study on The Oxidative Degradation of RO Concentrated Water by Ti/IrO2-RuO2 Electrode

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Abstract. Advanced treatment and reuse of wastewater is an effective way to solve the shortage of water resources in China. The advantages of RO Technology, such as better water quality and lower operating cost, have become the mainstream desalination technology for wastewater reuse. However, RO technology will produce a certain amount of concentrated water, which contains a large number of inorganic salts and soluble refractory organics. The efficient removal of refractory organics in this high salinity system has become the main bottleneck and problem faced by RO technology. In view of the difficulty of further biochemical treatment of the concentrated water in the RO unit of a sewage treatment plant, the electrochemical method is used to treat the concentrated water. The effects of electrode spacing, current density and reaction time on the treatment of RO concentrated water were discussed. The optimal operation parameters for the treatment of 300ml of the wastewater are as follows: plate spacing 1.5cm, current density 300A/m², reaction time 20min. Under the above conditions, the COD removal rate can reach 95%, and the lower the initial COD value, the higher the degradation efficiency.

1. Introduction
The RO process produces concentrated water with high pollutant concentration at the same time of the preparation of recycled water, and the concentrated water usually accounts for 1/3 of the recycled water. The COD of this kind of wastewater is generally over 100 mg/L, which can not be discharged directly, and the B/C is low, the conductivity is more than 3000μs/cm, the biodegradability is poor, and the treatment is very difficult. RO concentrated water treatment has become the bottleneck of double membrane process in the field of wastewater reuse. The treatment methods of RO concentrated water at home and abroad include improving recovery rate, direct or indirect discharge, comprehensive utilization, evaporation and concentration[1]. Among them, the improvement of recovery rate and direct or indirect discharge do not fundamentally remove pollutants; comprehensive utilization has great limitations for wastewater with complex pollutant components; evaporation and concentration consumes too much energy, which most enterprises cannot bear[2]. Therefore, the key to solve the problem of RO concentrated water treatment is to find a treatment method of highly effective degradation of pollutants. As a kind of advanced oxidation technology, electrochemical oxidation technology has the characteristics of strong degradation ability, no secondary pollution [3], low operation cost, mainly through the direct oxidation of the electrode surface, as well as the indirect oxidation of various free groups produced by the electrode, to degrade the organic pollutants in the electrochemical degradation, and the degradation effect is determined by the electrode material, test conditions and electrolyte composition Set [4]. Boron doped diamond electrode (BDD) has a high removal rate and electrical efficiency for organic pollutants. Pérez et al. [5] used BDD electrode to oxidize the concentrated reverse osmosis water produced by municipal tertiary wastewater treatment.
When the initial COD is 124.8 mg/L, all the COD can be removed in 8 hours, and the energy consumption is 6.4 kW·H/m³, but the expensive price of BDD electrode limits its application[4]. The resistance of Ti based Sb doped tin oxide (ATO) electrode is small, the over potential of oxygen evolution and the degradation efficiency of organic matter are high. However, there are few reports on the application of Ti/IrO₂-RuO₂ electrode in the degradation of RO concentrated water. In this paper, Ti/IrO₂-RuO₂ electrode is used to treat the concentrated water of a wastewater treatment plant in order to achieve the purpose of discharge of RO concentrated water up to the standard, and the best reaction conditions are explored.

2. Materials and methods

2.1. Preparation of Ti/IrO₂-RuO₂ Electrode

The prepared 5cm×10cm×1.5mm Ti plate is polished with 320 mesh abrasive paper to remove impurities and oxide layer on the surface of titanium matrix, then washed with deionized water, then soaked in 40% NaOH solution, ultrasonic degreased at 80 ℃ for 5 minutes, washed and dried. Then, the alkali washed Ti plate is immersed in 10% oxalic acid solution, heated and boiled for about 1 h, the Ti plate dissolves at high temperature and reacts with oxalic acid to form Ti oxalate, the surface of Ti plate produces brownish yellow substance, and the solution changes from colorless to brownish yellow. After boiling for 3 h, the surface of Ti plate lost metallic luster, and the surface was brown and uneven. Finally, the pickled Ti plate was stored in anhydrous ethanol. A certain amount of RuCl₃ꞏxH₂O, H₂IrClꞏ6H₂O and tetrabutyl titanate were dissolved in isopropanol, uniformly stirred by ultrasonic wave as coating solution, and a small amount of 37% hydrochloric acid was added to prevent hydrolysis. The coating solution is evenly applied on the surface of the treated titanium electrode with a brush. After coating, it is placed in an oven at 140 ℃ for drying. Then it is heated and oxidized in a muffle furnace at 450 ℃ for 15 min. After taking it out, it is cooled in the dryer and then brushed again. This process is repeated for 10 times.

2.2. Experimental Water Quality

The experimental water is from the third class concentrated water of the RO device of a sewage treatment plant in Tangshan City, Hebei Province. Main water quality indicators: COD 100-300 mg/L, pH 7.5±0.1, chroma 128 times, Cl⁻(3.5 ± 0.1) g/L, SO₄²⁻ 80-90g/L, with light yellow appearance. There are a lot of Ca₂SO₄, NaCl and other salts in the wastewater, the salinity is very high; in addition, there are a lot of surfactants, alkanes and aromatic hydrocarbons in the wastewater, which make the wastewater in a very stable emulsification state, and the treatment is difficult.

2.3. Experimental Device

The experimental reactor is made of plexiglass with a volume of 0.40L. The reactor specification is 12cm (length) × 4cm (width) × 12cm (height). The anode adopts the self-made Ti/IrO₂-RuO₂ electrode, the cathode adopts the pure titanium electrode, the effective area of the plate is 10cm × 10cm, and the spacing between the plates is adjustable. The DC stabilized power supply is used for power supply, and the experimental treatment water volume is 300mL.

2.4. Experimental Method

Put the anode plate and cathode plate in the electrolytic cell containing the wastewater to be degraded relatively parallel. The anode plate is connected with the positive pole of the DC power supply, and the cathode plate is connected with the negative pole of the DC power supply. Degrade the wastewater with different electrode spacing. Take samples every 10 minutes and measure the COD value of wastewater at different time points.
3. Results and Discussion

3.1. Effect of Plate Spacing on Degradation Effect
The change of COD value was investigated when \( d = 1.0 \text{cm}, 1.5 \text{cm}, 2.0 \text{cm} \) and \( 2.5 \text{cm} \). The experimental conditions are as follows: current density \( 300 \text{A/m}^2 \), adding \( 300 \text{ml} \) wastewater, initial COD of wastewater is \( 180 \text{mg/L} \), electrolysis time \( t = 40 \text{min} \), sampling and analysis every 10min. The results are shown in Figure 1.

![Figure 1](image1.png)

Figure 1. Influence of plate spacing on COD

The reason why the plate spacing is considered as a single factor is that the size of the plate spacing will affect the electric field strength of the solution between the plates, thus affecting the degradation effect of pollutants. It can be seen from figure 3.1 that when the distance \( d = 1.5 \text{cm} \), the COD value decreases the most, when \( d = 1.0 \text{cm} \), the COD value decreases the slowest, when the distance increases to more than 2\text{cm}, the effect of COD value decrease gradually becomes worse as the reaction proceeds. The analysis shows that the smaller the electrode spacing is, the greater the electric field strength is, so that the force between electrodes is enhanced, the conductivity is increased, the mass transfer effect in wastewater is increased, the migration rate of charged ions is increased, the generated \( \cdot \text{OH}, \text{O}_2^- \) can react with organic pollutants quickly, and the COD removal rate of wastewater is effectively improved. When the current density is fixed, with the increase of plate spacing, the field strength of pollutants in the solution between plates decreases. In addition, with the constant electrolyte concentration, the conductivity decreases with the increase of distance, and the current efficiency decreases, so that the degradation effect is weakened. However, if the distance is too small, it is not conducive to the electrochemical catalytic oxidation reaction. This is because when the distance between the two plates is very close, the solution between the plates is not easy to flow and exchange with the solution outside the plate, resulting in the uneven composition of the solution, resulting in concentration polarization, resulting in the waste of electric energy. If the control is not appropriate in the experiment, the contact between the positive and negative plates will cause short circuit or current load It can not only reduce the service life of the electrode, but also destroy the power supply and instruments, resulting in safety accidents. Therefore, the optimal plate spacing is determined as \( d = 1.5 \text{cm} \).

3.2. Effect of Current Density on Degradation Effect
The effects of current density on the degradation efficiency were investigated, and the changes of COD value at \( J=100 \text{A/m}^2, 200 \text{A/m}^2, 300 \text{A/m}^2 \) and \( 400 \text{A/m}^2 \) were investigated. The experimental conditions are as follows: the distance between plates is 1.5\text{cm}, 300\text{ml} \) wastewater is added, the initial COD of wastewater is 180\text{mg/L}, the electrolysis time \( t=40 \text{min} \), and the samples are taken every 10\text{min} for analysis. The results are shown in Figure 2.
0 1 02 03 04 0
0 40 80 120 160 200
COD(mg/L) Time/min

Figure 2. Influence of current density on COD

It can be seen from Figure 3.2 that the degradation effect under the condition of high current density is better than that under the condition of low current density. This is because the increase of current density and the acceleration of electron transfer speed between organic pollutants and electrodes further cause the concentration of active groups such as ·OH, O$_2^-$ with strong oxidation in the wastewater to increase, which is conducive to the progress of electrocatalytic oxidation reaction, thus improving the wastewater COD removal rate of. When the current density is more than 300A/m$^2$, the treatment effect does not improve significantly with the increase of current density. This is because when the current density is higher and the pollutants are less, side reactions will occur, there are more bubbles around the plate, the phenomenon of hydrogen evolution and oxygen evolution in the wastewater is serious, and the power efficiency is reduced. In conclusion, the best current density is 300A/m$^2$.

3.3. Effect of Reaction Time on Degradation Effect

The effect of electrolysis time on degradation efficiency was studied, and the change of COD value at $t = 10$min, 20min, 30min and 40min was investigated. The experimental conditions are: plate spacing = 1.5cm, current density = 300A/m$^2$, initial COD of wastewater is 180mg/L, and the results are shown in Figure 3.

0 1 02 03 04 0
0 40 80 120 160 200
COD(mg/L) Time/min

Figure 3. Effect of electrolysis time on COD

The electrolysis time has a great influence on the experimental results. The electrolysis time is related to the electrocatalytic effect, electric energy efficiency and other factors. The purpose of studying the electrolysis time is to fully degrade pollutants under high electric energy efficiency and improve the economy and practicability of electrochemistry oxidation catalysis. It can be seen from the figure that within 20 minutes before the reaction, with the increase of the reaction time, the COD value decreases rapidly. This is because in the early stage of the electrocatalytic oxidation reaction, the concentration of organics in the wastewater is relatively large, and the diffusion speed to the electrode plate is very fast. With the extension of the degradation time, the strong oxidation intermediates H$_2$O$_2$
and · OH generated on the anode plate surface. The increase plays a decisive role in the degradation of pollutants, and the COD value decreases rapidly. The electrolysis time continues to increase, and the reduction of COD value slows down. This is because in the later stage, with the decrease of pollutant concentration in the wastewater, the probability of its diffusion to the electrode surface becomes smaller, the excessive current density produces oxygen on the electrode surface, and the side reaction of oxygen evolution takes place, which leads to the waste of electric energy. Considering the treatment effect and economy, the best reaction time is determined as follows: 20min.

### 3.4. Effect of Initial COD Value of Wastewater on Degradation Effect

When the initial COD value is 100mg/L, 180mg/L and 250mg/L, the change of COD value is investigated. The experimental conditions are as follows: plate spacing =1.5cm, current density = 300A/m², electrolysis time t = 40min, sampling and analysis every 10min. The results are shown in Figure 4.

![Figure 4. Effect of initial value of wastewater on degradation effect](image)

It can be seen from the figure that when the initial COD value of wastewater is 250mg/L, the degradation rate of COD begins to decline. This is because the surface of the electrode plate has been saturated and the electrons in the solution can not contact with the electrode plate well to produce · OH, which leads to the degradation efficiency reduction. However, when the initial COD value of wastewater is below 180mg/L, the degradation rate of COD does not increase. This is because the content of solute in the reaction system is relatively high. Therefore, the optimal initial COD value of wastewater is 180mg/L.

### 4. Conclusion

1. The optimal reaction conditions for the degradation of RO concentrated water were determined by experiments. When the electrode spacing was 1.5cm, the current density was 300A/m², and the reaction time was 20min, the highest removal rate of COD was 95%.

2. The removal efficiency of RO concentrated water with COD of 100-180mg/L was about 95%, but when the initial COD value of wastewater was higher than 180mg/L, the removal efficiency decreased obviously.

### 5. Reference

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