

Original Article



Research on a Novel Combined Technology Treated High-Salt Organic Wastewater

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Abstract:

In this study, a novel combined technology treated high-salt organic wastewater was proposed by ozone oxidation-coupled electro dialysis technology. Both the decomposition law of organic matter and the migration rule of salt ions during the coupled process were analyzed. The results showed that without adjusting the pH, when the ozone concentration was 20 g/L and the ozone reaction time was 10 min, the removal rates of COD, UV254, and ammonia nitrogen were 53.89%, 42.20%, and 40.29%, respectively. The concentration changes of the major anions and cations were extremely small, and the separation rates of Cl⁻ and SO₄²⁻ were only 4.54% and 5.56%, respectively. The chromaticity varied from 2000 to 800. Ozone pretreatment improved the operating environment during electro dialysis. After electro dialysis treatment, the separation efficiencies of Cl⁻, SO₄²⁻, Na⁺, and K⁺ were significantly improved. Under conditions of 15 V and 1 A and a reaction time of 60 min, the separation efficiencies of Cl⁻, SO₄²⁻, Na⁺, and K⁺ were 94.24%, 86.37%, 96.12%, and 91.08%, respectively. The total desalination efficiency of the entire process is 92.24%. The combined process provides a new solution for the treatment of high salt and high organic wastewater.

Keywords: ozone coupled electro dialysis; high-salt organic wastewater; organic matter decomposition; salt separation

Introduction

As an emerging treatment technology, hydrothermal treatment (HTT) has received wide attention in the field of solid waste treatment owing to its advantages of better resource and energy recovery [1-4]. However, the generation of hydrothermal solutions from the hydrothermal process, which contain dissolved organic pollutants, has hindered the application of this technology to a certain extent [5]. Therefore, the necessary treatment is key to promoting the engineering transformation of this technology.

Currently, the treatment of hydrothermal solutions includes anaerobic digestion[6, 7], algae cultivation[8], advanced oxidation[9], nutrient recovery[10], and hydrothermal solution circulation application[11-13], etc. Chen Huihui (2017) from Fudan University used sludge

hydrothermal solution for anaerobic digestion, and the results showed that at a HTT temperature of 170°C, the methane production was 286 mL CH₄/g COD, which gradually decreased with the increase of HTT temperature[14]. Owing to the long period and slow reaction time of the anaerobic digestion process, the fermentation broth requires further treatment. Some researchers have proposed the use of a hydrothermal solution for microbiological cultivation to achieve efficient use of organic matter in the hydrothermal solution. Diego López Barreiro (2015) investigated the influence of the hydrothermal solution produced by HTT on microalgal growth and found that the response of microalgae species to the recycling of nutrients is strain-dependent: *P. tricornutum* and *S. almeriensis* were not able to grow satisfactorily in recovered aqueous by-

products. *C. vulgaris* and *N. gaditana* could grow by replacing 75% of the nutrients from the standard medium[10]. Du Zhenyi (2012) carried out the culture of *Chlorella vulgaris* using sludge hydrothermal solution and found that the undiluted hydrothermal solution had a certain toxic inhibitory effect on the growth of algae, and the culture of *Chlorella vulgaris* was significantly correlated with the dilution times of the hydrothermal solution[15]. Advanced oxidation technology can achieve the efficient detoxification of macromolecules through direct or indirect redox reactions with organic matter and free radical reactions, creating conditions for subsequent recycling or resourcing. M. Toufiq Reza (2016) applied wet oxidation technology for the treatment of cattle manure and sludge digestate[9]. The results showed that after the wet oxidation treatment, nitrogen-containing macromolecular compounds from solution products were converted and decomposed into short-chain organic acids (e.g., formic, acetic, succinic, propionic, and glycolic acids). However, such technologies are only used for pretreatment or deep treatment.

Unlike the hydrothermal solution produced by the HTT of ordinary biomass, when treating a hydrothermal solution containing a high content of salt and organic matter, the high concentration of salt ions also inhibits the decomposition of organic matter to some extent[5]. To realize the recycling application of hydrothermal solutions with high salt and organic matter contents, desalination is a necessary prerequisite for resource recycling. Owing to its excellent element recovery, electrodialysis technology is regarded as the most promising desalination technology and has been widely used in wastewater and brackish water desalination processes [16-18]. However, few studies have focused on industrial wastewater with high organic matter content derived from the hydrothermal process. High concentrations of

organic matter can significantly affect mass transfer during the electrodialysis process[19], leading to the attachment and accumulation of organic contaminants on the membrane surface, causing fouling of the membrane aperture, destruction of the membrane structure, and reduction of membrane life[20].

Based on the above research analyses, ozone oxidation coupled with electrodialysis was used in this study for the treatment of hydrothermal solutions with high salt and organic matter content. To investigate the decomposition and transformation of organic pollutants, ozone was used as a pre-treatment to oxidize the hydrothermal solution. After pre-oxidation, the effluent flows into the electrodialysis unit to further study the effect of current intensity, reaction time, and other parameters on desalination and the performance of the membrane module, laying the foundation for the recycling application of the high-salt and high-organic-matter hydrothermal solution.

1. Materials and Methods

1.1 Sources and Characteristics of the Experimental Hydrothermal Solution

First, dewatered sludge with a moisture content of 80% and incineration fly ash were mixed in an autoclave (FCF - 2 L, China) at a mass ratio of 4:1 (dry basis), and the liquid–solid ratio was adjusted to 4:1 by adding DI water. The autoclave was then sealed and heated to 180 °C for 60 min under anoxic conditions with stirring at 200 rpm. At the end of the reaction, the products were filtered via vacuum filtration to achieve solid - liquid separation, and the separated liquid phase was collected and stored in a refrigerator at 4 °C to obtain the experimental hydrothermal solution. The procedure was described in detail in our previous research [21, 22]. The characteristics of the hydrothermal solution are listed in Table 1.

Table 1 Characteristics of the Hydrothermal Solution

Parameters	pH	UV254	COD (g/L)	TP (mg/L)	NH ₄ -N (mg/L)	Chroma (multiple)
	7.02±0.01	14.13±0.67	32.94	0.72±0.23	535.15±45	2000
Parameters	Cl ⁻ (g/L)	SO ₄ ²⁻ (g/L)	Na ⁺ (g/L)	K ⁺ (g/L)	TDS (g/L)	EC (mS/cm)
	11.02±0.09	1.79±0.02	0.25±0.05	0.16±0.04	19.02±0.38	38.65±0.05

TDS: total dissolved solids; EC: Electrical conductivity

From Table 1, it can be seen that the concentrations of COD, $\text{NH}_4 - \text{N}$, Cl^- , SO_4^{2-} , chroma, and TDS are very high, which is related to the raw material and makes it difficult to deal with.

1.2 Experiments of Ozone Pre - oxidation for the Hydrothermal Solution

To investigate the effect of contact time of ozone with the hydrothermal solution, the experiment was carried out in a cylindrical reactor of plexiglass with a diameter of 80 mm and a height of 250 mm ($\text{H}250 \times \Phi 80$), with an effective volume of 0.5 L. An ozone generator with a rate of 20 g (O_3)/h was fed from the bottom of the reactor, and the gas volume was adjusted to 2 L/min for 60 min. The samples were collected at 5, 10, 20, 30, and 60 min and analyzed after passing through a 0.45 μm filter membrane for ammonia nitrogen, chroma, COD, UV254, and 3D fluorescence.

To investigate the effect of ozone concentration

on the hydrothermal solution, under the condition that the ozone reaction time was controlled at 10 min, and without adjusting the pH value and other parameters of the hydrothermal solution, the strength of the electric current and the amount of oxygen inlet were adjusted to control ozone generation at 16, 18, 20, and 25 g/h. Experimental samples were collected for further analysis.

1.3 Experiments of Electrodialysis Separation

Electrodialysis separation experiments were performed using the EX - 3BT electro dialysis unit provided by Hangzhou Lanran Technology Co., Ltd.. A schematic of the device is shown in Fig. 1. It consists of ten membrane pair units, each containing a cation exchange membrane (CEM) and an anion exchange membrane (AEM), which are alternately distributed to form the electro dialysis unit. The membrane size was 75×195 and the total effective membrane area was 0.055 m^2 , corresponding to an effective area of 0.0055 m^2 per unit.

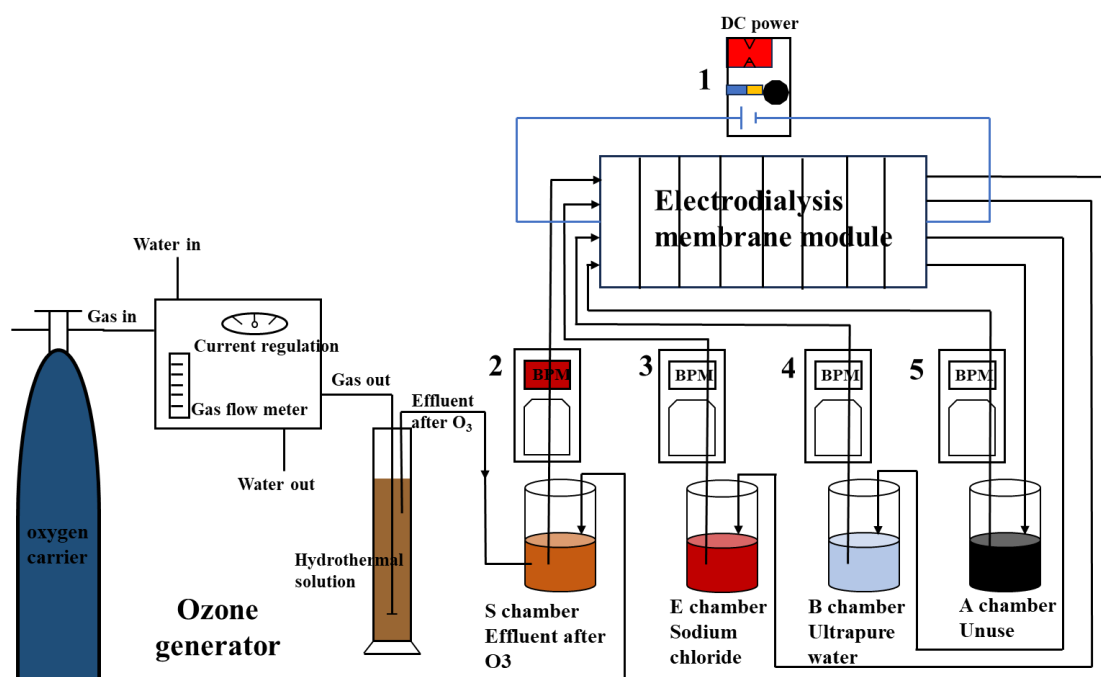


Figure 1 Ozone coupled Electrodialysis Device Diagram

The electro dialysis mode was selected, and four peristaltic pumps (2, 3, 4, and 5) were used to drive the hydrothermal solution to flow into the separation unit. The hydrothermal solution to be treated was placed in the dilute chamber (chamber S), the acid chamber (chamber A) was unused, ultrapure water was in the concentrated chamber (chamber B), and the circulation of the electrode

solution was carried out in the electrode chamber (chamber E). Sodium chloride (NaCl) at a concentration of 3% was used as the electrode solution. The flow rates of the dilute and concentrated chambers were set to 600 mL/h.

The flow rate of the electrode chamber was adjusted to 800 mL/h to ensure a better charge transfer. The electro dialysis experiments were

carried out using a DC power supply in 15 V constant voltage mode, and the current of the electro dialysis unit was sequentially adjusted to 0.5, 1.0, 1.5, and 2.2 A. The limiting current of the unit was 2.2 A. All experiments were carried out at a constant temperature of 25 ± 1 °C. Samples were collected at regular intervals (0, 5, 10, 20, 30, 60, 120, 150, 180, and 210 min) during the experiments, and the changes in electroconductivity in the dilute and concentrated chambers, pH, cumulative power consumption, cumulative energy consumption, and liquid level were recorded to determine the changes in their volume. The duration of the experiment was determined by the electro-conductivity in the dilute chamber, which was reported when the conductivity of the chamber was reduced to approximately 2 mS/cm; operation within the current limit region will result in concentration polarization[23].

To ensure complete ion exchange of mixed counterions to the membrane, before starting the experiment, the electrolyte solutions in the dilute chamber (S chamber), concentrated chamber (B chamber), and electrode chamber (E chamber) were all run at a flow rate of 80 L/h for approximately 4 h and then stopped, immersing the membranes in the solution for at least 10 h. Only in this way can a fully equilibrated ion exchange membrane be obtained to exclude experimental errors caused by incomplete adsorption on the ion exchange membrane, which may occur when the ion concentration is too low.

1.4 Analytical Methods

The chemical oxygen demand (COD) of the samples was determined using a portable COD tester; ammonia nitrogen ($\text{NH}_4\text{-N}$) was tested by spectrophotometry (HJ535 - 2009); the concentrations of anions (Cl^- and SO_4^{2-} ions) in the water samples were determined by ion chromatography (ICS - 90, Thermo, USA); and the concentrations of cations (Na^+ and K^+) were tested by inductively coupled plasma mass spectrometry (ICP-MS) [24]. All samples to be

tested were passed through a 0.45 μm filter membrane and then diluted to a certain proportion with DI water according to the test range before being measured and analyzed. Electrical conductivity (EC) and total salt content were measured using a conductivity meter. Chroma was determined using the dilution method. pH was measured using a pH meter. A fluorescence spectrophotometer (F - 7100) was used to determine the changes in the major organic pollutants in water.

The ion separation efficiency of the hydrothermal solution after electro dialysis was calculated using the following equation.

$$\text{Separation rate} = (\text{C}_0\text{V}_0 - \text{C}_t\text{V}_t) / \text{C}_0\text{V}_0 * 100\%$$

Here, C_0 is the initial concentration of the ion (including: Cl^- , SO_4^{2-} , Na^+ , and K^+); V_0 is the initial volume of the hydrothermal solution to be treated; C_t is the final concentration of the ion (including: Cl^- , SO_4^{2-} , Na^+ , and K^+) after electro dialysis; V_t is the remaining volume of the hydrothermal solution after electro dialysis.

2. Results and Discussion

2.1 Analysis of the Effect of Ozone Pre - oxidation

It is well known that ozone has high oxidation activity, which does not increase the salt content of wastewater in the case of no other salts participating in the reaction. Moreover, the decomposition product of ozone oxidation is oxygen, which does not cause secondary pollution[25], and is considered to be an ideal method for treating wastewater with a high salt and organic content. Therefore, the effect of ozone pretreatment under different conditions on the removal of organic matter from wastewater with a high salt content was initially investigated.

2.1.1 Changes in COD, and $\text{NH}_4\text{-N}$

Fig. 2 shows the changes in COD and $\text{NH}_4\text{-N}$ under different ozone reaction conditions. Fig. 2 (a) shows the effect of ozone action time and Fig. 2 (b) shows the effect of ozone concentration.

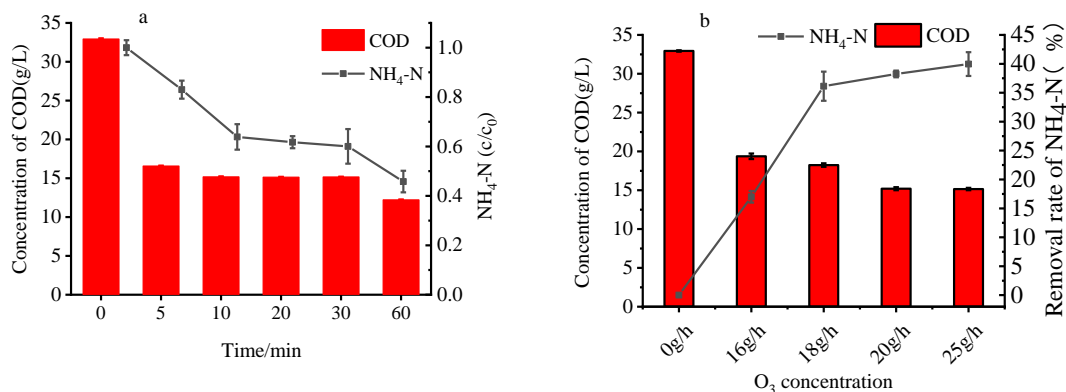


Figure 2 Changes in COD, and NH₄ - N under Different Ozone Conditions (a) Time (b) Concentration

As shown in Fig. 2 (a), the COD and NH₄ - N of the hydrothermal solution showed a gradual decrease with increasing ozone reaction time. In the first 5 min of ozonation, the organic matter decreases rapidly, and the COD concentration decreases from the initial 32.94 g/L to 16.58 g/L, with a decomposition rate close to 50%, and then the decomposition rate slows down. The NH₄ - N changed gradually after 10 min of ozone action, and the oxidation rate of NH₄-N was 36.13% in the first 10 min of the ozone reaction. This is due to the fact that the accumulation of ozone continues to increase with the extension of time, and in the initial stage, ozone quickly reacts with the substances that are relatively easy to decompose in the hydrothermal solution, and the organic matter decreases rapidly. With an increase in the reaction time, the easily degradable substances in the hydrothermal solution decomposed completely. Some refractory macromolecular substances cannot be immediately decomposed under the reaction of ozone, need to be decomposed into low molecular weight intermediate products, and then degraded. NH₄-N was oxidized and decomposed under the action of ozone during the initial process. After the easily degradable organic matter was decomposed, the stubborn organic matter was enhanced, and some surplus ozone still had the capacity to oxidize NH₄⁺ - N. Therefore, it was observed that the change in NH₄⁺ - N gradually flattened after 10 min. This is consistent with the results of UV254 and 3D fluorescence spectra (SM-Fig.1 and SM-Fig.2). In the first 10 min of

the reaction, the value of UV254 decreased significantly from the initial 14.10 to 8.15, and the degradation rate reached 42.20%, after which the change was gentle. Therefore, considering the treatment effects of COD, UV254, and NH₄ - N, the pre-oxidation time of the hydrothermal solution under ozone action should not be less than 10 min.

From Fig. 2 (b), it can be seen that the higher the concentration of ozone, the more fully it contacts and mixes with the organic matter, and the faster the COD decomposition. When the ozone concentration was increased from 16 to 20 g/h, under the same ozone reaction time (10 min), the COD decomposition rate increased by 21.88%. When the ozone concentration exceeded 20 g/h, the COD decomposition rate did not significantly change. As for NH₄ - N, with the increase in ozone generation concentration, the removal rate of NH₄ - N continued to rise, and until the ozone generation concentration exceeded 18 g/h, the removal rate of NH₄ - N gradually slowed. Combined with the comprehensive treatment effect of COD and NH₄-N, an ozone generation concentration of 20 g/h was selected for this experiment.

2.1.2 Changes in Cl⁻ and SO₄²⁻

Under the conditions of an ozone generation concentration of 20 g/h and a pre-oxidation time of 10 min, salt ions (Cl⁻ and SO₄²⁻) in the pretreated hydrothermal solution were detected and analyzed, and the results are shown in Fig. 3.

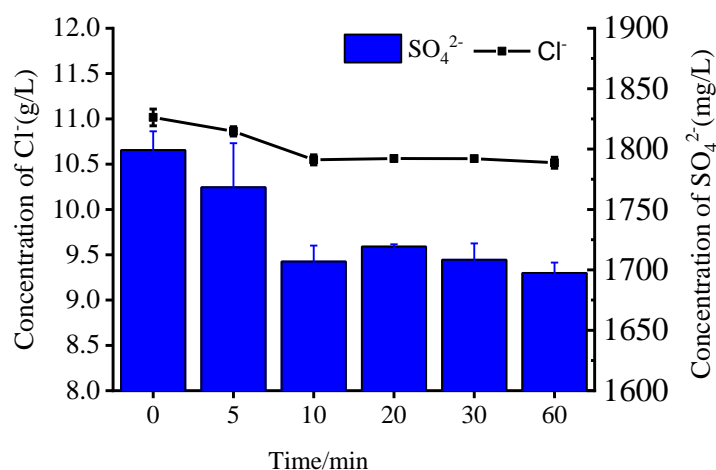


Figure 3 Changes in Cl⁻ and SO₄²⁻ for Different Ozonation Times

The variation in salt ions (Cl⁻ and SO₄²⁻) during the hydrothermal solution treatment process indicates that there was no significant change in the separation and removal of salt ions by the ozone pre-oxidation process. From Fig. 3, it can be observed that even after 60 min of ozone treatment, Cl⁻ and SO₄²⁻ in the hydrothermal solution decreased only slightly, with separation rates of 4.54% and 5.56%, respectively. Although it has been suggested in the literature that superoxide radicals produced by ozone can react with Cl⁻ [26], most ozone reacts with COD and NH₄-N for contamination degradation, while the effect on Cl⁻ and SO₄²⁻ is relatively minor. Because the cations Na⁺ and K⁺ do not participate in the ozone reaction, their concentrations were not measured during the experiments. Therefore, subsequent desalination operations are essential to achieve the application of hydrothermal circulation.

2.2 Evaluation of Electrodialysis Separation and Desalting Effect

Electrodialysis, as an efficient desalination

technology, is the directional movement of cation and anion ions in high-salt wastewater by means of the selectivity of the ion exchange membrane to ions under the action of a DC electric field, to achieve efficient salt separation [27]. For this reason, the effluent derived from ozone pre-oxidation of the hydrothermal solution flowed into the electrodialysis unit for desalination separation. The effects of parameters such as the current intensity and reaction time during the electrodialysis process on the desalination efficiency and performance of the membrane module are discussed in detail.

2.2.1 Change of Electroconductivity

The magnitude of conductivity reflects the strength of conductive particles in the wastewater, and salt ions, as excellent conductive particles in the wastewater, determine the magnitude of conductivity. Therefore, conductivity can indirectly reflect the salt ion concentration in the wastewater. Fig. 4 shows the variation in the conductivity of the effluent in the electrodialysis unit at different current intensities.

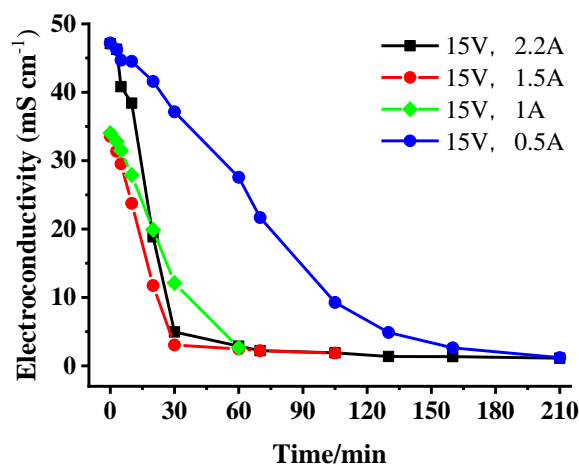


Figure 4 Variation of Conductivity with Reaction Time at Different Current Intensities

As shown in Fig. 4, with an increase in the current intensity, the conductivity of the effluent in the sample chamber after separation by the electro dialysis unit gradually decreased. Compared with the electro dialysis operation parameter of 15V, 0.5A, at the same electro dialysis treatment time, the conductivity of the effluent in the sample chamber decreased to more than 90% in only 30 min under the condition of 15V, 2.2A, while it took 200 min or even more under the condition of 15V, 0.5A. This is mainly due to the fact that the higher the current, the greater the current density, the faster the migration of cationic ions, and the higher the separation efficiency of salt ions. However, as shown in Fig. 4, with the prolongation of the electro dialysis reaction time, the conductivity of the effluent in

the sample chamber also decreases. Except for the condition of 15V and 0.5A, the anions and cations migrated completely during the entire separation process at a reaction time of 60 min, and the changes were not obvious. Combined with the calculation of accumulated energy consumption and accumulated electricity in the electro dialysis process (SM-Table 1), the experimental parameters of electro dialysis in this study were 15V and 1.0A, and the reaction time was 60 min.

2.2.2 Changes of Major Anions and Cations

To gain a deeper understanding of the migration rules of different anions and cations, the main anions and cations, such as Na^+ , K^+ , Cl^- , and SO_4^{2-} , were detected and analyzed in detail during the experiments. The results are shown in Fig. 5.

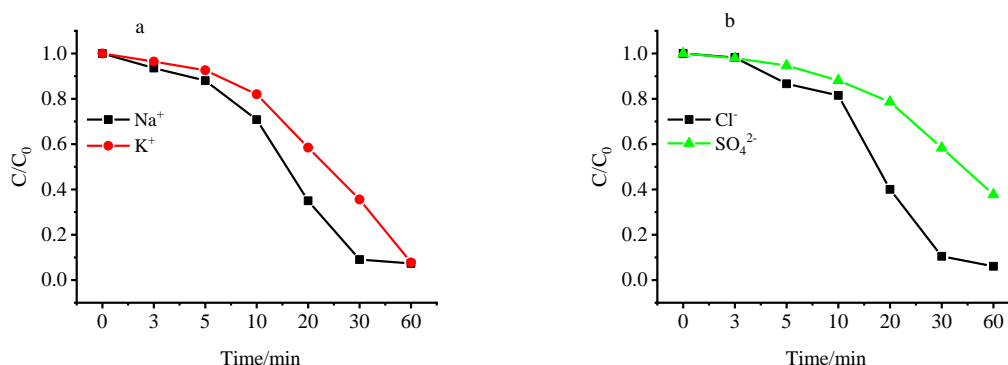


Figure 5 Main Cationic and Anion Separation Efficiency under Different Electro dialysis Reaction Times

(a) Separation Efficiency of Na^+ and K^+ ; (b) Separation Efficiency of Cl^- and SO_4^{2-}

Fig. 5 (a) shows the changes in the concentrations

of Na^+ and K^+ cations during the electro dialysis separation process at different times. It was found

that with an increase in the reaction time, the concentrations of Na^+ and K^+ at the outlet of the electro dialysis sample chamber decreased, and the concentration of Na^+ decreased much faster than that of K^+ . For Na^+ , the separation efficiency exceeded 90% when the reaction time was 30 min, whereas for K^+ , the reaction time needed to be 60 min to achieve a 90% separation efficiency. This is mainly due to the fact that Na^+ has a smaller volume and lower molecular weight than K^+ , and its migration speed is faster under the action of the same electric current. Combined with the volume change of the sample chamber before and after the electro dialysis process, the separation efficiencies of Na^+ and K^+ were 96.12% and 91.08%, respectively, at an electro dialysis reaction time of 60 min.

Fig. 5 (b) shows the changes in the concentrations of Cl^- and SO_4^{2-} anions during electro dialysis at different times. It can be seen that with the prolongation of the reaction time, the concentrations of Cl^- and SO_4^{2-} at the outlet of the sample chamber of electro dialysis decreased, and the concentration of Cl^- decreased faster than that of SO_4^{2-} , which was separated by more than 90% in the electro dialysis reaction for 30 min, while SO_4^{2-} was only about 60% in the reaction for 60 min. This is mainly due to the fact that compared with the divalent state of SO_4^{2-} , the monovalent state of Cl^- migrates faster under the action of the electric current. Combined with the volume

change of the sample chamber before and after the electro dialysis reaction, the separation efficiencies of Cl^- and SO_4^{2-} were 94.24% and 86.37%, respectively, for an electro dialysis separation time of 60 min. Combined with the volume changes of the dilute and concentrated chambers, the desalination efficiency of the entire process of ozone coupling with electro dialysis was calculated, and the results showed that the total desalination efficiency of the entire process reached 92.24%.

The above results indicate that small amounts of Na^+ and K^+ may still be present in the electro dialysis-treated effluent, which has not been completely separated. This may be related to other coexisting ions in the hydrothermal solution, such as calcium ions [20], or the change in membrane performance during the reaction process, which needs to be further explored.

2.2.3 Changes of Exchange Capacity and Membrane Resistance

To understand the effect of the ozone-treated hydrothermal solution after electro dialysis process on the electro dialysis membrane modules, the membrane modules before and after the electro dialysis experiments were removed, and the manufacturer was commissioned to test their membrane resistance and exchange capacity. The results are presented in Table 2.

Table 2 Performance Index Changes of Membrane Modules Before and After the Electro dialysis Process

Index	Resistance (0.5N NaCl) ($\Omega \cdot \text{cm}^2$)	Exchange capacity (mmol/g)	Moisture (%)
CEM before electro dialysis process	6.0	2.78	32
CEM after electro dialysis process	7.4	2.21	38
AEM before electro dialysis process	6.2	2.72	32
AEM after electro dialysis process	8.5	2.03	38

From Table 2, it can be seen that with the progress of the electro dialysis unit, the exchange capacity of the CEM decreased slightly less than that of the AEM, which decreased from 2.78 mmol/g to 2.21 mmol/g after 60 min of separation; while the AEM decreased by 0.69 mmol/g. The membrane resistance of the AEM increased much more than that of the CEM, which could be related to the concentration of anions. All of these changes in the performance index affect the separation of

anions and cations to a certain extent. Therefore, it is necessary to backwash the membrane to ensure its lifetime and normal exchange capacity after each electro dialysis operation experiment is completed.

3 Conclusion

To efficiently solve the problem of recycling and reuse of high-salt organic matter wastewater, a novel method of ozone oxidation coupled with electro dialysis technology was proposed in the

study. The following conclusions were drawn.

Without adjusting the hydrothermal pH value, when the ozone concentration was 20 g/L and the ozone reaction time was 10 min, the removal rates of COD, UV254, and $\text{NH}_4 - \text{N}$ in the hydrothermal solution were 53.89%, 42.20%, and 40.29%, respectively. The major anions and cations had a small rate of change, and the separation rates of chloride and sulfate were only 4.54% and 5.56%, respectively.

When the effluent after the ozone reaction was treated with electrodialysis, the separation efficiency of Cl^- , SO_4^{2-} , Na^+ , and K^+ ions increased significantly. At a voltage of 15 V, current of 1 A, and reaction time of 60 min, the separation efficiencies of Cl^- and SO_4^{2-} ions were 94.24% and 86.37%, respectively, and the separation efficiencies of Na^+ and K^+ ions were 96.12% and 91.08%, respectively.

Before and after electrodialysis separation, the exchange capacity of the electrodialysis membrane decreased slightly but not significantly, and the membrane resistance increased, which affected the separation of anions and cations to a certain extent. Therefore, it is necessary to backwash the membrane to ensure its lifetime and normal exchange capacity after each electrodialysis reaction is completed.

Ethical Approval

When conducting experiments, investigation or research, the approval of the ethics committee is required to ensure that the research process and results comply with ethical standards and ethical norms.

Consent to Participate and Public

All authors understand all aspects of the study and give consent, also every author makes contribution to the research. All authors consent to publish.

Authors Contributions

Shiqian Li: Formal analysis, Writing-review & editing; Zhan Chen: Methodology, Formal analysis, Data curation, Writing-original draft, Writing-review & editing, Funding acquisition, Project administration, Validation, Supervision; Lili Yang: Supervision; Lyu Yang: Investigation, Resources, Data curation.

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Declaration of Competing Interest

All the authors guarantee that it is our original research work and they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper, and there is no conflict of interests with other researchers.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author, upon reasonable request.

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