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To cite this article: Kuan He *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **227** 062043

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Application of homogeneous membrane electrodialysis in the treatment of high-salt organic wastewater

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Abstract. In this paper, a homogeneous membrane electrodialysis system was used to separate the high COD and high sulfate concentrated water from a non-ferrous metal plant. After continuous pilot test, the results showed that the homogeneous membrane electrodialysis method has the characteristics of low energy consumption, high concentration ratio, strong ion selective permeability and effectively remove organic matter. Therefore, the production cost can be reduced and the recycling of waste water resources can be realized.

1. Introduction

With the development of industry, the discharge of industrial wastewater is increasing. Industrial wastewater contains a large amount of solid suspended matter, metal ions, high concentrations of organic matter and salt substances [1]. The direct discharge of untreated industrial wastewater will not only damage the environment, but also pollute the drinking water source and cause harm to the human body. Conventional physico-chemical organisms and other methods have many drawbacks when directly used to treat industrial wastewater, such as high energy consumption, low salt rejection, and inability to effectively remove COD [2-5]. Therefore, how to effectively combine various water treatment processes to achieve material circulation, and comprehensive wastewater treatment is an important way to achieve zero discharge of wastewater.

In this paper, the RO concentrated water in a zero-discharge wastewater system of an enterprise is pre-concentrated to about 3% by using the reverse osmosis process with low operating energy consumption and low investment cost, and then enter the homogeneous membrane electrodialysis. The TDS on the freshwater side of electrodialysis is discharged after decreasing to 1%. After reverse osmosis desalting, RO produced water was reused, RO concentrated water was further concentrated and then returned to homogeneous membrane electrodialysis. This not only reduces the energy consumption and improves the operation efficiency, but also greatly reduces the operation cost.

2. Homogeneous membrane electrodialysis

Electrodialysis technology means that under the action of an electric field, the solute particles (such as ions) in the solution migrate through the selective permeable membrane to achieve the purpose of separation and purification of substances, widely used in food, chemical, water treatment and other industries [6-9]. In the homogeneous membrane electrodialyzer, the cation and anion membranes are intercalated, and a pair of electrodes are arranged at both ends of the membranes through a multi-layer separator. The raw water staggered into the separation chamber, and the ions concentration in the adjacent concentration chambers through the ion exchange membrane under the action of DC electric



field, thereby achieving the purpose of salt concentration and separation. Figure 1 shows the working principle of a homogeneous membrane electro dialyzer.

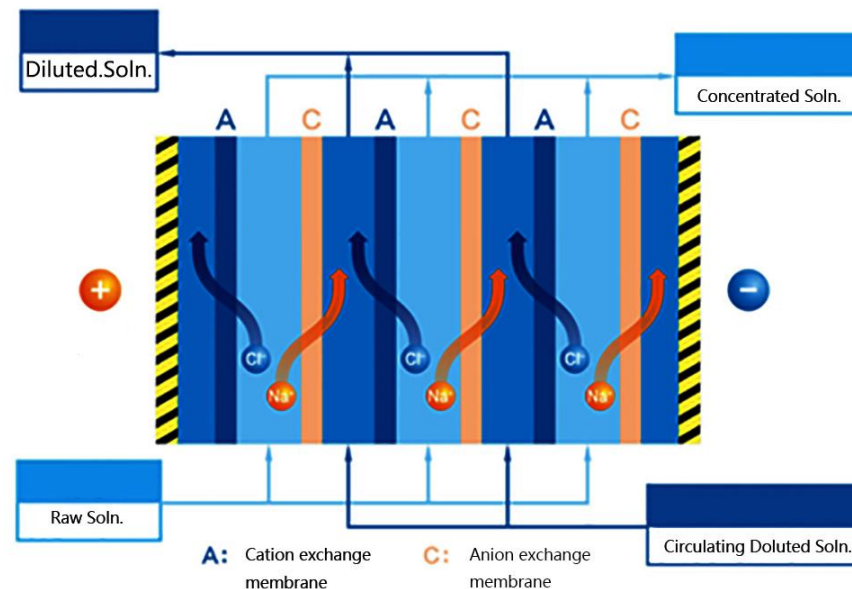


Figure 1. Schematic diagram of homogeneous membrane electro dialysis.

The homogeneous ion exchange membrane is formed by polymerizing a high molecular polymer to form a base film, and then chemically modifying to introduce a reactive group. At present, most of the homogeneous anion and cation exchange membranes produced in China, are made by slurry **coating** method [10]. Compared with heterogeneous membranes made by mixing ion exchange resin powder and polymer materials, the homogeneous membranes have the following characteristics:

2.1. Strong ion permeability

The selective permeability of ion exchange membranes determines the ion exchange capacity. Because the homogeneous membrane contained more active groups, therefore the cost of homogeneous membrane electro dialysis is lower when the same amount of ions are migrated.. Prakhari Prakash [11] used the Donnan membrane process (DMP) to recovery of alum from water treatment plant residues or sludge. In the process, the recovered Al³⁺ could be concentrated to a high value of over 4500 mg/L (80% recovery) with the homogeneous Nafion 117 membrane, but the recovery was relatively low (25% recovery) with heterogeneous Ionac 3470 membranes.

2.2. Low water loss rate

During the electro dialysis process, due to the concentration difference between the desalination and the concentration chambers and the ion hydration, water molecules migrate from the desalination chamber to the concentration chamber, resulting in water loss. Since the homogeneous membrane is tightly packed, avoid high concentration due to excessive loss of water on freshwater side. The water loss rate can generally be controlled at about 10%.

2.3. Stable physico-chemical properties

The membrane structure determines physical and chemical properties such as membrane resistance, mechanical strength, and stability. The homogeneous ion exchange membrane contains an insert polymer and a reinforced fabric. The surface of the membrane is chemically modified to have stable reactive groups, and the mechanical strength and thermal stability are stronger, so the service life is longer than that of the heterogeneous membrane. Moreover, the improved membrane preparation

process can make the homogeneous ion exchange membrane thinner and lower surface resistance. Consequently, it improves the efficiency of current transmission and reduces energy consumption.

2.4. *Effective separation of organic matter*

The homogeneous ion exchange membrane are dense and non-porous, allowing only ions and part of charged organic matter to pass through, and leaving the non-charged COD in the dilute chamber, thus achieving the purpose of separating organic matter.

Because homogeneous membranes have many advantages over heterogeneous membranes, it can reduce energy consumption. Feng Yunhua [12] analyzed the influence of membrane stack configuration, process flow and process parameters on energy consumption and desalination effect in EDI desalination process, and used desalination rate, energy consumption and electrical resistance to characterize the performance of EDI membrane stack, the results show that the energy saving of the membrane stack using the homogeneous membrane is about 27.8% compared with the heterogeneous membrane.

3. **Pilot test**

The RO concentrated water from a non-ferrous metal plant zero-emission pilot system, which mainly contained sodium sulfate, a small amount of calcium and magnesium ions and sulfite, Among them, sulfite leads to high COD. The specific composition is shown in Table 1.

Table 1. RO concentration water quality index.

	Solubility total solids (TDS)(mg/L)	Conductivity ($\mu\text{S}/\text{cm}$)	pH	COD (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)
RO concentrated water	28000	39000	8-9	282	59.98	6.96

The system adopts the method of homogeneous membrane electro dialysis and reverse osmosis. Firstly, the RO concentrated water is pre-concentrated to about 3% by reverse osmosis and then enters the homogeneous membrane electro dialysis. The TDS value of the fresh water after electro dialysis is reduced to 1% and discharged into the reverse osmosis desalting system. The fresh water produced by RO is reused. The concentrated water produced by RO is further condensed and then returned to the homogeneous membrane electro dialysis apparatus. Figure 2 shows the system flow.

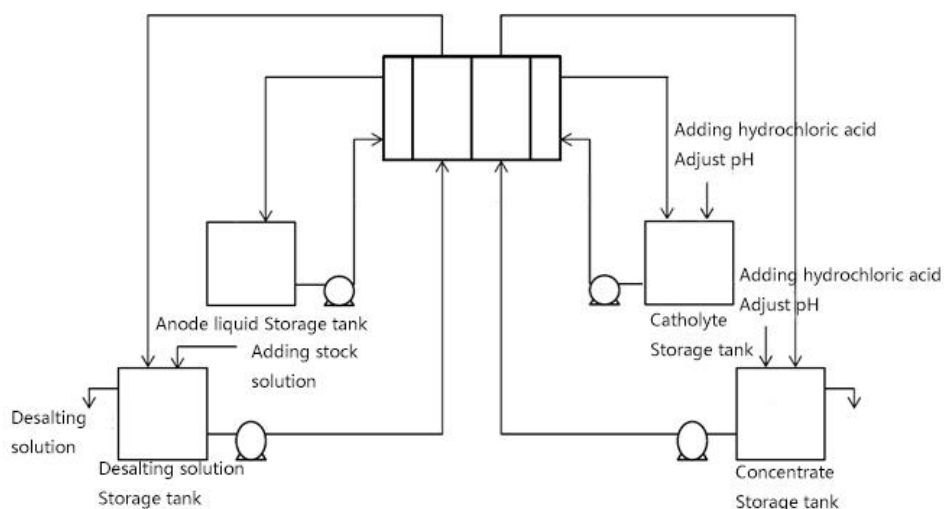


Figure 2. Flow chart of homogeneous membrane electro dialysis system.

3.1. Electrodialysis system

The original liquid of about 3% TDS is added to the desalting liquid storage tank by a peristaltic pump. The desalting liquid, concentrate liquid and polar liquid enter the electrodialysis tank by a circulation pump. When the desalination and concentrate TDS reached 1% and 20%, respectively, the system operated stably. The system equipment parameters are shown in Table 2.

Table 2. System equipment parameters.

Equipment	Specification	Quantity	Remark
Electrodialysis tank	10 pairs of membranes, single-piece effective membrane area 0.021m ²	1	CMV and AMV High efficiency diffusion diaphragm
Rectifier	DC 35V/10A	1	
Storage tank	5L	3	Desalting solution, concentrate, and polar solution (share one)
Circulating pump	Centrifugal pump, Q=600L/h	3	Desalting solution, concentrate, and polar solution (share one)
Feed pump	Peristaltic pump, Q max=220mL/min	1	

4. Results analysis

4.1. Salt mobility analysis

The migration efficiency of the salt is related to the exchange capacity and selective permeability of the membrane. The larger the ion exchange capacity of the membrane, the stronger the conductivity of the membrane and the faster the ion permeation efficiency is. After the system is operated continuously, the flow rate of the raw liquid is 6.6 L/h and the overflow amount of the concentrated liquid is 0.7 L/h.

The amount of salt measured from the homogeneous ion exchange membrane to concentrated solution is the actual amount of salt transported across the membrane, and the total amount of salt transported is 140g/h.

The electrodialysis system consists of 10 pairs of membranes, and the effective membrane area of a pair of membrane is 0.021m². The mass of salt migration per unit membrane area is 667g/m²·h.

The main salts of wastewater is Na₂SO₄ and the gram equivalent E is 71g/eq,. The salt transport equivalent per unit membrane area is 9.4 eq /m²·h .

In the key parameters of homogeneous membrane electrodialysis design, the salt migration equivalent e per unit membrane area is generally 9 eq /m²·h. Therefore, the salt migration rate of the wastewater by homogeneous membrane is at a high level, which can effectively carry out the salt migration and concentration.

4.2. Analysis of water loss rate

In the continuous test, the concentrate has no additional water, so the overflow is the water that passing through the side of the desalting liquid. The water loss rate is the ratio of the flow rate of the concentrate to raw liquid flow rate. So the water loss rate is 10.6%.

It can be seen from the calculation that due to the non-porous and uniform uniformity of the homogeneous membrane, the water loss rate could be controlled to about 10%, which has a great effect on increasing the concentration ratio.

4.3. Energy consumption analysis

The energy consumption of the electrodialysis system mainly consists pump and electrodialyzer membrane. The homogeneous ion-charged membrane is more conducive to ion migration and has the characteristics of low thickness and low electrical resistance [13-14]. The cation exchange membrane (CMV) and anion exchange membrane (AMV) used in the experiment are two kinds of high-

efficiency diffusion membranes with a membrane thickness of only 120 μm . Therefore, the current efficiency of homogeneous membrane electrodialysis is higher, and the operating energy consumption is only 30-50% of the ordinary heterogeneous membrane.

In the experiment, the water inflow is 6.6 L/h, the operating voltage is 12 V, the operating current is 4.1 A, and the conversion current efficiency is 80%. Therefore the energy consumption for processing one ton of water treatment is 9.32kWh/m³.

The average operating energy consumption was calculated by taking three test results, and the average operating energy consumption was 9.16 kWh/m³. However, thermal processes (MVR, multi-effect evaporation) overcome the latent heat of water phase change. For each ton of wastewater treatment, multi-effect evaporation needs 0.35 tons of steam and 10-15 kWh of electricity; MVR needs 30-50 kWh of electricity. The energy consumption of water treatment methods such as pressure membrane method (RO, DT/STRO) is affected by working pressure.

5. Conclusions

In this paper, the homogeneous membrane electrodialysis system was used to concentrate RO concentrated water from pilot-scale zero-discharge system of industrial wastewater. Compared with traditional thermal, pressure and heterogeneous membrane electrodialysis methods, the homogeneous membrane electrodialysis method not only consumed less energy, but also can effectively remove organic matter in the process of treating high-salt wastewater. It can provide water quality guarantee for subsequent evaporation crystallization, realize the resource utilization of crystalline salt and reduce production cost.

Electrodialysis technology has been widely used in the field of water treatment, which is of great significance for achieving zero discharge of wastewater. The homogeneous membrane electrodialysis combined with reverse osmosis (RO) and MVR technology is an important technical route for wastewater treatment. By analyzing the water quality characteristics and optimizing the process, zero wastewater discharge and resource recycling can be realized.

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