Study on the process of simultaneous desalting and boron removal from seawater

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Abstract. Two new combined technologies, reverse osmosis (RO) + electrod eionization (EDI) and reverse osmosis (RO) + ion exchange (IE), were studied for simultaneous desalination and boron removal of seawater. The results show that the RO system has excellent desalination performance under the experimental conditions, and can provide stable desalination rate for the subsequent processes of the two combined schemes. The boron concentration in water has little effect on the desalination rate of RO system, and the boron removal rate of RO system is between 47% and 50%, which provides a good early treatment for the subsequent process. The blank experiment shows that the salinity has little effect on the boron removal rate of RO-EDI equipment, and the boron removal rate is more than 93%, which has excellent and stable boron removal performance, but the water yield of RO-EDI equipment is low (less than 60%). The RO-IE system has a high water yield (> 70%), but the equipment has poor adaptability to influent boron concentration and salinity. The results of effluent water show that the boron concentration of raw water by RO-EDI combined process can be adapted to a wider range, and the influence of salinity is less. Considering comprehensively, RO-EDI process has more advantages and broad application prospects.

1. Introduction
With the worldwide lack of fresh water resources, seawater desalination technology has received high attention in recent years. As a trace element, boron mainly exists in sea water in the form of boric acid with a concentration of 4-6 mg/L, accounting for 76.4% of the total boron. Boron plays an irreplaceable role in the growth and development of human and animal. However, if boron is ingested in excess it can cause a series of adverse effects and even boron poisoning. In China, the upper limit of allowable concentration of boron is set as 0.5mg/L in the Hygienic Standard for Drinking Water (GB5749-2006). Therefore, it is of great practical significance to study the desalination and boron removal of seawater.

At present, the removal methods of high concentration of boron in wastewater have been studied more, mainly including adsorption method and chemical precipitation method. However, these methods do not meet the technological requirements of seawater desalination, and the future...
development trend of seawater boron removal is to combine multiple methods for simultaneous desalination and boron removal\cite{6-9}. Electrical deionization (EDI) as a continuous deep desalination means, without chemical regeneration agent, simple operation and stable operation. However, the requirements for inlet water quality are very strict and the pretreatment process is complex. Currently, reverse osmosis (RO) is commonly used as the pretreatment process\cite{10}. In addition, with the rapid development of material technology, especially the use of boron specific resin, ion exchange method (IE) has a good separation effect of high concentration of boron, high water yield, and good development prospect. However, the effect of its treatment of low concentration of boron remains to be studied\cite{11-14}.

Reverse osmosis seawater desalination is one of the most important seawater desalination technologies, so its boron removal effect. Fruit is also getting a lot of attention. Due to the natural seawater pH, the value of about 7.9-8.2\cite{15}. Therefore, boric acid mainly exists in molecular form throughout the year. On the one hand, boric acid molecules have no electrostatic repulsion with the charged membrane surface due to their charge neutrality. On the other side, the boric acid molecule has three hydroxyl groups, which can easily interact with the polymer groups on the surface of reverse osmosis membrane to form hydrogen. Bonds and diffuses through the membrane. In addition, the volume of boric acid molecule is small, so the reverse osmosis membrane can remove boron from natural seawater. The effect of division is poor for seawater desalination reverse osmosis system, the boron removal rate under normal test conditions is approximately 85-90%, but only in practical commercial application 78-80% even lower\cite{16-18}. And we know that when the solution pH value to 9, boric acid ionization increases, the solution contains boric acid dihydrogen ion. As the amount of borate increases, the electrostatic interaction between borate dihydrogen ions and the negatively charged reverse osmosis membrane is enhanced, which makes the membrane to the boron. The rejection rate increases, so it adjusts pH. The value of boric acid is an important means in the process of boric acid removal, and is often associated with other methods. The method is used simultaneously. At the same time, operating conditions such as membrane type, temperature, flow rate and pressure also affect the boron removal. It has a significant impact.

In this paper, for the purpose of seawater desalination and boron removal, the effect of the new combined technology RO-EDI and RO-IE to remove boron from seawater was studied, and the combined technology of synchronous desalination and boron removal was discussed, so as to provide technical support for engineering application.

2. Materials and methods

2.1. Raw water quality
Due to geographical reasons, seawater cannot be obtained in time for treatment and analysis in this process research, so the method of artificial simulation of seawater is adopted in the laboratory to provide the required salinity. The average salinity of the world's oceans is 35‰; The pH of seawater varies from season to season and from region to region. The pH of seawater varies very little, usually between 7.9 and 8.3, with an average value of 8.1. The prepared simulated seawater contains mainly NaCl, dissolved solid TDS of 35000 mg/L and pH of 8.1.

2.2. Test apparatus
The boric acid used in the experiment was purchased from Tianjin Damao Chemical Reagent Factory and analyzed to be pure. Sodium chloride was purchased from Xilong Chemical Co., Ltd., pure for analysis. The main experimental instruments and equipment are:

In view of the characteristics of reverse osmosis membrane for small-scale desalination, the reverse osmosis membrane element used in this experiment is the roll polyamide composite seawater desalination membrane made by Dow Company in the United States, the model is FilmTectM SW30HRLE-4040. FilmTectM SW30HRLE-4040 membrane element performance parameters are as follows: polyamide composite membrane.
EDI membrane reactor must cooperate with reverse osmosis system to play its role of deep purification, therefore, it for the inlet water quality requirements are more stringent than reverse osmosis. In this experimental system, the patented product of Guangzhou Jingyuan Seawater Desalination and Water Treatment Company, HJJ-EDI membrane heap for incoming water treatment, whose model is HJJ-2-EDIMD-B-1000, is adopted. Water quality requirements of EDI membrane pile influent: usually for the first stage reverse osmosis of permeable water, pH: 6.0 ~ 8.0, the best working pH range of the second stage EDI is 7±0.5, temperature: 5 ~ 35℃, influent pressure: ≤ 4 bar (60 psi), hardness (based on CaCO3) :< 0.5ppm, organic matter (TOC) :< 0.5ppm, oxidant: Cl2 < 0.05ppm, O3 < 0.02ppm, variable metal: Fe < 0.02ppm, Mn < 0.04ppm, H2S: < 0.01ppm. Silica: < 0.3 PPM. Total carbon dioxide: < 5 PPM.

IE system followed by RO system, there is no independent pressurization and other equipment, the flow rate is the flow rate after RO water, no other operation, IE equipment adopts the inner diameter of 100 mm, 1000 mm high plexiglase column, add 2/3 height of mixed ion exchange resin, Ion exchange resin using 717 type anionic resin and 732 type cationic resin according to 1:1 mixing.

UV-V is spectrophotometer, model 752, was purchased from Shanghai Spectral Instrument Co., Ltd.

In the experiment, the raw water is from the original water tank → pressurized water pump → sand filter column → activated carbon filter column → precision filter column → high pressure pump → reverse osmosis membrane stack → RO tank → EDI membrane stack (ion exchange) → production tank. The volume of the original water tank was 125 L, the sand filter column and the activated carbon column were made of plexiglass column with an inner diameter of 200 mm, and the precision filter column was made of plexiglass column with an inner diameter of 100 mm. For reverse osmosis and ion exchange treatment systems, the ion exchange resin column is made of a 100 mm plexiglass column with an inner diameter and is directly connected to the reverse osmosis back end. The function of the three filter columns in the front section is to ensure the normal operation of the reverse osmosis membrane reactor.

2.3. Analysis conditions

The desalination rate measurement in this experiment is mainly analyzed for RO device, RO-EDI system and RO-IE system. TDS of the sample is directly measured by TDS pen. Test using UV-visible spectrophotometer determination of boron concentration, its basic principle is under the condition of acid boron evaporate water samples with curcumin, generate complex called the rose of wellknown glycosides, the complex can be soluble in ethanol or isopropanol, had maximum absorption peak at 540 nm, the color depth is proportional to the content of boron.

3. Results and discussion

3.1. RO - EDI process

The RO system is regarded as a relatively independent system in the whole, and the high pressure pump operates at fixed frequency. The water production rate of RO system is stable at 75%, and the concentrated water valve is fixed after adjustment. Reverse osmosis, as the common core device of the two sets of devices, mainly plays the pre-treatment role of desalination and boron, and provides the prerequisite working conditions for the subsequent EDI and IE processes. Its performance directly affects the performance of the two sets of devices. The reverse osmosis experiment was carried out by this device, and the results show that: When the boron concentration of seawater is 4-6 mg/L, the desalination rate of RO system is stable in the range of 0.9935~0.9945, and it is little affected by the influent boron concentration. The boron removal rate of RO system is between 47% and 50%, which can play a better boron pretreatment effect.

EDI membrane stack is also A relatively independent system, and the membrane stack current is always guaranteed to be 2.48A. The membrane stack voltage is determined jointly by the membrane stack current and the water quality produced by the RO system, so the membrane stack current no
longer needs to be adjusted once it is adjusted. The water yield of the EDI membrane reactor is stable at 60%, the extreme water inlet flow of the EDI membrane reactor is 20 LPM, and the concentrated water inlet flow of the EDI membrane reactor is 50 LPM. The desalination rate of RO system is very high, so for EDI membrane reactor, its influent TDS value can be regarded as constant. The boron removal rate of RO-EDI membrane reactor is stable above 93% for both tap water and simulated sea water, indicating that the salinity has little influence on the equipment, and the difference in salinity between real sea water and simulated sea water can be ignored. The equipment has stable and good boron removal effect. With the increase of boron concentration, the removal rate of EDI decreased slowly, but the boron concentration had little influence on the removal rate, which mainly depended on the previous filtration and reverse osmosis and other corresponding treatment facilities, which ensured that the influent water of EDI reached the limit of its technical requirements. At the same time, EDI well made up for the low boron removal rate of reverse osmosis.

3.2. RO - EDI process
Also, given the high desalination rate of reverse osmosis, influent TDS can be considered a fixed amount for an ion exchange system. Under the same conditions as EDI, the relationship between the boron removal rate of the ion exchange system and the boron concentration of the reverse osmosis effluent is discussed. The boron removal rate of RO-IE process for tap water is significantly higher than that of simulated seawater, and IE process is more sensitive to the salinity of influent water, which may be because the ion exchange between influent salt ions and resin affects the boron removal effect. In addition, the boron removal efficiency of RO-IE system decreases rapidly with the increase of boron concentration. When the influent boron concentration increases from 2.0 mg/L to 7.0 mg/L, the boron removal rate of the ion exchange system decreases from 86.3% to 66.5%, which is a great decrease. In addition, since the theoretical water yield of IE device is 100%, the measured water yield after the combination of RO device can also reach more than 70%, which is higher than that of RO-EDI process.

3.3. Comparison of two processes

| influent boron concentration / (mg/L) | RO-EDI effluent boron concentration / (mg/L) | RO-IE effluent boron concentration / (mg/L) |
|--------------------------------------|-------------------------------------------|-------------------------------------------|
| 2.11                                 | 0.12                                      | 0.28                                      |
| 3.24                                 | 0.19                                      | 0.33                                      |
| 4.19                                 | 0.20                                      | 0.42                                      |
| 4.86                                 | 0.30                                      | 0.48                                      |
| 6.20                                 | 0.47                                      | 0.90                                      |
| 7.13                                 | 0.68                                      | 1.45                                      |

It can be seen from the above table that with the increase of influent boron concentration, the influent boron concentration increases. According to the Sanitary Standard for Drinking Water (GB5749-2006), the upper limit of allowable concentration of boron is 0.5 mg/L. When 4.86 mg/L, the boron concentration of the effluent is lower than the standard value, and its applicable boron concentration range is small. When the influent boron concentration, at 6.20 mg/L, the boron concentration of RO-EDI effluent meets the requirements of water quality standard. Considering that the boron concentration in seawater ranges from 4 to 6 mg/L, the boron treatment capacity of RO-EDI combined process meets the requirements. From the point of view of boron concentration in raw water, RO-EDI system is more advantageous. In addition, it can be seen from Table 1 that the boron removal rate of RO-EDI system is higher than that of RO-IE system. The blank experiment shows that the salinity
adaptability of RO-EDI system is higher under the two simulated objects of tap water and seawater. The calculation of water yield shows that the latter is 10% higher than the former. Considering comprehensively, the synchronous desalination and boron removal, RO-EDI process is more advantageous.

4. Conclusion
The results show that the RO system has excellent desalination performance under the experimental conditions, and can provide stable desalination rate for the subsequent processes of the two combined schemes. Boron concentration in seawater is negatively correlated with RO desalination rate. For artificial seawater with salinity of 35‰, when boron concentration is 4-6 mg/L, desalination rate drops from 0.9945 to 0.9935, and the overall decrease is very small. The boron removal rate of RO system is between 47% and 50%, which can play a better boron pretreatment effect. Both tap water and simulated sea water, the boron removal rate of RO-EDI membrane reactor is stable above 93%, indicating that the influence of salinity on the equipment is small, and the boron removal stability of the device is good, but the water yield is low (less than 60%).

The RO-IE process has poor adaptability to the salinity of raw water, and the boron removal rate of tap water is obviously higher than that of artificial seawater. The effect of boron removal decreases rapidly with the increase of boron concentration. When the influent boron concentration increases from 2.0 mg/L to 7.0 mg/L, the boron removal rate of RO-IE system decreases from 86.3% to 66.5%, which is a large decrease, but the water production filtration rate is higher (> 70%). The results of effluent showed that the boron concentration in raw water of RO-EDI combined process was more suitable for a wider range.

In conclusion, the RO-EDI process is more advantageous for the synchronous desalination and boron removal of seawater for the production of drinking water source. It can further improve the water production rate and realize the industrial application as soon as possible, and has a broad prospect.

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