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Study on pretreatment of seawater electrolysis for desalination

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ABSTRACT

The results of seawater electrolysis for pretreatment with self-made diaphragm electrolyzer and ruthenium titanium oxide electrode are presented in this study. The influences of stirring and different concentrations of Cl^-, Mg^{2+}, and Ca^{2+} ions on chlorine evolution reaction were investigated. Experiments of electrolyzing natural seawater were performed to evaluate the effect of current density and water velocity on product water quality and the rate of chlorine evolution. The results show that the rate of the reaction is determined by electrochemical step at low current density ($<10\,mA/cm^2$), and at higher current density, the diffusion of chloride ions is the rate-determining step. The contents of calcium and magnesium have little influence on chlorine evolution reaction. Under the optimum operating conditions of current density at $20.0\,mA/cm^2$ and water velocity at 14 L/h, the product water meets the criteria for feeding reverse osmosis desalination, and the rate of the chlorine production is 1.75 mL/s. In addition, the mechanism of purification is discussed.

Keywords: Electrolysis; Chlorine evolution; Reaction; Seawater pretreatment; Desalination

1. Introduction

Acute water shortages have stimulated the investigation and application of various approaches to seawater desalination, the market of which grows rapidly and is supposed to double to more than $70 billion in the next 20 years [1,2]. With the development of membrane technology, reverse osmosis (RO) has been applied commercially for many years as a major desalination technology [3,4]. However, RO membranes are sensitive to various types of pollutants, such as suspended solids, colloidal species, organic matters etc. Membrane fouling seriously decreases membrane productivity and causes deterioration of product water quality [5]. Therefore, the pretreatment process is necessary to supply good feed water. With conventional pretreatment including clarification, sand filtration and cartridge filtration [6], it is difficult to produce high-quality feed water for RO. In addition, chemical treatment with coagulants should be used prior to integrated membrane technology [2].

Attention was focused on electrochemical treatment techniques due to their versatility and environmental compatibility [7,8]. In the last decades, electrochemical processes such as electro-coagulation,

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electro-flotation, and electro-oxidation have frequently been used to treat various industrial wastewaters [9–11]. In recent years, seawater electrolysis has been studied for hydrogen production [12], chlorine evolution [13–15], and disinfection process for desalination [16], but not for pretreatment of seawater. In our previous work, one-step electrolyzing seawater pretreatment for RO [17] was investigated.

In this study, mixed ruthenium titanium oxide electrodes were placed in a self-made diaphragm electrolyzer. The sludge of magnesium hydroxide was produced in cathode, which adsorbed suspended solids, colloidal species, and organic matters. It was similar to the process of conventional adsorption [17]. Chlorine (Cl_2 and HOCl) was formed in the anodic reaction, which was subsequently used for neutralizing alkaline water from the cathode chamber and disinfection for desalination. Therefore, a new form of pretreatment consisting of seawater electrolysis without addition of any coagulants may be adequate.

This work examines the possibility of application of seawater electrolysis as pretreatment for RO desalination by the investigation on the chlorine evolution and the optimal process of pretreatment under continuous conditions.

2. Experimental

2.1. Preparation of electrolyte

The natural seawater samples were collected from the Bohai-Sea and were directly used for analysis and electrolytic treatment. The characteristics of the seawater samples are shown in Table 1. The electrolytes of different concentrations of Cl^-, Mg^{2+}, and Ca^{2+} ions were prepared using pure NaCl, $MgSO_4$, and $CaSO_4$ to analyze the chlorine evolution. The detailed concentrations of the solutions are summarized in Table 2.

Table 1
Characteristics of the natural seawater samples

Parameters	Values
Turbidity (NTU)	41.27
COD_{Mn} (mg/L)	3.58
Colority (mg/L)	125
SDI_{15}	Out of range
Mg^{2+} (mg/L)	1,385
Ca^{2+} (mg/L)	417
Cl^- (mg/L)	20,218
pH	7.64

Table 2
Different concentrations of the electrolyte

No.	Cl^- (g/L)	20 g/L Cl^-	
		Mg^{2+} (g/L)	Ca^{2+} (g/L)
1	4	0.6	0.2
2	8	0.9	0.3
3	12	1.2	0.4
4	16	1.5	0.5
5	20	1.8	0.6
6	24	2.1	0.7

2.2. Polarization curves

The electrochemical experiments were conducted at ambient temperature with the electrochemical measurement system (LK3200A, China) in solutions with different concentrations of Cl^-, Mg^{2+}, and Ca^{2+} ions. Anode polarization curves were obtained at the scan rate of 0.01 V/s from 0 to 4 V with a conventional three electrode system, of which the working electrode was ruthenium titanium oxide ($Ti/Ru_{0.3}Ti_{0.7}O_2$) anode with an electro-active area of 2 cm^2, and the reference electrode and counter electrode were Ag/AgCl and Pt, respectively. A stirrer (JB-1A, China) was used to analyze the rate-determining step of chlorine evolution reaction in seawater.

2.3. Pretreatment procedure

The flow diagram of pretreatment process is shown in Fig. 1. The diaphragm electrolyzer, consisting of the anode chamber (200 mm × 180 mm × 150 mm) and cathode chamber (40 mm × 180 mm × 150 mm), was used in the pretreatment process of electrolysis seawater. The two parallel plate electrodes were $Ti/Ru_{0.3}Ti_{0.7}O_2$ with an effective area of 400 cm^2. The electrodes were connected to a DC power (Zhong

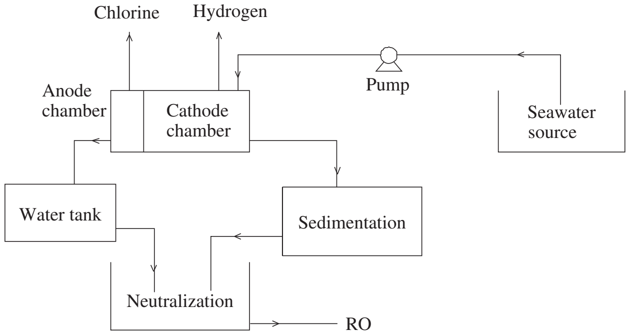

Fig. 1. Flow diagram of electrolysis seawater for pretreatment process.

CE Electronics Co. Ltd; 0-10 A; 0–60 V) equipped with ammeter and voltmeter to control the current density for electrolysis. Raw water was pumped to the electrolyzer and then electrolyzed. After sedimentation, the cathodic water was neutralized from the anode chamber. The product water was examined using a turbidity meter (HANNAs HI 93703-11, Italy), Simple SDI (182-10025, USA), pH meter (PHS-3E, China), and micro-electrophoresis meter (JS94G+, Shanghai, China).

The experiments were carried out at seawater velocity of 12 L/h, with constant current from 5 to 9 A and interval 1 A. The optimum flow rate was estimated with the current density of 20.0 mA/cm^2 and the seawater velocity at 10, 12, 14, 16, and 18 L/h, respectively.

3. Results and discussion

3.1. The rate-determining step of anode reaction

The polarization curves were measured in solutions with different concentrations of Cl$^-$ ion, and the results are showed in Fig. 2. It may be observed that the curves show inflection points at the potential of 1.0 V, suggesting that the chlorine is formed. Moreover, the increase in the relative amount of Cl$^-$ ions decreases the anode potential. Fig. 3 shows the comparison of polarization curves with and without stirring in natural seawater. The potentials obtained increase linearly with an increase in the current density at the range of 1.0–1.2 V, and the subsequent potential observed with stirring is clearly low, especially at a higher current density.

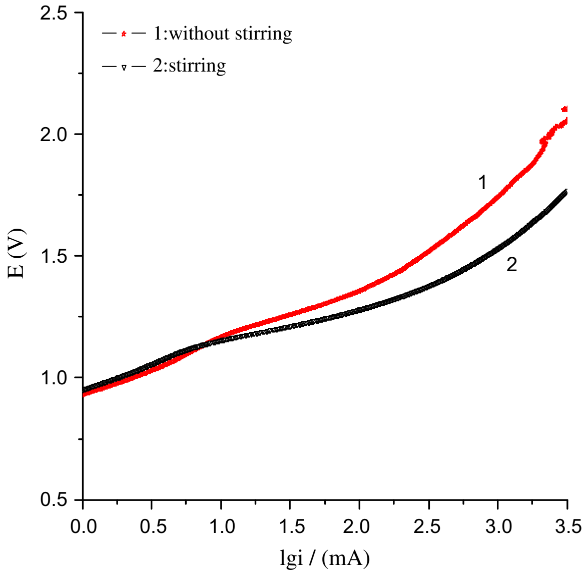

Fig. 3. Anode polarization curves in seawater with and without a stirrer.

As mentioned previously, the straight line of E-lgi relation shows that the anode reaction is in accordance with the Tafel equation, and the rate of the reaction is determined by the electrochemical step at a lower current density of 10 mA/cm^2. However, for a higher current density, the mechanism of the anode reaction changes and the electron transfer is replaced by slow chloride ion diffusion. Thus, the pretreatment of seawater electrolysis is operated at a current density more than 10 mA/cm^2 with stirring.

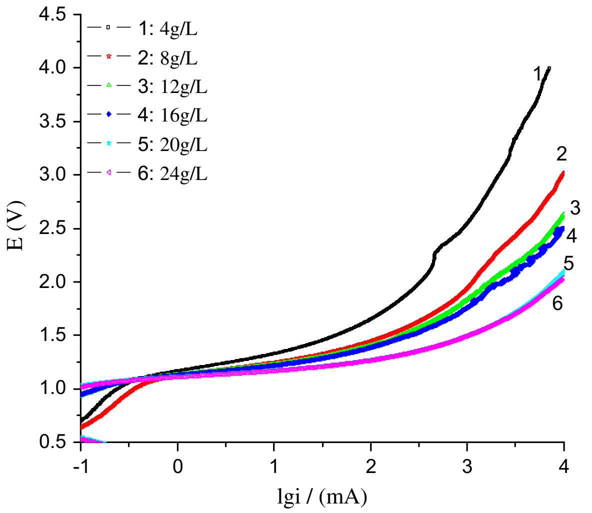

Fig. 2. Anode polarization curves in different concentration of Cl$^-$ ion.

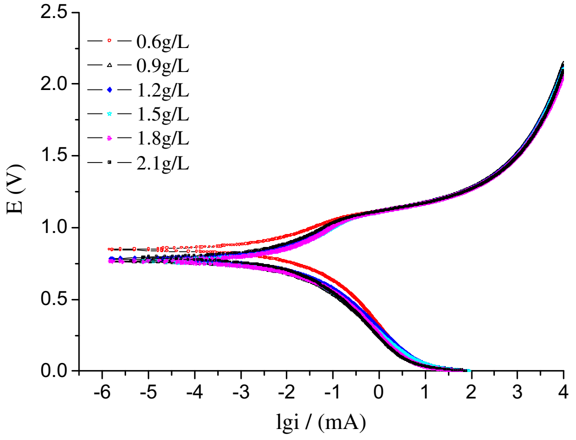

Fig. 4. The effect of magnesium ion on chlorine evolution reaction.

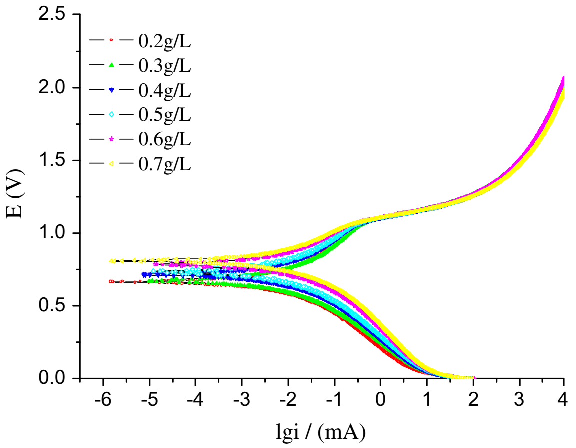

Fig. 5. The effect of calcium ion on chlorine evolution reaction.

3.2. Effects of calcium and magnesium ions on anode reaction

Figs. 4 and 5 show that the polarization curves were measured in solutions with different concentrations of magnesium and calcium ions. It is clear that Mg^{2+} and Ca^{2+} ions have almost no effect on the chlorine evolution reaction. Magnesium sulfate and calcium sulfate added to control the concentrations might not take part in the anode reaction, and the addition amount is far lower compared with Cl^- ions. Therefore, the formation of magnesium hydroxide and calcium hydroxide to flocculate and purify seawater is feasible, and simultaneous production of chlorine and hydrogen.

3.3. Current density

The seawater electrolysis experiments have been run with water velocity of 12 L/h at five different current densities from 12.5 to 22.5 mA/cm^2. The results, expressed in parameters of COD_{Mn}, turbidity, SDI_{15}, and pH, are shown in Table 3.

It is obvious that the COD_{Mn} and turbidity removal yields increase with the current density, and the values of SDI_{15} decrease from 4.4 to 2.1. This can be explained by the fact that more dissolution of hydroxyl and magnesium ions generate monomeric or polymeric magnesium hydroxides, which boost the quality of product water due to sweep coagulation at higher solids loading [18]. In addition, more bubbles are produced to improve the mixing and removal processes [19]. In the low range of current density, as the hydroxyl generated is few, the sludge of magnesium hydroxide formed has small dimension and is not allowed to an efficient adsorption of seawater pollutants. However, the COD_{Mn} removal has no significant increase when the current density is up to 20.0 mA/cm^2. It is implied that the dissolved organics are hardly removed after the organic suspended matters effectively removed.

Table 3
The quality of product water at various current density

Current density (mA/cm^2)	Turbidity removal (%)	COD_{Mn} removal (%)	Values of SDI_{15}	Values of pH
12.5	78.79	33.84	4.4	6.57
15.0	81.99	41.91	3.7	6.85
17.5	88.73	56.65	3.2	7.12
20.0	99.57	68.24	2.7	7.23
22.5	99.83	69.11	2.1	7.37

The pH value is often considered as an important index of RO feed water. Table 3 shows the values of pH increase with the current density increasing. This result may be explained by the fact that at low current density, the cathode produces few hydroxyls leading to be low pH value of water in cathode chamber, and the chlorine generated all dissolves in water of anode chamber. Thus, after neutralizing, the pH of product water is becoming lower. For high current density, there is no change in acidity of anode water since it is saturated with Cl_2, and the redundant chlorine is collected by sodium hydroxide. However, more hydroxyls formed results in high value of pH in cathode chamber. Therefore, the pH value of product water has increased after acid–alkali neutral reaction.

The electrolysis process is known as in situ chlorine generator. The production of chlorine, the optimal current for electrolysis and the rate of chlorine formation were investigated in natural seawater. Fig. 6 shows the rate of chlorine evolution as a function of current density at water velocity of 12 L/h. It is obvi-

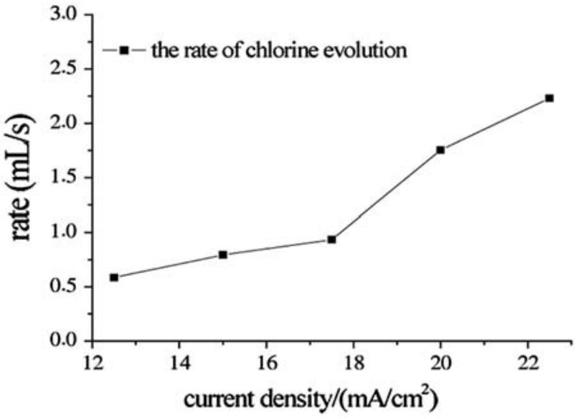

Fig. 6. The rate of chlorine evolution at different current density.

ous that with the increasing of current density, the rate tends to increase gently at first and then grow sharply (>18 mA/cm^2). It may depend on the properties of the electrode, especially the electro-catalysis. The result shows that the reaction is speeded up when the current density reaches to 17.5 mA/cm^2 and the rate of the chlorine evolution is 1.75 mL/s at the current density of 20.0 mA/cm^2.

On the basis of the above laboratory observations, current density is a significant parameter in seawater electrolysis process. At low current density, the product water does not meet the criteria for feeding RO membrane desalination installation. The precipitation, such as magnesium hydroxides, is easily adsorbed onto the anode electrode, leading to be weak removal process. At higher current density, the rate of gas evolution is fast and more hydrogen gas generated scours the precipitate by agitation effect. Thus, the precipitation is hardly adsorbed onto the electrode. Taking the cost into consideration, the current density of 20.0 mA/cm^2 is chosen for electrolysis pretreatment, at which the turbidity removal, SDI$_{15}$ and COD$_{Mn}$ removal is 99.57%, 2.7 and 63.22%, respectively.

3.4. Water velocity

From Fig. 7, it can be easily seen that the turbidity removal decreases with water velocity at the current density of 20.0 mA/cm^2. This may be explained by the fact that the volume of diaphragm electrolyzer is fixed and the large water velocity means the shortage of hydraulic residence time, which leads to a spot of magnesium hydroxide and there is not enough reaction time to adsorb and flocculate the pollutants from new water. Therefore, high water flow results in low turbidity removal, and much lower water velocity is better. However, the cost is becoming one of the important parameters that greatly determines the application process of seawater pretreatment. With comprehensive consideration, water velocity of 14 L/h is selected, at which turbidity, COD$_{Mn}$ and SDI$_{15}$ is 0.36 NTU, 1.27 mg/L, and 2.4, respectively.

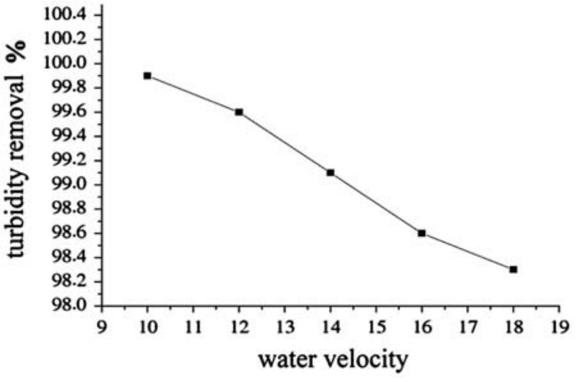

Fig. 7. The influence of water velocity on turbidity removal.

3.5. Mechanism of pretreatment

Fig. 8(a) shows the influences of electrolysis time on Mg^{2+}, Ca^{2+} ions and pH value. It is obvious that the concentration of magnesium dramatically decreased from 15 to 40 min, revealing 69.82% reduction. Before 15 min and after 40 min the decreasing rate is retarded. The concentration of calcium decreases from 40 min, before which it has no significant change. This phenomenon can be explained that the K_{sp} constant of magnesium hydroxide is 1.8×10^{-12} which is much lower than 5.5×10^{-6} of calcium hydroxide. From 20 to 40 min, there is a platform region of pH with the increase of electrolysis time, where much more magnesium hydroxide may

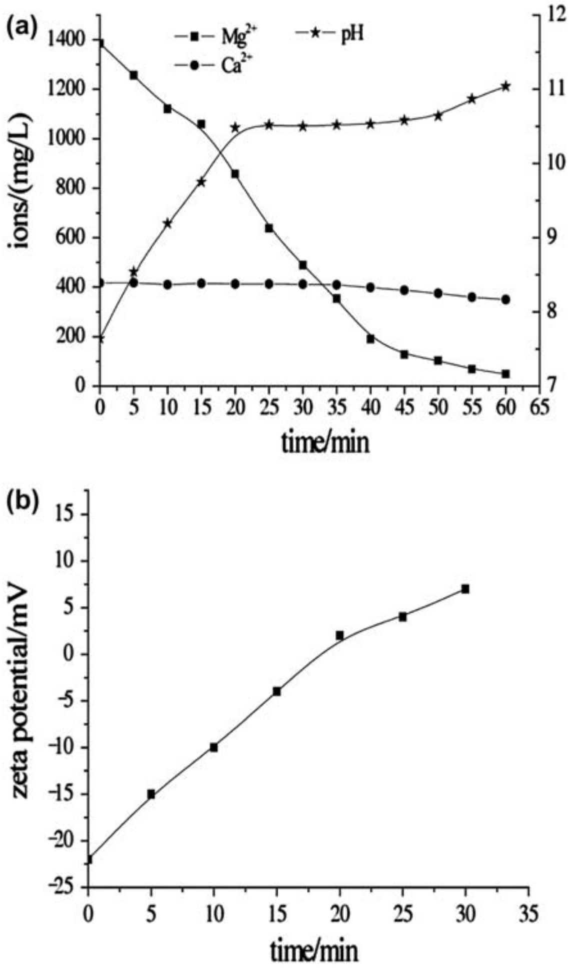

Fig. 8. The curves of Mg^{2+}, Ca^{2+}, pH (a) and zeta potential (b) vs. time.

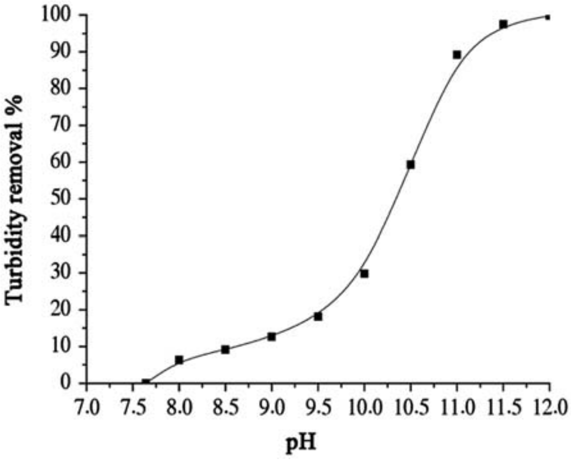

Fig. 9. The influence of pH on turbidity removal.

be formed. As Fig. 9 shows, the turbidity removal increases with pH values, especially at pH of 10.5. Therefore, we suppose that the magnesium hydroxide plays an important role in seawater purification.

Fig. 8(b) shows the zeta potential of suspension in seawater as a function of electrolysis time at 20.0 mA/cm^2. The zeta potential of particles increases with electrolysis time and 0 V is observed at about 18 min. It means that charge neutralization may be occurred at zeta potential of 0 V because the zeta potential of raw seawater is negative but suspension has the opposite potential. Longer than 18 min, sweep coagulation may play the main role in purification. Thus, the mechanism [17] can be described that magnesium ions have the double electronic shell compression, which decreases the zeta potential of pollutants, resulting in coagulation. In addition, magnesium hydroxide precipitate acts as an efficient coagulant with the action of sweep coagulation due to its structure of large adsorptive surface area.

4. Conclusions

The experiment of seawater electrolysis for pretreatment was studied. It demonstrates that the process is a simple and new effective method for seawater pretreatment for RO systems. Under optimum operating conditions at a current density of 20.0 mA/cm^2 and water velocity of 14 L/h, ions diffusion is the rate-determining step of the anode reaction and the rate of chlorine evolution is 1.75 mL/s. Moreover, various concentrations of magnesium and calcium ions have no significant influence on chlorine evolution. High turbidity removal and low value of SDI$_{15}$ are achieved due to the gelatinous suspension of magnesium hydroxide which removes the pollutants from seawater by the adsorption and coagulation. COD$_{Mn}$ of 1.27 mg/L is obtained because of the disinfection of chlorine generated in anode.

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