



## In *Desalination*, from 1987 to 2009, the birth of a new seawater pretreatment process: Electrocoagulation—an overview

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### ABSTRACT

In the first journal in the desalination world, *Desalination*, during the last 20 years, there is the birth of a new seawater pretreatment process: electrocoagulation (EC). In order to note some facts of this birth, relate its context, and understand its circumstances, this review concerns a brief description of the application of EC as a new seawater pretreatment process throughout the work of Sanfan and Qinlai (1987) until the work of Yi *et al.* (2009) via the work of Sanfan (1991); all of them are published in *Desalination*. The first paper (1987) discusses the mechanism of removing some ions from the brackish water using EC method. Experiment results present some major parameters for the EC process. The most important one in operation is electric current density (CD). Moreover, the first paper suggests the method of selecting optimum density and some ways could raise economic property of EC and could reduce handling costs. In the paper of Sanfan (1991) the further research results of improving economic property of EC method are discussed. In order to reduce the cost and raise the handling efficiency, five different technological processes are set up and studied. The best one was the using Fe electrode and aerating for raw water combine with reusing flocs. It can reduce 60% of handling cost in comparison withal electrode and remove 75% of hardness. Finally, Yi *et al.* (2009) use a simple and new effective electrochemical method (EM) prior to reverse osmosis for seawater desalination. The influences of three main factors in EMs—CD, operating time and sedimentation time on the efficiency of pretreatment—have been investigated. It is shown that the EM is very effective for removal of turbidity. The qualities of the raw and the treated seawater have been measured using UV–Vis spectrometry. The morphologies and the particle size distribution of the resulted sludge have been characterised by scanning electron microscopy (SEM) and a particle size analyser, and the mechanism of the EM has been analysed theoretically. Raw seawater with a turbidity of 54.1 NTU, 94.48 mg L<sup>-1</sup> SS after EM pretreatment at 26.30 mA cm<sup>-2</sup> CD for 40 min reduces the turbidity to 1.00 NTU. The time taken for the same depletion of turbidity in case of 39.45 mA cm<sup>-2</sup> CD is 35 min, and the absorbance of the curve decreases when EM treatment is applied. The experimental results reveal that particular size in seawater agglomerate and get bigger after EM treatment, and the turbidity removal is enhanced by charge neutralisation and sweep coagulation. The sludge generated from the process is found to have larger specific surface areas at higher CD from SEM observation, leading to better treatment efficiency.

*Keywords:* Seawater; Desalination; Pretreatment; Coagulation; Electrocoagulation; Boron

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## 1. Introduction

Reverse osmosis (RO) is gradually becoming an effective approach to solving the shortage of fresh water resources in coastal cities [1–4]. But the existence of suspended substances, colloids, microorganisms and soluble organic macromolecules [5] in seawater will pollute the RO membranes [6], leading to a drop in filtrate flux and an increasing trend in transmembrane pressure. As a result, pretreatment is an absolutely necessary process of the RO system [7–12].

Electrochemical treatment techniques have attracted a great deal of attention [13–15] because of their versatility and environmental compatibility. In the last decade, electrochemical treatment has frequently been used to treat various industrial wastewaters successfully [16, 17]. In fact, electrochemical methods (EMs) use the electron as the main reagent, which is a “clean reagent” [3, 18]. The degradation products in the oxidation of contamination are often carbon dioxide, water, nitrate and sulphate, etc. These processes can operate at ambient temperature without needing temperature control [3].

Contamination removal can be achieved either by electro-oxidation with insoluble anodes [17] or by electro-coagulation (EC) using consumable materials [19–22]. In an electro-oxidation process, the pollutant is destroyed in the bulk solution by the role of strong oxidants generated by the electrochemical reactions. EC involves the generation of coagulant *in situ* by the dissolution of metal [23] from the anode with simultaneous formation of hydroxyl ions and hydrogen gas at the cathode. This process produces the corresponding aluminium or iron hydroxides and/or polyhydroxides. The generated gas also helps to float [24] the flocculated particles at the water surface [3].

However, in order to note some facts of this birth, relate its context, and understand its circumstances, this review concerns a brief description of the application of EC as a new seawater pretreatment process throughout the work of Sanfan and Qinlai (1987) [25] until the work of Yi *et al.* (2009) [3] via the work of Sanfan (1991) [26]; all of them are published in *Desalination*.

## 2. Pretreatment process of brackish water using electrocoagulation

In areas where only brackish (salty) ground water is available [25], the choice of the water desalination method [27–29] between electrodialysis (ED) and RO is now feasible and possibly economical [25, 30]. But the presence of scale leads to operating difficulties and/or loss of efficiency in ED and RO [31]. It plugs the membranes; it increases the electrical or hydraulic resistance and the power consumption. Therefore, pretreatment of salty water prior often proves necessary. One of the purposes

of the pretreatment [32–36] is the removal or at least the reduction of the concentration of ions which can be components of scale. Some methods, e.g. chemical softening and ion exchange, for the prevention of scale in pretreatment processes are known, but many of them are quite expensive [25].

A new method of pretreatment for ions removal, EC has been tried and laboratory tested in China. In this paper [25] the mechanism of removing some ions from the brackish water using EC method is discussed. Changing some major factors, the experimental comparison among various different salty waters has been made. Results have been found quite effective, especially for the water of high-alkalinity, high-hardness and high-salty [25].

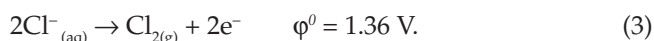
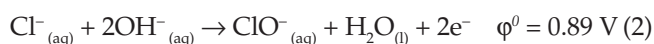
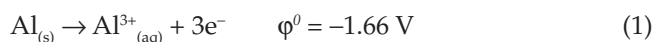
### 2.1. Mechanism of electrocoagulation

Some ions in the brackish water can be removed partly by EC through filtration or sedimentation. The removal percent depends on the kinds of ions.  $Mg^{2+}$ , one of the major constituents in the brackish water, is the highest in removal,  $HCO_3^-$  and  $Ca^{2+}$  are higher,  $SO_4^{2-}$  is less,  $Cl^-$  is the least, and  $Na^+$  and  $K^+$  are hardly removed at all. It is a more complicated process relating to the complexation, the adsorption and the precipitation [25].

#### 2.1.1. Electrode reaction

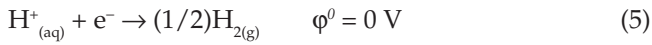
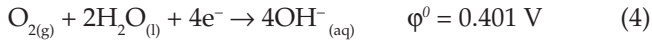
EC is known for an electrolysis method which process results in electrode reaction with metal electrode (as Al or Fe) in brackish water under the action of a direct current (DC) field. What form of the reaction will take place at electrodes? It lies on the electrode potentials of metals. At the cathode, higher potential matter goes into solution first, at the anode, less potential has a prior reaction [25].

Using Al plate electrodes for the brackish water purification, the anode reactions are (25°C)



The reducing potential of dissolving aluminium among these three reactions is less than the other two although aluminium has an excessive potential. The difference between any two potentials is much more than 0.2 V, otherwise they would have been analysed at the same time. It turns out that only metal Al is dissolved in the water at the anode. The other two reactions would not have taken place [25].

The cathode reactions are (25°C)



Judging from electrode potentials, *Reactions* (4) and (5) will take place first. In the raw water, it contains less dissolved oxygen, less in the ground water. The natural water is an alkaline water as usual, which hydrogen concentration is less than  $10^{-7}$  N. On condition that the passing electric current is high enough when EC is in operation, it certainly causes all in all of  $\text{O}_{2(\text{g})}$  and  $\text{H}^+_{(\text{aq})}$  attaching on the electrode plate in the retarding layer. It results in the taking place of *Reaction* (6). The  $\text{H}_{2(\text{g})}$  and  $\text{OH}^-_{(\text{aq})}$  will be ionised from the water. It was proved to be that much gas bubbles have formed at the cathode in EC. Thus three electrode reactions may proceed at the same time and the third one is mainly [25].

For the electrode reactions to occur and keep proceeding in the instance of single unit (only one pair of electrodes), an electrical voltage is given as follows [25]:

$$E = \varphi_a - \varphi_c + IR = \varphi_{at} - \varphi_{ct} + \eta_+ + \eta_- + IR, \quad (7)$$

with  $E$ : a voltage which is capable of maintaining a DC electric field;

$\varphi_{at}$ ,  $\varphi_{ct}$ : the theoretical electrode potential at anode or at cathode;

$\eta_+$ ,  $\eta_-$ : an excessive potential of anode, or cathode;

$I$ : current between two electrode plates;

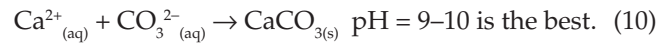
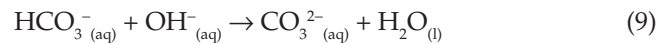
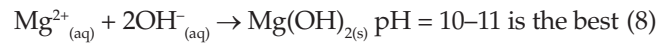
$R$ : resistance in solution [25].

The excessive potential (or resistance in solution) increases with the raise of current density (CD). As a result, the additional voltage of EC unit is not kept constant. If it is less than  $E = \varphi_{at} - \varphi_{ct}$ , the unit would failed in operation [25].

### 2.1.2. Ions movement and polarisation precipitation

$\text{Al}^{3+}_{(\text{aq})}$  and  $\text{OH}^-_{(\text{aq})}$ , passing the retarding layer from the surface of electrode into the solution, their diffusion rates can be obtained from Fick's law. In the same time, under the action of electric field, all of the ions in solution with the products of electrode reaction are travelling by electrostatic attraction: the cations tend to cathode; the anions to anode. Their moving velocities determine on the potential gradient between two electrodes. The diffusion and moving actions are both helpful to reaction products apart from the reaction

points speedily. It avoids concentration raising and thus increasing the electrode potential rapidly. Then it keeps the additional voltage constant. Although that, on account of the reaction product at cathode  $\text{OH}^-_{(\text{aq})}$  and the cations  $\text{Ca}^{2+}_{(\text{aq})}$ ,  $\text{Mg}^{2+}_{(\text{aq})}$ , accumulating to the cathode from the solution, their concentration products are over each of their solubility product. Scale precipitation would occur on the surface of cathode and in the retarding layer while the CD is high enough. The reactions are as follows [25]:



These precipitation reactions can easily occur in the retarding layer and not in the solution. It may be proved as following calculus, the solubility product of  $\text{Mg}(\text{OH})_2$  is [25]

$$K_s = [\text{Mg}^{2+}] [\text{OH}^-]^2 = 5.0 \times 10^{-12} \quad (25^\circ\text{C}). \quad (11)$$

Provided the concentration of  $\text{Mg}^{2+}$  in the raw water is  $10 \text{ meq L}^{-1} = 5.0 \times 10^{-3} \text{ mol L}^{-1}$ , when  $[\text{OH}^-] \geq 3.16 \times 10^{-5} \text{ mol L}^{-1}$ , they may be precipitated as magnesium hydroxide. At that time  $\text{pH} > 9.5$  is necessary. In addition, a good many of the product at cathode  $\text{OH}^-$  is consumed which will form  $\text{Al}(\text{OH})_3$  foremost (the solubility product of aluminium hydroxide is  $1.0 \times 10^{-32}$ ). The result from experiments have presented that the pH in the finished water of EC is less than 9,  $\text{pH} = 7.5\text{--}8.5$  is in general. Therefore the reaction in the solution to precipitate  $\text{Mg}(\text{OH})_2$  is too difficult to go on [25].

### 2.1.3. Flocs forming and their adsorption

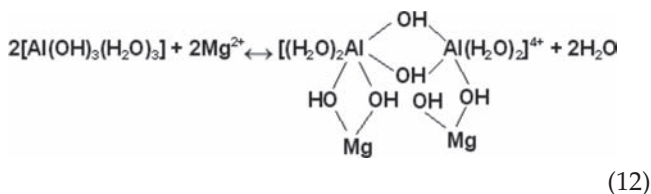
EC in operation would produced  $\text{Al}^{3+}$ ,  $\text{OH}^-$  and formed as  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ , or its hydrolyse products as  $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ ,  $[\text{Al}(\text{OH})_2(\text{H}_2\text{O})_4]^+$ ,  $[\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3]$ ,  $[\text{Al}(\text{OH})_3(\text{H}_2\text{O})_2]$ ,  $[\text{Al}(\text{OH})_4(\text{H}_2\text{O})]^-$  and other polyhydroxyl polynuclear complex ions. Finally, the aluminium species that are formed depend on the pH of the water. When  $7 < \text{pH} < 8.5$ ,  $[\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3]$  is in quantities and other polymeric cations of aluminium hydroxide are in small amount. They may be formed flocs in EC process [25].

In the finished water of EC the removal percent of  $\text{HCO}_3^-$  is 50–70% in general,  $\text{Ca}^{2+}$  is 40–60%. In process of EC on the cathode plate  $\text{OH}^-$  are provided into the solution continuously. It causes the equilibrium of carbonic acid lost. The reaction is described above as

Reaction (9). As we know the ionisation equilibrium constant  $k = 4.7 \times 10^{-11}$ , only when  $\text{pH} > 8.35$ , this reaction may be occurred. But in the finished water of EC the  $\text{pH} < 8.5$ , it seems that  $\text{CaCO}_3$  precipitation (solubility product is  $4.8 \times 10^{-9}$ ) mainly presents in the retarding layer of cathode. Besides, a large part of  $\text{HCO}_3^-$  tending to  $\text{CO}_3^{2-}$  and  $\text{CaCO}_3$  may be occurred around the flocs. In the course of forming aluminium hydroxide polymer, there are various middles of hydroxyl complex with a good many positive charges. The anions are attracted around the flocs thus creating a cloud of 'counter-ions' in which concentration of the  $\text{OH}^-$  and  $\text{HCO}_3^-$  increases. When carbonic acid equilibrium is lost, precipitates  $\text{CaCO}_3$  may produce and coagulation is achieved with adsorption of these targets. A large number of flocs present in the water uniformly, moving continuous and the precipitates are caught in the meshes thus causing the removal of  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  [25].

The removal of  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  is based on the principle of solubility products, as well as of  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ . The difference between each of their solubility products is obviously. The solubility product of  $\text{Mg}(\text{OH})_2$  which only as  $5.0 \times 10^{-12}$ , is less than of  $\text{CaCO}_3$ , so the removal percent of  $\text{Mg}^{2+}$  is the highest. The solubility product of  $\text{CaSO}_4$  among them is the most as  $6.1 \times 10^{-5}$  so the removal of  $\text{SO}_4^{2-}$  is less than of  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  or  $\text{Ca}^{2+}$ , as less than 20% in general [25].

In proper conditions, the high polymer aluminium hydroxide to form bridges and/or cross-links as following reaction may be occurred [25]:



Besides, the flocs carrying charges will attract those charges of opposite sign. It depends on the  $\text{pH}$  in solution whether the flocs carrying positive attract the anions as  $\text{SO}_4^{2-}$  or  $\text{Mg}^{2+}$ . Colloidal particles carrying opposite charges also may be attract each other, such as  $\text{CaCO}_3$  forms negatively charged colloids which will neutralise the positively charged colloids as  $\text{Mg}(\text{OH})_2$ , hence agglutination and precipitation are possible [25].

#### 2.1.4. Properties of electrocoagulation

The property of electrolyse method is mainly of that the  $\text{Al}^{3+}$  dissolved at anode has strong activation.  $\text{Al}^{3+}$  and  $\text{OH}^-$  are both equal-equivalently produced at the cathode and anode simultaneously, thus keeping proper range of  $\text{pH}$ . The distance between two electrodes is

only a few centimetre. All above are the superior conditions of forming flocs rapidly. It needs only 15–20 s from occurrence of  $\text{Al}^{3+}$  till forming flocs. The detention time of water in the unit is only 30–120 s. It is far less than the time 20 min or so which is need for mixing and flocculation in coagulation as usual. It causes the loading of EC unit is some dozens of times larger than of the chemical coagulation (CC) units [25].

As mentioned above, the removal of ions in the water is mainly by means of flocs adsorption. It is achieved by the actions of decreasing surface free energy, electrostatic attraction, 'bridge binder' and Van der Waals forces. A constant quantity of flocs can adsorb a limited quantity of matter. Its amount of adsorbate in equilibrium is under the influence of many factors such as the kinds of adsorbate,  $\text{pH}$  of solutions and the contact conditions of them each other etc. From the adsorption isotherm, the more the solution concentration of adsorbate, the more the amount of adsorbed on a unit weight of adsorbent. That is to say, in EC process flowing through the same current, producing the same quantity of flocs, if the amount of ions required to remove in the raw water increases, in spite of the decrease in removal percent, the removed matter greatly increases in quantity [25].

Some ions in raw water may be removed by the flocs in EC that is effective as well as in CC. The amount of dosing chemical in CC is far less than of aluminium dissolved in EC for removal some ions, thus the amount of flocs forming is few in coagulation. Moreover in CC alkalinity of raw water need to be consumed in hydrolysis. It is hardly to form precipitates as  $\text{Mg}(\text{OH})_2$  or  $\text{CaCO}_3$ , so its removal of ions is nothing. If the alum dosing in CC is increased to the level of EC and dosing  $\text{OH}^-$  proportionally, the effect of removal ions may be obtained. This conclusion can be proved in experiments as shown in Table 1 [25].

#### 2.2. Experimental details

The small-sized experimental EC device is made of Plexiglas (Fig. 1). Its dimensions are that length is 18 cm, width is 13 cm, and height is 10 cm. The distance between two electrodes is 5 cm, and total area of electrodes is 5 cm, and total area of electrode plates is  $0.3 \text{ m}^2$  [25].

The water sample type 1 and type 2 consist of different ions (Table 2). By exchanging the water sample type, the total salty, the discharge and the electric CD we probed into the adaptability using EC dealt with the different type of brackish water and their reasonable operation parameters [25].

#### 2.3. Results and discussion

The ions such as  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  can be removed from the water samples partly by EC with



Table 1  
Effect contrast between EC and CC [25].

Type	Chemical <i>et al.</i>	Dosing Al <sup>3+</sup>	Raw water meq L <sup>-1</sup>		Finished water meq L <sup>-1</sup>	
			Alkalinity	Hardness	Alkalinity	Hardness
EC	Current 3.04 A Flow 10 L h <sup>-1</sup>	be equal to 10 meq L <sup>-1</sup>	9.013	38.0	3.77	30.2
CC	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O	0.5 meq L <sup>-1</sup>	9.013	38.0	8.89	37.85
	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O	10 meq L <sup>-1</sup>	9.013	38.0	0.42	36.0
	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O + NaOH	10 meq L <sup>-1</sup> + 10 meq L <sup>-1</sup>	9.013	38.0	5.03	28.4

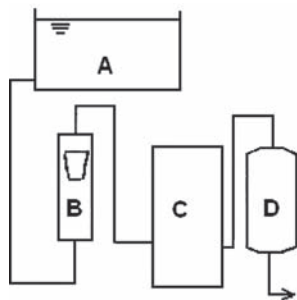


Fig. 1. Experimental flow chart (A: steady elevated water tank; B: flow regulator; C: EC device; D: filter) [25].

the increasing of the discharge their removal percents decrease and with the raising of the electric CD their removal percents increase. The sequence in quantity of removal percents is Mg<sup>2+</sup> > HCO<sub>3</sub><sup>-</sup> > Ca<sup>2+</sup> > SO<sub>4</sub><sup>2-</sup>, but the removal percent of Cl<sup>-</sup> is less than 10% and K<sup>+</sup>, Na<sup>+</sup> are nearly unchanged [25].

Regardless the types of brackish water, the result of experiment shows that EC can bring the effect of removing ions into full play. For same salty though the removal percent of type 1 is less than the type 2, the quantity of ions removed is much increased than the last one. For same type of water though the removal percent of sample of salty 7000 mg L<sup>-1</sup> is less than the sample of 3500 mg L<sup>-1</sup>, the quantity of ions removed is much increased than the last one. These show that EC device for pretreatment of brackish water with either ED or RO is feasible particular for high-hardness and high-salty brackish water (Figs. 2 and 3) [25].

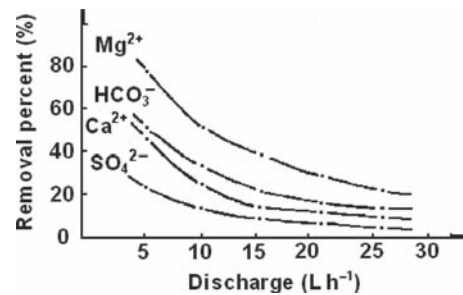


Fig. 2. The change of removal percent with discharge (CD is 10 A m<sup>-2</sup>, salty of type 1 is 3500 mg L<sup>-1</sup>) [25].

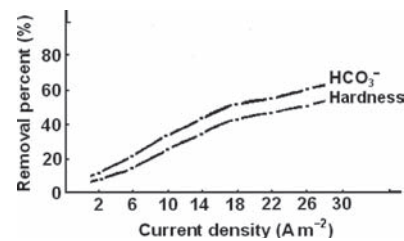


Fig. 3. The change of removal percent with CD (discharge is 15 L h<sup>-1</sup>, salty of type 1 is 3500 mg L<sup>-1</sup>) [25].

### 2.3.1. Operation parameters for the EC process

For treating objects are different, the operation parameters for the purification can not be referred to the pretreatment of brackish water. Recording to the experiment

Table 2  
The various ions concentration in different type of water sample [25].

Type of water sample	Equivalent percentage							Total salty
1	Cation	Ca <sup>2+</sup>	12.16	Mg <sup>2+</sup>	11.80	Na <sup>+</sup>	76.04	3500 mg L <sup>-1</sup>
	Anion	SO <sub>4</sub> <sup>2-</sup>	24.19	Cl <sup>-</sup>	68.38	HCO <sub>3</sub> <sup>-</sup>	7.43	
2	Cation	Ca <sup>2+</sup>	30.72	Mg <sup>2+</sup>	38.76	Na <sup>+</sup>	30.52	3500 mg L <sup>-1</sup>
	Anion	SO <sub>4</sub> <sup>2-</sup>	65.00	Cl <sup>-</sup>	19.89	HCO <sub>3</sub> <sup>-</sup>	15.11	

results the operation parameters were presented for reference [25]:

- Applicable water quality: total salty > 2500 mg L<sup>-1</sup> or hardness > 10 meq L<sup>-1</sup>.
- Removal percent of hardness: 35–50%.
- Flowing velocity between plates: 5–10 mm s<sup>-1</sup>.
- Distance between electrode plates: 3–10 mm.
- Retention period: 1.5–4 min.
- Electric CD: this is most important operation parameter [25].

The trial run is carried out according to the device property, water quality and the diagram of electric CD with energy consumption per unit removal percent can be obtained. The best electric CD is determined in this diagram. For example, according to Fig. 2, the process can be carried on as follows [25].

(1) Energy consumption corresponding with electric CD is obtained:

$$W = \frac{i \times A \times V}{Q} \times 10^{-3}, \quad (13)$$

with  $W$ : electric energy consumption to treat per ton water (kWh m<sup>-3</sup>);

- $i$ : electric CD in operation (A m<sup>-2</sup>);
- $A$ : total area of electrode plates (m<sup>2</sup>);
- $V$ : operation voltage (V);
- $Q$ : discharge (L h<sup>-1</sup>).

(2) Energy consumption of removing 1% hardness is obtained:

$$\omega = \frac{W}{n} \times 10^{-2} \times 10^3 = \frac{W}{n} \times 10, \quad (14)$$

with  $\omega$ : electric energy consumption of removing 1% hardness (wh m<sup>-3</sup> %);

- $n$ : removal percent corresponding with each  $W$  [25].

### 2.3.2. Ways to improve the economical characteristics of EC

As the removing ions effect of EC depends on the consumptions of electric energy and Al electrode, the consumptions become the major target to appraise the economical characteristics of EC. In above-mentioned experiments, handling 3500 mg L<sup>-1</sup> of salty brackish water per ton require to consume 60–80 g Al and 0.7–1.1 kWh electric energy then 4–10 eq hardness could be removed. This consumption is expensive for pretreatment process for brackish water. In order to reduce the costs and raising the handling efficiency, three different methods have been tested [25].

Firstly, the iron and aluminium electrodes mixed in an EC device was used. The proportion of Fe electrodes and Al electrodes is 2:1. The handling effect is better than Fe electrodes or Al electrodes alone. Secondly, the floccule was reused. This method can make full use of adsorption of floc and reduce handling costs. That the floccule separated from handled water was mixed with raw water can remove 20% hardness when EC device is no electric current at the same time and reduce 15% consumption at the same removal percent. Lastly, Fe electrodes and aerating for influent of raw water was used. Though the Fe electrode is much sharp the Al one and the same effect of handling was obtained, the large number of matters such as Fe<sup>2+</sup>, FeC<sub>2</sub>, Fe(OH)<sub>2</sub> and Fe(SO<sub>4</sub>) in water after handling by EC can make water become green or yellow. This phenomenon is caused by depletion of oxygen in water. For this reason the aerating for influent is necessary. This method can reduce 40–50% of costs comparing with Al electrodes at the same removal percent. Experiment results proved that above-mentioned methods can all raised economic property of EC and reduced handling costs for pretreatment process of brackish water. But it is the best operation way in EC to combine Fe electrodes and aerating for influent of raw water with reusing floccules [25].

Sanfan and Qinlai [25] concluded the following.

(1) It was feasible that the EC device was used for pretreatment of brackish water before the desalination by ED or RO. As it can reduce hardness and alkalinity in raw water meanwhile, it can remove opacity and various heavy metals ions, it would be disappear or reduce the deposition and scale in ED or RO.

(2) The major mechanism of removing some ions from the brackish using EC method was: firstly, it can turn some ions round flocs into precipitation a adsorbed by aluminium and/or iron hydroxide polymer then it can be removed with floccules, lastly, the carrying charges flocs will directly adsorb the ions and colloids with opposite charges.

(3) The electric CD was the most important operation parameter [25].

### 3. Economic property of pretreatment process of brackish water using electrocoagulation

The work of Sanfan (1991) is the continuation of the work of Sanfan and Qinlai (1987). It concerned more studies on economic property of pretreatment process of brackish water using EC method. As the experimental results are practically the same in the work of Sanfan and Qinlai (1987), we are satisfied with mentioning here in this review the main conclusions of the work of Sanfan (1991).

1. The Fe is used instead of Al as electrode of EC for pretreatment of brackish water is feasible. At the same percentage reduction, it can greatly reduce the cost of pretreatment.
2. The mechanism of removing ions by EC is that the suitable condition is formed round flocs and  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and some ions change into hard dissolution chemical compounds at there, then they are adsorbed by hydroxide polymer of iron and/or aluminium and removed by ways of sedimentation and filtration.
3. The key to using Fe electrode is aeration for raw water. It can oxidise  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and form floc having property of adsorption.
4. In all of processes, the Fe electrode and aerating for raw water combine with reusing flocs is best in technical and economic [26].

#### 4. Pretreatment of seawater by a one-step electrochemical method

Most studies [3] have focused on the efficiency of a specific pollutant removal, manipulating parameters such as conductivity, pH, CD, electrode materials [16], etc., and explore the fundamental mechanisms involved in the electrochemical processes. From an electrochemical point of view, the choice of electrode material is of great importance as electrode material can influence the mechanism, efficiency, and consequently the products of anodic reaction. Dimensionally suitable anode (DSA) materials have been widely studied for application in organic oxidation [3]. DSA materials are beneficial for treating wastewater as they present relatively longer lifetimes, higher current efficiency, and lower cost compared to traditional electrode materials such as Pt. The most common DSA material is the  $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  anode, which has been extensively used in the chlor-alkali industry for a number of years [3].

In this study [3], insoluble electrodes were placed in an electrochemical cell without an ion exchange membrane, and the final production such as magnesium hydroxide adsorbed the colloidal pollutants, organic particles and solid suspends, similar to a conventional adsorption process. The resulted chlorine and hydrogen lead to turbulence by reaction of  $\text{Cl}^-$  in anode and reduction of  $\text{H}_2\text{O}$  in cathode, which destabilise the colloid to flocculate generating bigger particles. Polyacrylamide (PAM) was also added in order to get quick sedimentation. In this paper [3], one-step electrolysis seawater pretreatment for RO is discussed. It is easy to manipulate, the whole process is environmentally friendly without secondary pollution, and the process also provided various benefits: One of the by-products,  $\text{Cl}_2$ , could be

used in sterilisation,  $\text{H}_2$  is an important energy, and the sludge is useful for acid wastewater neutralisation. As of now, similar research has not been reported [3].

#### 4.1. Experimental details

Samples of seawater were collected from the Bohai Sea [3], then directly used for analysis and electrochemical treatment. Its properties are shown in Table 3 [3].

The electrochemical reactor was made of Plexiglas with the dimensions of 100 mm × 100 mm × 120 mm. The DSA ( $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ ) anode and iron cathode fully immersed in seawater were connected to a digital DC power supply (WY10A-1) which supply the system with 1–3 A, corresponding to a CD of 13.15–39.45 mA cm<sup>-2</sup>. Each electrode dimensions were 95 mm long and 80 mm wide. The gap between the electrodes was 50 mm. The polarity of the electrodes was reversed intermittently every 30 min in order to prevent precipitate from being adsorbed onto electrodes. One mL PAM of 0.5 g L<sup>-1</sup> was added into 1 L raw seawater to get quick sedimentation [3].

The effect of the electrochemical treatment was determined by analysis of the turbidity at different operating conditions. Turbidity was measured by a turbidity meter (LP2000-11, Hanna, Italy). Zeta potential (ZP) was measured by a micro-electrophoresis meter (JS94G+, Shanghai, China). Concentrations of ions were determined by ion chromatography (DX-120, Dionex, USA). The Silt Density Index (SDI) is an empirical test developed for representing the potential for fouling of the membranes by finely suspended particles present in feed water to the membranes, which bases on the time required to filter a volume of feed water through a 0.45 μm filter paper at a feed pressure of 30 psig at start and then after 5, 10 and 15 min of continuous filtration, according to ASTM standard test method D 4189-82. However, for high SS water such as raw seawater, SDI cannot be measured as the pollutants plug the pores of micron filter paper. Only the SDIs of electrochemical treated seawater were measured. A L340304 spectrophotometer was used to record the UV–Vis spectra within a 200–400 nm wavelength range. The morphologies were observed by a Hitachi-3500N scanning electron microscope

Table 3  
Parameters of the raw seawater samples [3].

Parameter	Value
Temperature (°K)	289
pH	8.29
SS (mg L <sup>-1</sup> )	94.48
Turbidity (NTU)	54.1
COD <sub>Mn</sub> (mg L <sup>-1</sup> )	8.47
Content of $\text{Mg}^{2+}$ (mg L <sup>-1</sup> )	1256.37
SDI <sub>15</sub>	Out of range

(SEM) at an acceleration voltage of 3 kV. A LS13320 laser diffraction particle size analyser was used to analyse the sludge produced by the electrochemical process [3].

## 4.2. Results and discussion

### 4.2.1. Effect of current density and operating time

CD combines the effect of cell current and effective surface area of electrodes. CD during electrochemical experiments is varied by changing cell current. Fig. 4 portrays the effect of CD on electrochemical experiments at constant electrode surface areas. After 50 min of electrochemical treatment, 74.3, 99.1 and 99.7% turbidity from the liquid phase was found to be transferred to sludge phase at current densities of 13.15, 26.30 and 39.45 mA cm<sup>-2</sup>, respectively. SDI<sub>15</sub> values under these operating conditions are 2.95, 2.04, 1.57 correspondently. The maximum limit as influent quality standard to RO system for turbidity (1.0 NTU) was obtained after 40 and 35 min of electrochemical treatment with 26.30 and 39.45 mA cm<sup>-2</sup> CD, respectively. SDI under these conditions is 2.78 and 1.96 correspondently. Therefore, effective removal of turbidity from the supernatant by electrochemical treatment has been observed at higher current densities [3].

At higher CD, more dissolution of hydroxyl with high-rate-formation of monomeric and/or polymeric magnesium hydroxides results in significant improvement in turbidity removal. Due to elevated dissolution rate of ions, more sludge is generated, which boosts the turbidity removal due to sweep coagulation at higher solids loading. At the same time, more generated bubbles improved the mixing and removal processes [3].

There was no significant variation at 30 min when polarity of electrodes was reversed at current densities of 26.30 and 39.45 mA cm<sup>-2</sup>. Because at higher CD, precipitate was hardly adsorbed onto electrodes as more

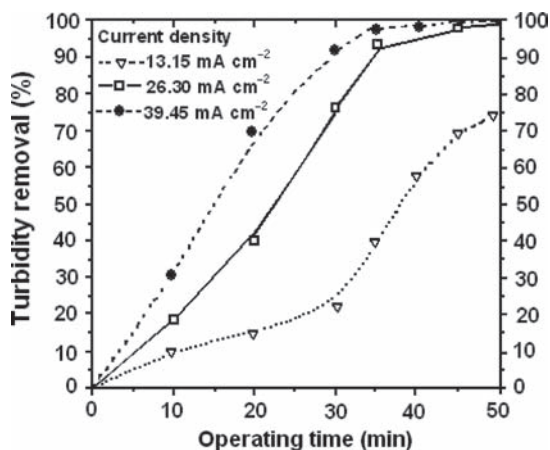


Fig. 4. Turbidity removal at different current densities and operating times [3].

gas generated improve the agitation effect. A significant increase in the turbidity removal was observed when the polarity of electrodes was reversed at 13.15 mA cm<sup>-2</sup> CD since at low CD precipitate was adsorbed onto electrodes, leading to a weak removal process. Once the polarity was reversed, precipitate on electrodes was scattered into the seawater and enhanced the removal effect [3].

### 4.2.2. UV-Vis spectra

The UV-Vis spectra of the raw and electrochemically pretreated seawater under operating conditions of CD 39.45 mA cm<sup>-2</sup> and operating time 35 min are shown in Fig. 5. They were two continuous curves without peaks at the higher absorbance range from 240 to 340 nm. The absorbance around 240 nm decreased by 88% (decreases from 2.25 to 0.20) when electrochemical treatment was applied. The results indicate that there was a significant colour reduction of the raw seawater after the electrochemical treatment was applied [3].

### 4.2.3. Zeta potential

Fig. 6 shows the variation of ZP as a function of the operating time at CD of 39.45 mA cm<sup>-2</sup>. The ZP of

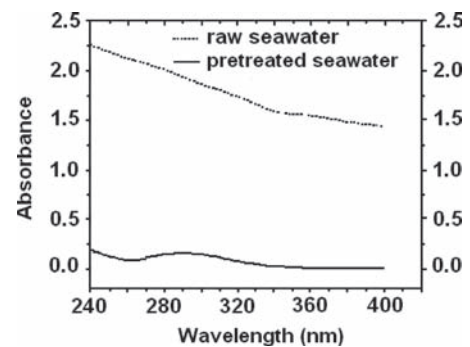


Fig. 5. UV-Vis spectra of raw and pretreated seawater [3].

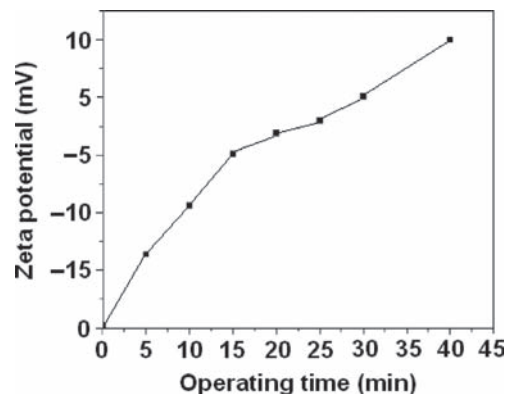


Fig. 6. Curves of ZP varying with residence time [3].



suspension in raw seawater was about  $-15$  mV and increased rapidly with operating time. However, as the operating time was longer than 15 min, the ZP increased slightly. This result means charge neutralisation occurred when ZP of particles was close to zero and sweep coagulation took place at the longer time that caused precipitation of amorphous hydroxide. Therefore, we could consider the operating time of 15 min as the charge neutralisation point [3].

4.2.4. Effect of sedimentation time on turbidity removal

At the end of the electrochemical pretreatment, the sample was poured into a graduated cylinder for precipitation of flocs. As Fig. 7 shows, when sedimentation time was increased (up to 30 min) the removal efficiency of turbidity increases. But after 30 min, the rate of turbidity removal is relatively constant since the adsorption capacity of flocs becomes exhausted [3].

4.2.5. Particle size analysis

According to Fig. 8, the size of suspended particles in raw seawater ranged from 0.03 to 10  $\mu\text{m}$  with two

peak particle sizes of 0.15 and 3.2  $\mu\text{m}$ . However, the size distribution of the particles in sludge produced by electrochemical process under CD of  $39.45 \text{ mA cm}^{-2}$  and operating time of 35 min was broader, and had two peaks at 5 and 80  $\mu\text{m}$ . The first peak eliminated gradually as the sediment time went by, at the same time the turbidity and SDI reduced. The result indicates that particle size got bigger after electrochemical process. And the particles with sizes varying from 1 to 5  $\mu\text{m}$  had a higher impact on SDI than particles with size above 5  $\mu\text{m}$  in seawater, which is coincident with the opinion of Teng et al. [37]. Magnesium hydroxide produced by the electrochemical process could adsorb microorganisms, colloids, and emulsion in seawater, which coagulate to easy sedimentation [3].

4.2.6. Scanning electron micrographs

The size and morphology of the resulting sludge solids produced under different current densities of 13.15, 26.30 and  $39.45 \text{ mA cm}^{-2}$  for 35 min were further examined by SEM analysis. And the SDI values of correspondent treated seawater were 3.76, 2.05, 1.68, respectively. As shown in Fig. 9(a), it is quite remarkable that all

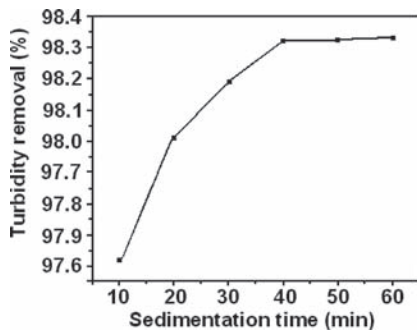


Fig. 7. Effect of the sedimentation time on the removal efficiency of turbidity [3].

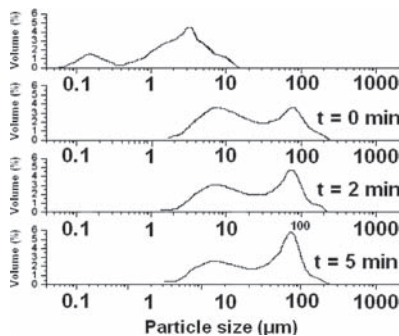


Fig. 8. Particle size distribution for different sediment time [3].

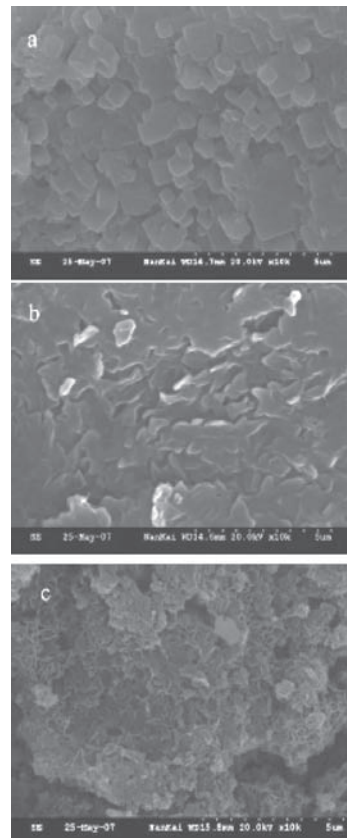


Fig. 9. SEM images of the sludge produced under different CD. (a)  $13.15 \text{ mA cm}^{-2}$ ; (b)  $26.30 \text{ mA cm}^{-2}$ ; (c)  $39.45 \text{ mA cm}^{-2}$  [3].

particles present straight flake structure and distribute uniformly under CD of  $13.15 \text{ mA cm}^{-2}$ . When the CD increased to  $26.30 \text{ mA cm}^{-2}$ , the granules have a smooth outer surface with bigger particle sizes, which were usually irregular or polygonal in shape. As shown in Fig. 9(b), the sludge produced under  $39.45 \text{ mA cm}^{-2}$  CD has a netlike structure with a large number of irregular pores in it. It indicates that sludge generated under higher CD have larger specific surface areas, which lead to a better treatment efficiency [3].

#### 4.2.7. By-products

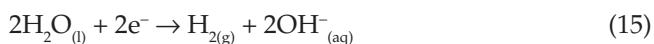
Quality and quantity of sludge produced during water treatment is of industrial importance. If improperly managed, this waste can pose dangerous health and environmental consequences. In this paper, 20 mL sludge was added to 150 mL steel pickling waste liquor which was diluted for 10 times. Its qualities were measured after precipitation for 3 h at room temperature. As shown in Table 4, the results meet the standard of the national third-class Integrated Wastewater Discharge Standard (IWDS)GB 8978–1996 [3].

#### 4.2.8. Electrochemical mechanisms

Electrochemical seawater pretreatment is a process consisting of creating magnesium hydroxide flocs where adsorption and precipitation are not formed by delivering chemicals to the system, but result from an electron reaction on the electrodes. Electrochemical pretreatment is based on the fact that the stability of colloids, suspensions and emulsions is influenced by electric charges. Therefore, if additional electrical charges are supplied to the charged particles via appropriate electrodes, the surface charge of particles is neutralised and several particles combine into larger and separable agglomerates [3].

The possible mechanisms for the production of  $\text{Mg}(\text{OH})_2$  and the removal of turbidity can be summarised in Reactions (15)–(20) [3].

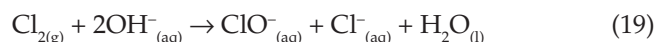
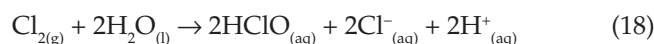
Cathode:



Anode:



Solution:



The pH value around cathode increased during the electrolysis process. According to Alexeev's research [38], two major reactions are effective in liquid–solids separation when pH is increased, i.e., the calcium carbonate  $\text{CaCO}_3$  precipitation and the magnesium hydroxide  $\text{Mg}(\text{OH})_2$  precipitation. The role played by each reaction depends on the primary particles and the ions contained in solution. Since the concentration of magnesium is higher than calcium in seawater, we deduce that magnesium plays a more important role in pretreatment [3].

As shown in Fig. 10, the turbidity removal becomes significant at pH 10.5. At pH 12, a high efficiency plateau appeared where nearly all the measurable turbidity is eliminated. In fact, the abatement increases rapidly when the pH value is about the theoretical value of  $\text{Mg}(\text{OH})_2$

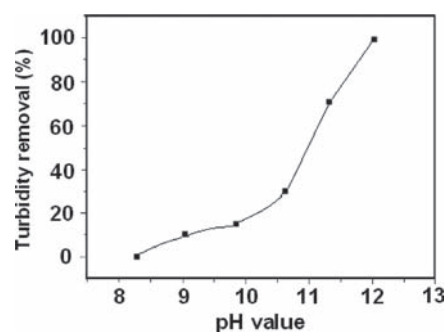


Fig. 10. Turbidity removal relating with pH in the vicinity of the cathode [3].

Table 4  
Acid waste liquid quality before and after treatment [3].

Parameter	pH	Turbidity (NTU)	Colourity	CODCr (mg L <sup>-1</sup> )	Cr <sup>6+</sup> (mg L <sup>-1</sup> )	SS (mg L <sup>-1</sup> )
Raw wastewater	1.64	40.15	0.172	1427	0.724	0.1002
Treated wastewater	7.89	5.11	0.02	445	0	0.002
Third-class of IWDS	69	–	–	1000	–	400

Table 5  
Concentration of main ions [3].

Parameter	Cl <sup>-</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>
Raw seawater (mg L <sup>-1</sup> )	20169.31	10792.11	359.70	1256.37	283.54
Treated seawater (mg L <sup>-1</sup> )	12997.57	10706.92	292.58	131.47	267.36
Sludge (%)	2.03	1.96	0.10	22.26	0.11

precipitation, i.e. 11.3 [3], while there is no significant change in turbidity removal at pH between 9 and 9.5, at which calcium carbonate is easily precipitated [3].

The magnesium hydroxide produced in *Reaction* (20) remains in the aqueous stream as a gelatinous suspension, which could remove the pollutants from seawater either by complexation or by electrostatic attraction. The mechanism [3] can be described as follows.

1. The double electronic shell compression of magnesium ion decreased the ZP of pollutant, leading to coagulation.
2. The hydrophobicity of pollutant increases steeply as  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  is adsorbed on the surface, which is the resulting product of reaction between magnesium ion and water molecular, leading to a improvement in flocculation.
3. The structure of the magnesium hydroxide precipitate provides a large adsorptive surface area and a positive electrostatic surface charge, which enables the precipitate to act as a powerful and efficient coagulant with the action of charge neutralisation and sweep coagulation [3].

The concentrations of main ions in raw seawater in the resulting sludge and in electrochemically pretreated seawater (under operating conditions of CD 39.45 mA cm<sup>-2</sup> and time 35 min) are shown in Table 5. The concentrations of Na<sup>+</sup>, Ca<sup>2+</sup>, and K<sup>+</sup> have no significant changes before and after electrochemical pretreatment, while the concentration of Mg<sup>2+</sup> decreased from 1256.37 to 131.47 mg L<sup>-1</sup>, and the mass fraction of Mg<sup>2+</sup> in sludge is much higher than any other cation. This also confirms that magnesium hydroxide represents a main role in seawater purification [3].

It is evident that the concentration of chloride decreased after electrochemical process, as shown in Table 5. The products in *Reactions* (18) and (19) may decompose organic macromolecule through their strong oxidation. The high energy of the particulate suspension resulted adsorption of the contaminants, breaking of emulsions and aggregation of the destabilised phases to form flocs [3].

The hydrogen produced from *Reaction* (15) may remove the dissolved organics or any suspended materials by flotation [3].

Yi *et al.* [3] concluded the following.

The one-step EM demonstrated in this communication is a simple and new effective method for pretreatment of seawater RO system. Raw seawater with a turbidity of 54.1 NTU, 94.48 mg L<sup>-1</sup> SS after electrochemical pretreatment at 26.30 mA cm<sup>-2</sup> CD for 40 min reduces the turbidity to 1.00 NTU. The time taken for the same depletion of turbidity in case of 39.45 mA cm<sup>-2</sup> CD is 35 min, and the absorbance of the curve decreases when electrochemical treatment is applied. The experimental results revealed that particular size in seawater agglomerate and get bigger after electrochemical treatment, and the turbidity removal is enhanced by charge neutralisation and sweep coagulation. The sludge generated from the process is found to have larger specific surface areas at higher CD from SEM observation, leading to better treatment efficiency [3].

## 5. Why electrocoagulation as seawater pretreatment process?

### 5.1. Seawater pollutants need electric field action

Seawater reverse osmosis (SWRO) desalination [9, 39] is being increasingly emphasised as a strategy for conservation of limited resources of freshwater. Although desalination [40–42] has been developed for the last few decades, the SWRO operation is still affected by membrane fouling [43]. The membrane fouling of SWRO has a significant impact on operation of desalination plants. The SWRO foulants consist of (1) biofouling (48%), (2) inorganic colloids (18%), (3) organic compounds (15%), (4) silicites/silicates (13%), (5) mineral deposits (6%) and (6) coagulants (5%) [9, 44]. Organic compounds in seawater consist of particulate organic matter (POM > 0.45 μm) and dissolved organic matter (DOM < 0.45 μm) [45]. The concentration of the organic matter (OM) in seawater is relatively low (about 1–3 mg/L) and consequently the portion of organic foulant is small in comparison with inorganic constituents. However, seawater organic matter (SWOM) is a more difficult problem to be solved in the SWRO as it leads to biofouling [9].

Due to its SWRO foulants (consisting of biofouling, inorganic colloids, organic compounds, silicites/silicates and mineral deposits) [9], EC as seawater pretreatment

process is proved [3,25] efficient to remove such seawater components. This efficiency may be attributed to the applied electric field in seawater which is highly rich in ions (i.e. dissolved salts, salinity  $\sim 35 \text{ g L}^{-1}$ ). Moreover, the electrode polarity, i.e. anode (+) and cathode (-), plays a great role in the electrostatic (due to ionic charges) and electrodynamic (when mechanical agitation is introduced) separation process. Thus the generated ionic mobility increases the collisions between the sea water components and the produced metal species when dissolved anode is used, i.e.  $\text{Al}^{3+}/\text{Fe}^{2+}$  which acts by charge neutralisation and sweep coagulation when  $\text{Al}(\text{OH})_{3(s)}/\text{Fe}(\text{OH})_{2(s)}$  are later formed [3,15].

### 5.2. Replacement of traditional water treatment methods

On one hand [32], traditional methods of water treatment such as coagulation, flocculation, sedimentation and filtration are being replaced by membrane processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and RO [46–51]. The membrane processes are economical, relatively less chemical intensive, and environmentally friendlier than traditional methods [32]. However, membrane fouling is a major impediment in successful use of membrane process for water treatment. On the other hand, EC process is proved efficient in water treatment [13] substituting traditional methods of water treatment (especially coagulation, flocculation, sedimentation). Consequently, EC process may be kept in mind as a promising seawater pretreatment method.

### 5.3. Disinfection by-products in desalination systems

When chemical disinfection [28] is applied before or after desalination systems, compounds may be formed that pose potential risks to the health of human and aquatic organisms or impact aesthetic quality of drinking water. The formation and speciation of disinfection by-products (DBPs) in desalination systems is affected by the elevated concentrations of bromide and iodide in seawater and desalinated product water. To gain insight into DBPs likely to be formed in desalination systems, DBP studies conducted in saline source waters, coastal power stations and existing desalination systems are reviewed [28]. Chlorination is the most common disinfectant used in current desalination systems, with chloramines and chlorine dioxide gaining more popularity for disinfection of desalinated water. When seawater or RO permeate is chlorinated, bromoform ( $\text{CHBr}_3$ ) and brominated haloacetic acids (e.g. monobromoacetic acid, dibromoacetic acid, bromochloroacetic acid) are found to be the prevalent DBP species. Under conditions typically encountered in desalination systems, concentrations of these DBPs in the product drinking water

are below levels of concern set by regulating agencies. Less information is available on the formation of other haloorganic DBPs in desalination plants. Among DBPs identified in saline drinking waters, haloacetonitriles (HANs), mutagen X compounds (MX), halonitromethanes (HNMs) and cyanogens bromide (CNBr) pose potential concerns, especially when desalinated waters are blended with organic-matter rich source waters [28].

To substitute chlorination in water treatment and wastewater purification, several electrochemical processes [13] have been successfully studied. However, there is formation of chlorine ( $\text{Cl}_{2(g)}$ ) in some conditions: *Reaction (3)* (see *Section 2* of the work of Sanfan and Qinlai) which concerns  $\text{Cl}^-$  transformation to  $\text{Cl}_{2(g)}$  is electrochemically minimised but *Reaction (16)* (see *Section 4* of the Work of Yi et al. (2009)) which also concern  $\text{Cl}^-$  transformation to  $\text{Cl}_{2(g)}$  is not electrochemically minimised due to the use of a no 'sacrificial' anode (DSA).

### 5.4. From flotation to electrocoagulation

In desalination plants design [24,52–54], various techniques have been proposed for pretreatment, even other membranes such as UF. Nevertheless, may be among the more conventional belongs nowadays flotation (usually, in its dissolved-air option for bubbles generation), followed by filtration and preceded by screening. Flotation constitutes a high rate, effective and familiar separation process for oil, grease and suspended solids, like the algae. In potable water treatment, the process chain of flocculation–flotation–filtration is rather a common concept. The paper of Peleka and Matis [24] presents a review of this interesting area with focus on sustainable development. Furthermore, flotation is an induced phenomenon in EC process:  $\text{H}_{2(g)}$  production from cathode and  $\text{O}_{2(g)}$  from anode (in some conditions) especially one the electrodes are horizontally placed in the electrochemical device. This electrochemical characteristic may be counted as a supplementary advantage of EC as seawater pretreatment process.

### 5.5. From coagulation to enhanced coagulation in seawater pretreatment

Ma et al. (2007) studied the pretreatment with enhanced coagulation (EnC) and a UF membrane for seawater desalination with RO [11]. The application of RO for desalination process has increased rapidly with the construction of large RO plants. Although there have been considerable improvements in membrane materials and operation experience, the fouling of membranes is a significant problem up to the present. There have been many instances of fouling of RO membranes caused by the presence of iron and silica. Biomineralisation is



usually believed to be caused by microorganisms metabolising at iron and silica present. Its formation process was studied and described first [11], then the EnC with Fe(VI) and UF membrane treatment process for pretreatment of RO for desalination has been investigated in a laboratory for 3–4 months. The main aim is to reduce the feed water pollution, such as turbidity, iron, silica and algae, microbial contamination in order to control biofouling and mineralisation on the membrane surface. The results showed that the biomineralisation formation process is the adsorption of organism and the biosorption of inorganics onto the organic matrix. The pretreatment results show that turbidity is less than 0.5 NTU, iron concentration never exceeds  $0.2 \text{ mg L}^{-1}$ , silicon concentration must not exceed  $0.1 \text{ mg L}^{-1}$ , and the removal rate of algae and microbial is more than 98%, thus the biomineralisation formation is avoided [11].

What is interesting to note here with this paper [11], is the fact that the concept of EnC is transferred from water treatment to seawater pretreatment [55] due to the importance of EnC in dissolved OM removing as explained in our paper [15] in which we also explain EnC as a link between coagulation and EC in the concept of natural OM removal.

#### 5.6. Electrocoagulation: a new approach for the removal of boron

The World's Health Organisation (WHO) has established that high levels of boron [56] in drinking water have detrimental effects on human reproduction and has set as a general recommendation a limit of  $0.5 \text{ mg L}^{-1}$  of boron (as B) in drinking water [57]. Boron has also been found to be toxic for certain crops, notably citrus plants, when present in irrigation water at levels greater than  $0.3\text{--}0.5 \text{ mg L}^{-1}$ .

Whilst RO is very efficient to reject most of the salts present in sea or brackish water, its rejection of boric acid is poor under standard conditions. Seawater contains an average of  $5 \text{ mg L}^{-1}$  of boron present as boric acid [57], but ranges from  $0.5$  to  $9.6 \text{ mg L}^{-1}$  [58]. It is well known that boron compounds in seawater do not dissociate into ions at low or natural pH [58]. The membranes available presently for seawater desalination remove only 60–80% of the boron in the first pass. This means that the first pass permeate contains between 1 and  $2 \text{ mg L}^{-1}$  of boron, depending on the water temperature and membrane conditions [57].

Using EC as a new method to treat boron containing effluent/wastes has been studied by Xu *et al.* [22]. With combined mechanisms of adsorption and precipitation, the EC is very effective to remove boron; 82% of boron from model waters ( $[\text{B}]_0 = 250\text{--}500 \text{ mg L}^{-1}$ ) can be removed at a current density of  $62.1 \text{ A m}^{-2}$  (equivalent

to 3.3 as molar ratio of Al:B). In the treatment of industrial effluents, the EC can effectively remove boron and arsenic simultaneously, the [As] was reduced from 15 to  $<0.1 \text{ mg L}^{-1}$ . A multistage EC configuration was even more effective and the boron removal percentage was  $>99.9\%$ , i.e., after the fifth stage EC treatment, boron concentration can be decreased from  $500 \text{ mg L}^{-1}$  to less than  $0.5 \text{ mg L}^{-1}$ . Chemical adsorption with freshly formed  $\text{Al}(\text{OH})_3$  flocs played a dominant role in the removal of boron from the wastes. Pre-pH adjustment was not necessary with the EC in the treating of low pH wastes, whilst all other technologies need to raise the solution pH to neutral status [22].

Xu *et al.* [22] concluded that the advantages of using the EC for the treating of boron containing effluent/wastes have been confirmed by their study but this needs a validation through a pilot- or full-scale trial [22].

As a perspective, EC may be optimised to remove boron and play its fundamental role as pretreatment process – even [22] if a multistage EC configuration was more effective.

## 6. Pretreatment perspectives

In the past, conventional pretreatment (i.e., coagulation, flocculation, acid treatment, pH adjustment, addition of anti-scalant and mediafiltration) was usually used [48]. The main problem in using conventional pretreatment is corrosion and corrosion products. For example, in the acid dosing system, corrosion of metallic surfaces and corrosion products will roughen the surface of the equipment, which provides active sites for precipitation of more scale deposits [59–61]. In addition, this pretreatment is known to be complex, labour intensive and space consuming [62].

The last years have seen significant advancements [63] in pretreatment including improvements in conventional ones [64–68] practiced for long. The number of pretreatment options [69] available to treat the raw water is many-fold. With the advent of membrane technology, there can be marked improvement in the design and operation philosophy making retrofit and operation simplified [55, 70]. An overview of Table 6 indicates that it is feasible to combine UF/MF with RO, which is a well-established technique for water desalination and re-use in the Middle-Eastern States. The emerging UF technique holds greater hopes for the pretreatment, providing a filtrate quality that is free of suspended solids and microorganisms [55,71].

Finally, as recent EC developments, new published papers [72–73] in *Desalination* open a great pretreatment perspective concerning the industrial application of EC as seawater pretreatment process.

Table 6  
Comparison of conventional and MF/UF pretreatment [55].

	Conventional pretreatment	MF/UF pretreatment	Benefits
Capital costs	Cost competitive with MF/UF	Slightly higher than conventional pretreatment. Costs continue to decline as developments are made.	Capital costs of MF/UF could be 0–25% higher, whereas life cycle costs using either of the treatment schemes are comparable.
Foot print	Calls for larger foot print.	Significantly smaller footprint.	Foot print of MF/UF could be 30–50% of conventional filters.
Energy requirements	Less than MF/UF as it could be gravity flow.	Higher than conventional.	MF/UF requires pumping of water through the membranes. This can vary depending on the type of membrane and water quality.
Chemical costs	High due to coagulant and process chemicals needed for optimisation.	Chemical use low, dependent on raw water quality.	Less chemicals.
RO capital cost	Higher than MF/UF since RO operates at lower flux.	Higher flux is logically possible resulting in lower capital cost.	Due to lower SDI values, RO can be operated at 20% higher flux if feasible, reducing RO capital costs.
RO operating costs	Higher costs as fouling potential of RO feed water is high resulting in higher operating pressure. One experiences frequent cleaning of RO membranes.	Lower RO operating costs are expected due to less fouling potential and longer membrane life.	The NDP (net driving pressure) is likely to be lower if the feed water is pretreated by MF/UF. Membrane cleaning frequency is reduced by 10–100%, reducing system downtime and prolonged element life.

## 7. Conclusions

This paper concerns a brief description of the application of EC as a new seawater pretreatment process throughout the work of Sanfan and Qinlai (1987) until the work of Yi *et al.* (2009) via the work of Sanfan (1991); all of them are published in *Desalination*. The main conclusions from this review are as follows.

1. It was feasible that the EC device was used for pretreatment of brackish water before the desalination by ED or RO. As it can reduce hardness and alkalinity in raw water meanwhile, it can remove opacity and various heavy metals ions, it would be disappear or reduce the deposition and scale in ED or RO. The major mechanism of removing some ions from the brackish using EC method was: firstly, it can turn some ions round flocs into precipitation a adsorbed by aluminium and/or iron hydroxide polymer then it can be removed with floccules, lastly, the carrying charges flocs will directly adsorb the ions and colloids with opposite charges. The electric CD was the most important operation parameter [25].
2. The work of Sanfan (1991) is the continuation of the work of Sanfan and Qinlai (1987). It concerned more studies on economic property of pretreatment process of brackish water using EC method. Sanfan (1991) concluded that: the Fe is used to instead of Al as electrode of EC for pretreatment of brackish water is feasible. At the same percentage reduction, it can greatly reduce the cost of pretreatment. The mechanism of removing ions by EC is that the suiTable condition is formed round flocs and  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and some ions change into hard dissolution chemical compounds at there, then they are adsorbed by hydroxide polymer of iron and/or aluminium and removed by ways of sedimentation and filtration. The key to using Fe electrode is aeration for raw water. It can oxidise  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and form floc having property of adsorption. In all of processes, the Fe electrode and aerating for raw water combine with reusing flocs is best in technical and economic [26].
3. Yi *et al.* [3] concluded that the one-step EM demonstrated in this communication is a simple and

new effective method for pretreatment of seawater RO system. Raw seawater with a turbidity of 54.1 NTU, 94.48 mg L<sup>-1</sup> SS after electrochemical pretreatment at 26.30 mA cm<sup>-2</sup> CD for 40 min reduces the turbidity to 1.00 NTU. The time taken for the same depletion of turbidity in case of 39.45 mA cm<sup>-2</sup> CD is 35 min, and the absorbance of the curve decreases when electrochemical treatment is applied. The experimental results revealed that particular size in seawater agglomerate and get bigger after electrochemical treatment, and the turbidity removal is enhanced by charge neutralisation and sweep coagulation. The sludge generated from the process is found to have larger specific surface areas at higher CD from SEM observation, leading to better treatment efficiency [3].

4. The generated ionic mobility increases the collisions between the sea water components and the produced metal species when dissolved anode is used, i.e. Al<sup>3+</sup>/Fe<sup>2+</sup> which acts by charge neutralisation and sweep coagulation when Al(OH)<sub>3(s)</sub>/Fe(OH)<sub>2(s)</sub> are later formed [3, 15].
5. EC process is proved efficient in water treatment [13] substituting traditional methods of water treatment (especially coagulation, flocculation, sedimentation). Consequently, EC process may be kept in mind as a promising seawater pretreatment method.
6. The concept of EnC is transferred from water treatment to seawater pretreatment [55] due to the importance of EnC in dissolved OM removing as explained in our paper [15] in which we also explain EnC as a link between coagulation and EC in the concept of natural OM removal.
7. The interesting question which maybe asked is: "how many times that seawater would be re-circulated in EC device to be desalinated? In other words, is it possible that EC process could be a treatment process more than a pretreatment process?

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