Hardness Removal from Drinking Water Using Electrochemical Cell

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ABSTRACT

In this work, the removal of hardness was studied from tap water taken from Aljadriya municipal water network-Baghdad. A parallel plate electrochemical cell was constructed using two graphite electrodes as anode, and three aluminum electrodes as cathodes. The electrodes were connected to a power supply that provides direct electrical current to the cell. Results showed that a removal efficiency of 85% can be obtained at pH of 7.5and electrical voltage of 28.5 volt with retention time of 60 minutes. The high efficiency for hardness removal suggested that the electrochemical technique might be used as an alternative technique for hardness removal.

Keywords: aluminum electrodes; electrochemical; graphite electrodes and water hardness

إزالة العسرة من مياه الشرب باستخدام التقنية الكهروكيميائية

الخلاصة

في هذا البحث تم دراسة إزالة عسرة الماء من عينة مأخوذة من ماء الإسالة في منطقة الجادرية في بغداد. تم بناء خلية كهروكيميائية باستخدام أقطاب من مادة الكرافيت كقطب موجب(المصعد)، وثلاثة أقطاب من مادة الألمنيومك قطب سالب(المهبط). وتم ربط الأقطاب بشكل أحادي إلى مصدر تيار مستمر. الهدف هو دراسة كفاءة التقنية المذكورة في إزالة عسرة الماء تحت ظروف مختلفة. أظهرت نتائج البحث انه يمكن الوصول إلى كفاءة 85% عند الأس الهيدروجيني 7.5 وجهد كهربائي 28.5 فولت مع زمن استبقاء الماء لمدة 60 دقيقة. بينت نتائج البحث أمكانية استخدام التقنية الكهروكيميائية كطريقة فعالة لإزالة عسرة الماء.

INTERDUCATION

Hard water is water of high mineral content specifically calcium and magnesium. Hard water is not a health risk, but a nuisance because of mineral build-up on fixtures and poor soap and detergent performance in addition to industrial risks. Fresh water from almost all sources contains some level dissolved minerals in

the form of positively and negatively charged ions. Common positively charged ions include calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium (Na^{+1}), and potassium (K^{+1}). Common negatively charged ions include chloride (Cl^{-1}), sulfate (SO_4^{-2}), and bicarbonate (HCO_3^{-1}). These species dissolve in water as rain interacts with the Earth's surface and subsurface over long periods of time. Various physicochemical techniques for removing metal ions from water supplies include chemical precipitation, adsorption, ion exchange, extraction and membrane processes are employed. WHO Recommendation for drinking water's hardness is based on maximum 500 mg/l calcium carbonate [1]. Of different technologies which need adding chemicals for water softening, are chemical precipitation and ion exchange and those which do not need to add chemicals; include reverse osmosis, electrodialysis, nanofilteration, crystallization, distillation and evaporation [2, 3, 4, 5, and 6]. These techniques have some problems such as increased sludge, permanent water hardness, water salts like sodium, annual high operation costs, sediment formation on membrane, which require an effluent post treatment and disposal of residual sludge [7, 8, and 9]. Recently, growing demand for high quality water has justified the development of modern and low cost technologies for hard and very hard water softening [2, 3, and 10]. In recent years, the electrochemical precipitation as a new method of desalination of brackish water has been studied and the technical feasibility has been confirmed [11]. Electrochemical scale removal offers many advantages: environmental compatibility, no need to handle and dose chemicals, accessibility to automation and convenient process control [10]. The main difficulty is disposal of the precipitated scale. Most of the deposit adheres to the cathode leading to an increase in electrical resistance. Among of the effective factors on the electrochemical precipitation process is the electrical current. The cost of process is determined pay the consumption of electrode and electrical energy, which is economic due to the main advantages of method [2, 3]. On the other hand the change in the efficiency is related to the changes of these two parameters the electrical energy and the electrodes consumption. The aim of this study is to investigate the capability of electrochemical process in removal of water hardness as an alternative technique and the effect of experimental parameters such as electrical potential, contact time, electrode spacing and the consumption of electric power.

Principle of The Electrocamical Scaling

Many brackish water sources contain alkaline scale forming ions which are prone to precipitate $CaCO_3$ and $Mg(OH)_2$. Although the possibility of electrochemical scale removal has long been recognized, industrial application of this technique is rather limited and technical information in the literature is scant. Electrolytic scale removal is based on the generation of a high pH environment around the cathode by the following cathodic reactions [11]:

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^{-1} \qquad\qquad ....(1)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^{-1} \qquad\qquad .... (2)$$

The high alkaline environment acts to convert the HCO_3^- ion into the CO_3^{-2} form. The ensuing high super saturation level of $CaCO_3$ promotes its precipitation:

$$OH^{-1} + HCO_3^{-1} \longrightarrow CO_3^{-2} + H_2O \qquad \qquad ….(3)$$

$$Ca^{+2} + CO_3^{-2} \longrightarrow CaCO_3 \downarrow \qquad \qquad ….(4)$$

The high pH conditions also promote precipitation of magnesium hydroxide:

$$Mg^{+2} + 2OH^{-1} \longrightarrow Mg(OH)_2 \downarrow \qquad \qquad ….(5)$$

In the conventional equipment currently used for hardness reduction in the water is in contact with both the cathode and the anode electrodes. The cathode performs two functions: it generates alkalinity and serves as a scale deposition surface. There is no medium separating the cathodic and anodic environments. High pH conditions prevail only in a thin boundary layer near the cathodic surface while the bulk of the water is at the feed pH level. Consequently, the precipitation reaction occurs only in the water film adjacent to the cathodic surface. Periodic removal of the scale accumulating on the cathode is essential, the performance of electrolytic scale removal installations. Recent publications [12, 13] indicate a revived interest in the study of electrochemical precipitation of $CaCO_3$.

Materials and Methods
  The study was conducted by using a electrolytic cell (Fig. 1) with two graphite electrodes as anode, and three commercial aluminum electrodes as cathode with dimensions of 100×100 mm (Fig. 2), the distance between anode & cathode used in industry was 5-30 mm, [14, 15] in this study was used 10 mm and 40 mm apart from each other. The reactor was an acrylic tank, with a capacity of approximately 2.5 liters. The dimensions were 15 cm in length, 15 cm in height and a 15 cm width. The cell connected to a D.C. power supply (alternative to direct current converter) fitted with a voltage regulator. The two Electrodes of graphite were connected as monopolar and the cathode was connected as monopolar.
  Hardness rate was measured using EDTA Titrimetric method based on techniques mentioned in [1]. Removal rates of the hardness were calculated by the following Eq. (6):[7].

$$R = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \ (\%) \qquad \qquad …. (6)$$

Where
R (%) is the removal rate of hardness, C_{in} (ppm) is the feed concentration, and C_{out} (ppm) the effluent concentration.
 Water samples were used from tap water of Baghdad location; Al-jaderea, the total

hardness and Alkalinity of the water were respectively 330 and 144 mg/L, as calcium carbonate.

5 ml samples were drawn at different time intervals of 10, 20, 30, 40, 50 and 60 minute's then total hardness and alkalinity were measured. Many variables were investigated for its effect on the hardness removal efficiency from tap water such as, electrical potentials that ranged from 10 to 28.5 volt, and retention time ranged from 10 to 60 minutes and electrode spacing from 1 to 4 cm were investigated.
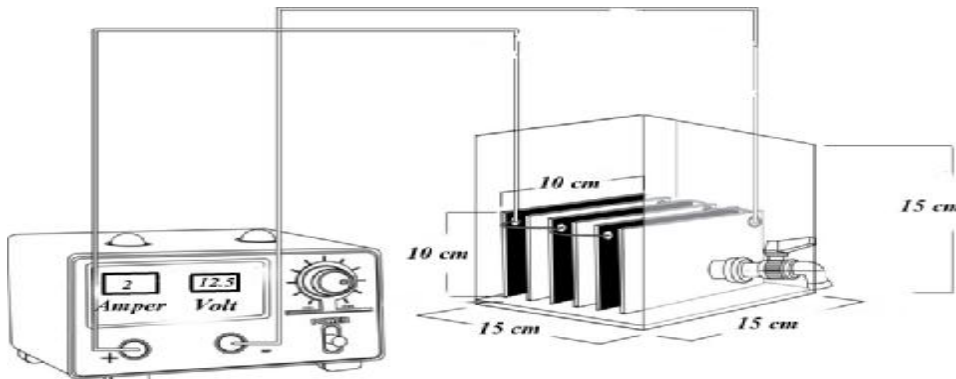
Figure (1) Schematic diagram of electrolytic cell
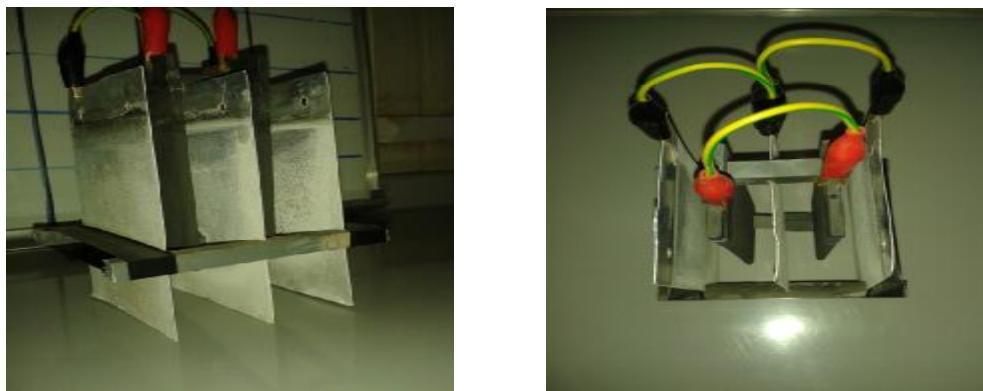
Figure (2) photography of two graphite electrodes as anode, and three commercial aluminum electrodes as cathode

Results and Discussion
Effect of applied voltage and time intervals:
Experiments were performed at five different voltages: 10, 12.5, 17, 21.5 and 28.5 V. The maximum voltage of 28.5V was assumed as optimum voltage throughout this study,

because the high current density increased the energy consumptions and that increased operational costs. On the other hand the nature and concentration of electrolyte, pH value and the concentration of pollutants in water also affect the oxidation process, if the concentration of electrolyte is high, the conductivity of water was also high and then the lower cell voltage for a given current density could be used to reduce energy consumption and cost [16].

Fig. (3), shows that the percentage removal of total hardness has been increased by increasing in retention time and increase in applied voltage. The highest removal efficiency was 85% that achieved in electrical potential of 28.5V and time interval of 60 minutes. An initial pH of 7.5-8 (process tends towards neutral pH under all conditions).

The degree of hardness acceptable for finished water varies with the consumer or industry served. According to the (AWWA) [1] established a water quality goal for total hardness of 80 to 100 mg/l as calcium carbonate. Table (1) shows a classification of water hardness; it has often been proposed that ideally water should have a total hardness of 75 to 85 mg/l (as $CaCO_3$). In this study, results indicate that the total hardness was carried out 50 ppm with 5 amp. and 28.5 volt.

Table(1) Classification of water hardness [1]

Water situation	Hardness mg/L as CaCO3
Soft	0 to75
Moderate	75 to 150
Hard	150 to 300
Very Hard	Above 300

These results can be explained by the fact that, increasing current density will increase the density of bubbles while their size decreases the flotation efficiency increases. It is also observed that the aggregation of the induced flocs, while increasing hydrogen evolution. Since the effective surface and retention time of larger bubbles are less comparing to small ones and this leads to an increase in the efficiency of hardness removal. And consequently the size of bubbles, with decrease of electrical current, the required time for achieving similar efficiencies increases. These findings are in line with the results of [17], which is a study in relation to arsenic removal by electro coagulation method.
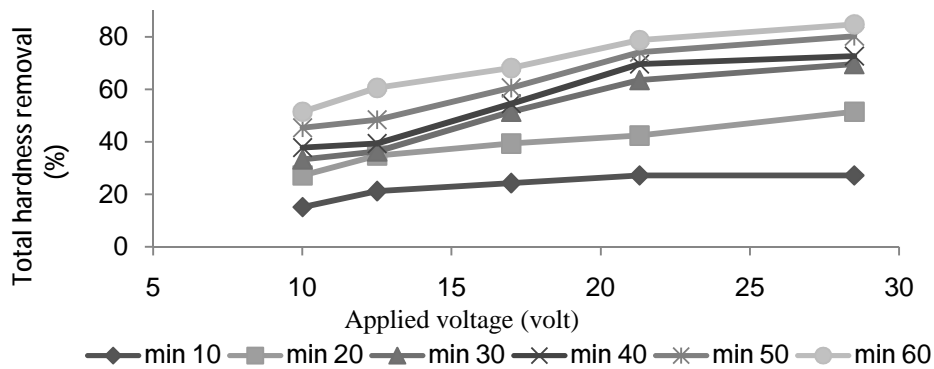
Figure (3) .Effect of applied voltage on the removal efficiency of total hardness at different operating times

As shown in Fig. (4), the concentration of hardness in the case of constant potential difference and pH, are decreased by increasing the retention time. This is because the cathodically evolved H_2 bubbles float that cause removal of hardness particles, according to the reactions in alkali conditions eq. (1), H_2 moves upward and causes flotation.

Increasing the operation time from 10 to 60 min, applied voltage of 10 V resulted in a decrease in total hardness from 330 mg/l to 210 mg/l. It is also observed when the applied voltages of 28.5V reduce total hardness from 330 mg/l to 50 mg/l. In addition that at higher concentrations of total hardness (330 mg/l) the removal rate approximately reaches maximum value at certain period approximately 60 minutes, applied voltage of 28.5V.

The results show that most of the hardness are removed in the first 60 min of process and this is also found by [18] in their studies on Cr^{+6} removal by electro coagulation process.
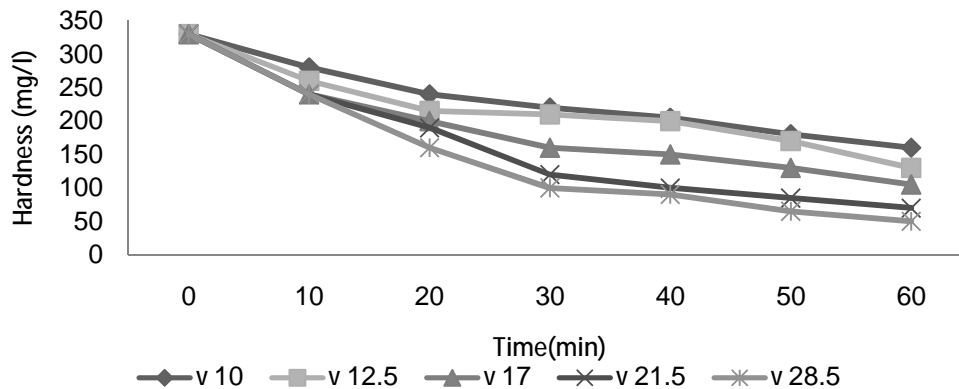

Figure (4) Effect of retention time on the total hardness removal at constant potential difference

Effect of electric power consumption:

Energy consumption and sacrificial electrodes are very important economical parameters in EC process. The electric power consumption of the process is calculated per m^3 of the waste solution using the equation that [19]:

$$E_{EC} = UIt_{EC} / V \qquad\qquad \dots (6)$$

Where

E_{EC} is the specific power consumption (kW.h/m^3). U is the cell voltage in volt (V), I is the current in ampere (A), t_{EC} is the time of electrochemical Processes in hour (h) and V is the solution volume in cubic meter (m^3). The time of operation is increased from 10 to 60 min. As shown in Fig. (5), it is clear that increasing the current density will increase the power consumption and percentage removal efficiency.

The increase in power consumption can be ascribed to the increased polarization on the two electrodes by increasing the current density [20].

To throw some light on the role of current density in the economy of the process the ratio (% removal efficiency/power consumption) is plotted versus applied voltages as shown in Fig. (6), the results show that the ratio dramatically decreased from 12.9 to 1.5 by increasing the applied voltage from 10 to 28.5 volt with time of operation at 60 min, which suggests that the economy of the process is favored by low current densities.
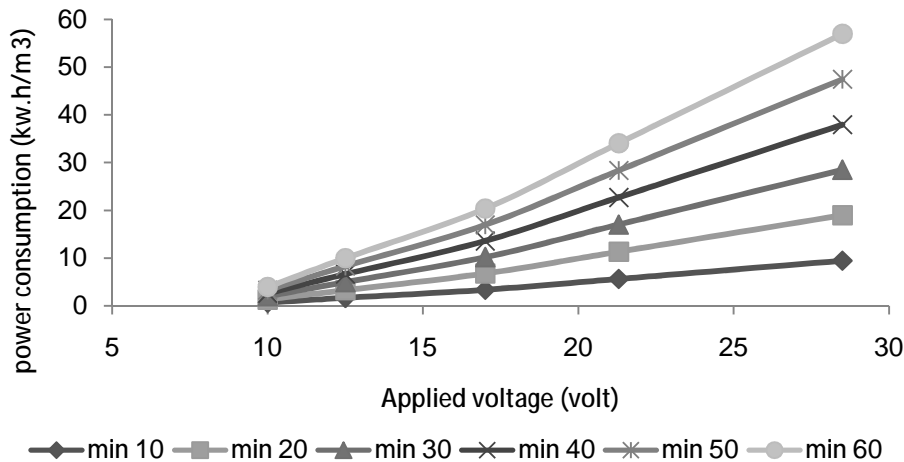
Figure (5) .Energy consumption vs applied voltage at different Operating times
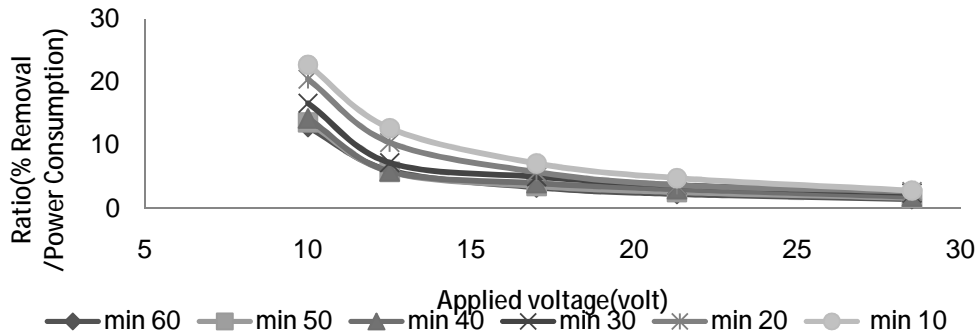
Figure(6) Ratio (% Removal efficiency/power consumption) vs applied voltage at different operating times

Effect of Electrode Spacing:

   Different electrode spacing or inter-electrode distances resulted in significant differences in removal efficiencies. The highest removal efficiency was observed at 2 cm inter-electrode distance Fig. (7)**.** There was no significant change in pH for different electrode spacing. Removal efficiencies varied from 85% at a distance of 2 cm to 50% at 4 cm. These results were similar to those observed in various other studies where the optimum inter-electrode distances were found to be 2 cm for removal of lead and 2.5 cm for removal of cadmium and copper in studies with laminate steel electrodes [21].

   In parametric studies with distillery wastewater [22] and biodigester effluent [23], the optimum electrode spacing was found to be 1 cm. Another parametric study for removal of arsenic and chromium found the optimum electrode spacing to be 1.4 cm [24]. Kumar et al. [25] found that 2 cm was optimum for removal of COD (chemical oxygen demand) from biodigester effluent.
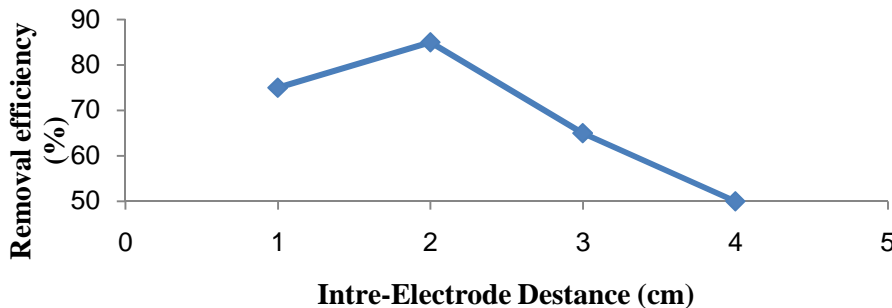

Figure (7) Total Removal efficiencies with different inter-electrode distances

Effect of pH and temperature on the removal efficiency:

   pH and temperature affects mostly indirect oxidation processes. It is no clear, how pH affects the efficiency of oxidation [16, 26]. As mentioned above, our study assumes that the process tends towards neutral pH (7.5-8) under all conditions.

As shown in Fig. (8), experiments were carried out at three different temperatures 25, 35 and 40°C. It was observed that the rise of temperature had some effect in the increasing of the efficiency. The results show in Fig. (8) had consistence with Pretreatment of Brackish Water Using DC-Electro coagulation **-** reported in the literature [27].
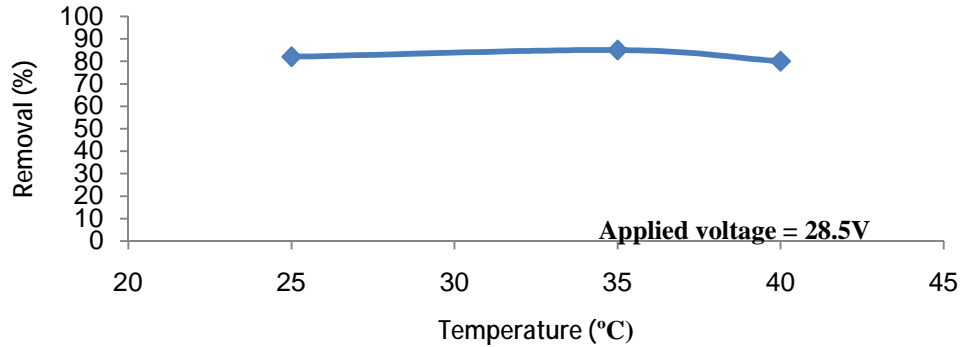
Figure(8) Effect of temperature on the removal efficiency

Comparison of observed and other previous studies:

Table (2) summarizes literature hardness removed by electrochemical and electro coagulation in water sources.

Table (2)Comparison of observed and other previous studies

Reference	Pollutants	Current or current density	Cell voltage (V)	Electrode materials, electrode Connections	Treatment efficiency (%)	Mode
Malakootian. M. and N.Yousefi, [26]	Tap water		20 V	Al/Al plate	80.6%	Continuous
Daneshvar et al., [27]	Brackish water hardness	22 A/m^2		Fe/Fe plate	90%	Continuous
Agostinho et al. [28]	Tap water	36 A	12V	Steel/Al	80%	Batch
Sanfan and Qinlai [29]	Brackish water:hardness, SO4_, Cl_	2–30 A/m^2	1.3–3.6	Al/Fe plate	60–80	Continuous
Gnusin et al. [30]	Natural water	10–500 A/m^2		Steel/Al - Monopolar		Continuous
Daneshvar et al. [31]	Brackish water	1–22 A/m^2	1.1–3.1	Al/Fe plate	40–76	Continuous
Daneshvar et al. [32]	Brackish water:hardness, SO4_, Cl_	22 A/m^2		Fe and steel plate	40–90	Continuous
Present study	Tap water		28.5 V	Graphite/Al plate	85%	Batch

CONCLUSIONS

A series of experiments was performed in order to find the effects of operating parameters for hardness removal from tap water by electrochemical cell of a batch operation. Hardness removal was affected by current density, time intervals, distance between electrodes and some effect of temperature.

Five experiments were conducted and removal efficiencies increased from 52% to 85% as applied voltages were increased from 10 to 28.5 Volts, at different operating times, the best conditions for hardness removal found in this study were an electrical current of 28.5 V, an initial pH of 7.5-8 (the process tends towards neutral pH under all conditions.), and 2 cm distance of electrodes an electrolysis time of 60 minutes resulting in hardness removal maximum efficiency of 85% was observed . Under these conditions, the energy consumption was 0.057 kWh/l. Thus, it was demonstrated that the process may be used as pretreatment method for removing hardness from water.

The results of the present study and other related studies show that electrochemical process in comparison to other techniques has some important advantages such as simple equipments, convenient operation, decrease or no need for using chemical matters, rapid sedimentation of produced flocs and less sludge production.

On the other hand it seems that electrochemical process cannot be applied for removal of water hardness in large water treatment plants, because in the electrooxidation technology, the focus of research should be on the reduction of operational cost and energy consumption and the development of efficient and stable electrode materials. High energy consumption and high operational costs can be the limiting factor in the further full-scale application. More pilot scale studies and practical large-scale studies are required.

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