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Separation of zinc ions from synthetically prepared brackish water using electrodialysis: effect of operating parameters

Ammar Fadel[b], Ridha Lafi[a], Anissa Aouni[a], Amor Hafiane[a,*], Saci Nacef[b]

[a]*Water and Membrane Technologies Laboratory, CERTE, Borj Cédria, Tunisia, Tel. +216 79 325 750; emails: ridha.lafi@yahoo.fr (R. Lafi), aouninoussa@hotmail.com (A. Aouni), Tel. +216 79 325 750; Fax: +216 325 802; email: amor.hafiane@certe.rnrt.tn (A. Hafiane)*

[b]*Laboratoire de Génie des Procédés Chimiques (LGPC), Department of Chemical Engineering, Ferhat Abbas University, Setif 1, Algeria, Tel. +213 780413600; email: ammfad@yahoo.fr (A. Fadel), Tel. +213 550473190; email: Nacef_s@yahoo.fr (S. Nacef)*

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ABSTRACT

The removal of zinc(II) at low concentrations from an aqueous saline solution was investigated using a five-compartment electrodialysis cell. In this work, the effect of key operating parameters such as initial zinc ions concentration, solution pH, applied voltage, and feed flow rate on process efficiency was studied. The separation performance was evaluated in terms of mass transfer, energy consumption, and current efficiency. The results showed that increasing the initial concentration of Zn(II) and applied voltage improves the cell performance. However, separation performance decreases with an increase in the flow rate. It was also found that specific power consumptions (SPC) are strongly dependant on ionic strength as the increase of ionic strength leads to an increase of the solution conductivity. Zinc removal rate and SPC were virtually constant and increased sharply when pH values ranged in the alkaline region.

Keywords: Electrodialysis; Zinc removal; Salted water

1. Introduction

Industrial activities such as mining, mineral processing, and extractive metallurgy of zinc, lead, and cadmium ores, steel production, coal burning, and waste incineration are the main causes for zinc to pollute the environment. Zinc is one of the most important heavy metal contaminants of surface and ground water despite the fact that trace amounts are considered as an essential element for life, acting as a micronutrient [1]. Free zinc ion in solution is highly harmful to plants and invertebrates. Trace amounts of free zinc ions can cause heavy damage to the environment and even kill some organisms. Excessive intake of zinc can promote deficiency in other dietary minerals [2,3]. The World Health Organization recommends the maximum acceptable concentration of zinc in drinking water as 3 mg/L [4]. Therefore, it is necessary to remove these hazardous metal ions from liquid wastes at least to a limit accepted by national and international regulatory agencies before their discharge into the environment [5].

The conventional methods of treatment of zinc from contaminated water include precipitation, ion exchange, membrane separation, solvent extraction, etc. [6,7]. These techniques were found not to be efficient

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*Corresponding author.

due to either being extremely expensive or inefficient to reduce zinc ions from saline water [8–10].

Today, electrodialysis is playing an increasingly important role in separating, concentrating, and recycling heavy metal ions. Electrodialysis (ED) is a membrane process for the separation of ions across charged membranes from one solution to another using an electric field as the driving force. This process has been widely used for the production of drinking and process water from brackish water and seawater, treatment of industrial effluents, recovery of useful materials from effluents, and salt production [11]. It is a technology that is well suited for pollution prevention. It accomplishes this task with low levels of pollution generation and high energy efficiencies relative to current technologies [12].

Literature survey concerning the treatment of water containing heavy metals by electrodialysis shows that in most cases the effluents treated contain high concentrations of metal ions, whereas the studies dealing with low metal concentrations effluent are scarce. Since heavy metals are toxic even at low levels in aqueous solutions, they pose a threat to the water quality of aquifers that receive them. The objective of this work is to investigate the removal of ionic zinc at low concentrations in the range of 2.5–10 mg/L, from salted aqueous solutions. Electrodialysis separation of zinc was studied as a function of main physico-chemical parameters such as flow rates, applied voltage, initial feed concentration, solution pH, and ionic strength.

2. Materials and methods

2.1. Chemicals

All chemicals used are of analytical reagent grade and were used as received. $ZnCl_2$ (7646-85-7), NaCl (7647-14-5), NaOH (1310-73-2), and HCl (7647-01-0) were supplied by Sigma-Aldrich. The different Zn(II) solutions were prepared by dissolving the reagents in distilled water.

2.2. Membranes

In the electrodialysis setup, three cation-exchange membranes and two anion-exchange membranes (AEM) were placed between an anode and a cathode. The flow channel width between two membranes was 0.5 mm. The charged groups were sulfonated copolymers at the cation-exchange membrane and quaternary ammonium groups at the anion-exchange membrane. The surface area of each membrane corresponded to approximately 64 cm^2. The characteristics of these membranes, according to the manufacturer, are listed in Table 1.

2.3. Electrodialysis experiments

The experiments were carried out using an electrodialysis cell supplied by PCA (Polymer Chimie Altmeier GmbH) and PCCell GmbH, Heusweiler (Germany). The ED setup consists of a feed tank, where Zn(II) solution is stored, of three centrifugal pumps ($p = 84$ W) equipped each with a flow meter and three valves to control feed flow rate in the four compartments of ED cell which are separated from each other through ion-exchange membranes.

A schematic view of an ED cell is presented in Fig. 1 [13].

As the electrical power is applied to the stack while electrolyte streams flow through the stack, cations travel in the direction of electrical field and pass through the cation-exchange membranes, but are repulsed upon the AEM. Likewise, anions moving in the opposite direction pass through the AEM, but are repulsed upon the cation-exchange membranes. As a result of this phenomenon, there are two streams: the dilute stream which is increasingly depleted of electrolytes and the concentrate stream which is increasingly enriched with electrolytes. The electrodialysis system was operated in a continuous mode (Fig. 2).

During the experimental, the volume of dilute, concentrate, and the electrode rinse solution was equal to 2 L. The same solution was used as the initial concentrate and dilute. Before each experiment, the pH value of the solution was adjusted with dilute HCl or NaOH. Flow rates of the dilute and the concentrate streams were measured by flow meters. The flow rate of the electrode rinse solution was fixed at 80 L/h for all experiments. Total voltage drop in the membrane stack as well as on the electrodes was measured.

After the completion of each experiment, cleaning solutions of 0.1 mol/L Na_2S0_4 and distilled water were circulated through the ED cell for 30 min in order to remove any deposits.

2.4. Analytical methods

The pH solution was determined by means of a digitally calibrated pH meter type 654 Metrohm AG, Switzerland, equipped with a glass electrode. The conductivity was measured by a conductometer type 712 Metrohm AG. The concentration of zinc in the aqueous solution was estimated using atomic absorption spectroscopy (AAS vario6 spectrometer), operated

Table 1
PCA standard cation and AEM characteristics

Membrane	Thickness (μm)	Ion exchange capacity (meq g^{-1})	Chemical stability (pH)	Permselectivity	Functional groups	Surface potential (Ω cm^2)
PC-SK	130	≈1	0–11	>0.93	$-SO_3^-$	0.75–3
PC-SA	90–130	≈1.5	0–9	>0.96	$-NR_4^+$	1–1.5

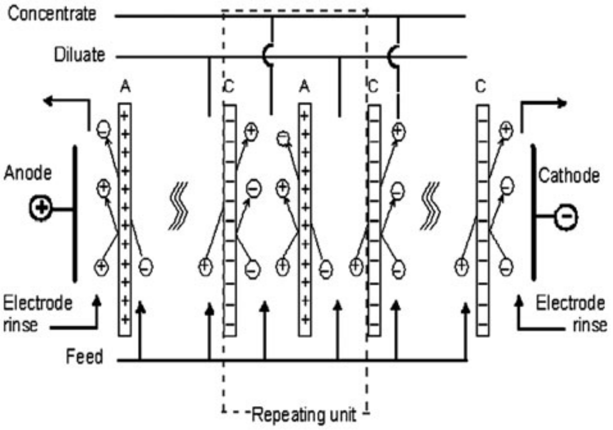

Fig. 1. A schematic view of an ED cell.

with an air-acetylene flame and equipped with a zinc hollow cathode lamp.

2.5. Data analysis

The electrodialysis performance was evaluated in terms of five parameters, namely the demineralization rate (DR), the removal of zinc (*R*), the flux (*J*), the specific power consumptions (SPC), and the current efficiency (CE).

The DR reflects the amount of total salt removed. It can be calculated from conductivity values using the following equation [14–16]:

$$\mathrm{DR}\ (\%) = 100\left(1 - \frac{EC_t}{EC_0}\right) \tag{1}$$

where EC_0 and EC_t (μS/cm) are the conductivity of the dilute solution before and after treatment, respectively.

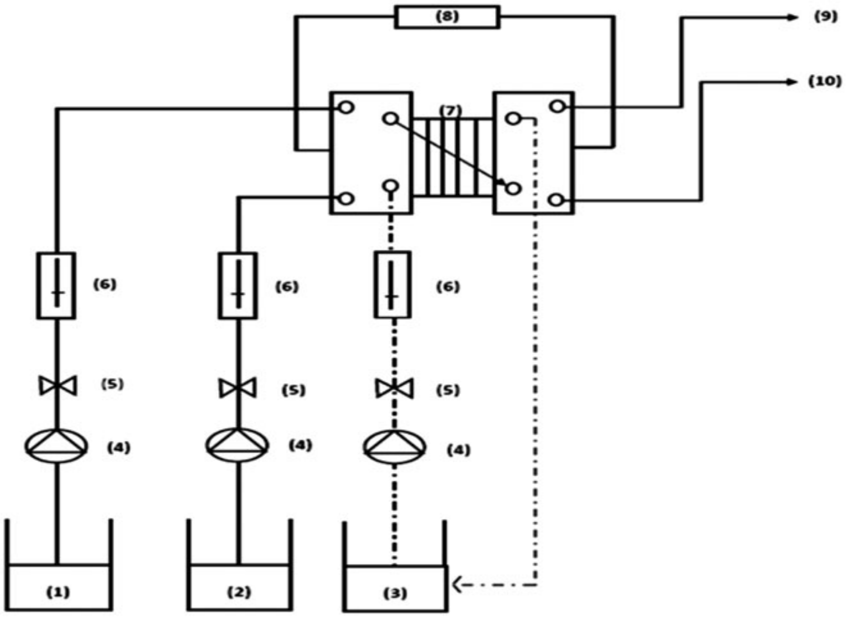

Fig. 2. A simplified diagram of the ED setup working in the continuous mode.
Notes: (1) The tank of rinsing solution, (2) The tank of solution that to be treated, (3) The tank of concentrated solution, (4) Pump, (5) valve, (6) Flow meter, (7) Electrodealysis cell, (8) DC generator, (9) Diluted solution, and (10) Concentrated solution.

The removal of zinc was defined as:

$$R(\mathrm{Zn})\ \% = 100\left(1 - \frac{C_t}{C_0}\right) \tag{2}$$

where C_t (mol/L) is the zinc concentration in the dilute compartment and C_0 (mol/L) is the initial concentration of zinc in the feed.

The flux value was evaluated in order to compare the zinc transport from feed to receiver phase. It was determined by using the following equation [17,18]:

$$J\,(\mathrm{mol/cm^2\,s}) = \left(\frac{V}{A}\right)\left(\frac{\Delta C}{T}\right) \tag{3}$$

where V (L) is the volume of receiver phase, A (cm^2) is the effective membrane area, ΔC (mol/L) is the transported amount of zinc at time t, and T (s) is the period time.

SPC can be described as the energy needed to treat unit volume of solution. It was calculated using the following equation [19]:

$$\mathrm{SPC} = \frac{E\int_0^t I(t)\,dt}{V} \tag{4}$$

where E (V) is the applied potential, I (A) is the applied current, V (L) is the dilute stream volume, and t (s) is the time.

The CE is a measure of how effective ions are transported across the ion-exchange membranes for a given applied current. It is defined as the fraction of coulombs utilized for the salt removal and may be calculated using the following equation [20]:

$$\mathrm{CE} = \frac{FzQ(C_0 - C_t)}{NI} \tag{5}$$

where C_0 and C_t (mol/m^3) are feed and dilute concentrations, respectively, z is the charge of ion, F is the Faraday constant (96,485 A s/mol), Q is the dilute flow rate (m^3/s), N is the number of cell pairs (two in this study), and I (A) is the current.

3. Results and discussion

3.1. Effect of initial Zn(II) concentration

The effect of initial zinc concentration on the separation performance was investigated using different zinc concentrations (2.5, 5, 7.5, and 10 mg/L) keeping the NaCl concentration, the pH, and the flow rate constant at 0.05 mol/L, 3, and 10 L/h, respectively. Three voltages (3, 9, and 15 V) were applied across the entire assembly.

As shown in Fig. 3(a) the DR decreased slightly with the increase in the initial zinc concentration. This is linked to the little increase in total conductivity of feed solution. Fig. 3(b) shows that zinc removal rate R (Zn) is strongly dependant on the feed solution. For instance, the removal of zinc, at $E = 9$ V, increased from 62 to 82% with the increase in initial zinc concentration from 2.5 to 10 mg/L. This increase of the separation performance is related to the presence of a sufficient quantity of ions near the membrane surface [21].

The increase in initial zinc concentration induces an increase in the zinc transport flux (Fig. 3(c)) but it doesn't have an effect on the SPC (Fig. 3(d)). These results can be explained by competitive transfer that appears between zinc ions and sodium ions. The CE (Fig. 3(e)) increased when the initial zinc concentration increased, owing to the increase in the number of ions crossing the membrane from the dilute to the concentrated solution with time.

3.2. Effect of applied voltage

The effect of applied voltage on the retention of zinc by electrodialysis was studied at ionic strength, pH, and flow rate of feed solution fixed at 0.05 mol/L, 3, and 10 L/h, respectively. According to Fig. 4(a), the DR increases with the increase of the applied voltage. We observe different regions in the obtained curve. In the first part ($E \le 5$ V), the DR increases only slightly with increasing voltage value. In this voltage range, there are a few transports of ions between the dilute and concentrate compartments. In this region, low ionic fluxes are obtained (Fig. 4(c)) due the evolution of the resistance of electrodialysis stack. From the variation of SPC in this same region, we observe that the resistance of the stack is relatively high and the applied voltage is not high enough to overcome the resistance of membranes and to induce the transports of several ions.

In the second part (5 V $\le E \le$ 15 V), Fig. 4(a) shows a linear increase of the DR with the applied voltage. It can be observed that the increase in the applied voltage increases the rate of ion transfer through the membranes. The amount of ions transported through the membrane is proportional to the electrical field, which represents the driving force responsible for the transfer of the ions through the ED stack. Indeed, the

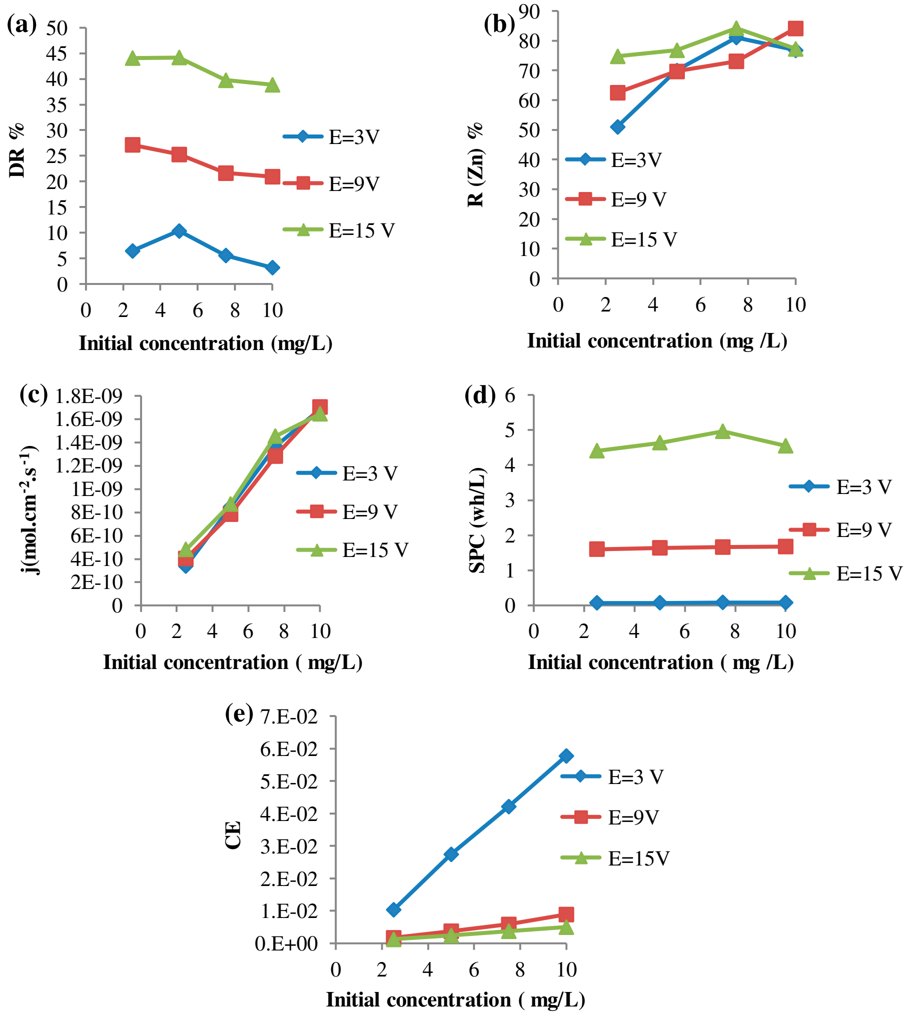

Fig. 3. Effect of initial zinc concentration on: (a) DR, (b) the zinc removal *R* (Zn), (c) zinc flux *J* (Zn), (d) SPC, and (e) CE. (Ionic strength 0.05 M, pH 3, flow rate 10 L/h).

inset of Fig. 4(c) shows that the metal flux through the ion-exchange membranes significantly increased when increasing the applied voltage.

In the third part ($E \geq 15$ V), the evolution of DR with the applied voltage is less important. At this stage, there is no increase in the current density and the limiting current density is reached.

The rate of zinc removal shown in Fig. 4(b) increases from 57 to 99% with an increase in the applied voltage from 1 to 15 V. Also, the SPC according to Fig. 4(d) increases with an increase in the applied voltage. This is obvious as the SPC depends on the applied voltage and the current. The CE decreases with increasing applied voltage (Fig. 4(e)), which means that the induced current is not merely used for the transport of zinc ions.

3.3. Effect of flow rate

The flow rate of dilute compartment varied from 4 to 10 L/h keeping constant the ionic strength, the pH, and the zinc concentration of feed solution at 0.05 mol/L, 3, and 5 mg/L, respectively. Experiments were performed by applying three voltages: 3, 9, and 15 V. As shown in Fig. 5(a) and (b), the DR and zinc removal rate decreases with an increase in the flow rate. This can be explained by the remaining time of ions inside the compartments of the cell. When the flow rate is high, ions do not have enough time to be transferred between compartments [22]. From Fig. 5(c) the flux of zinc J_{Zn} increases with an increase in the feed flow rates. This may be related to the decrease in the thickness

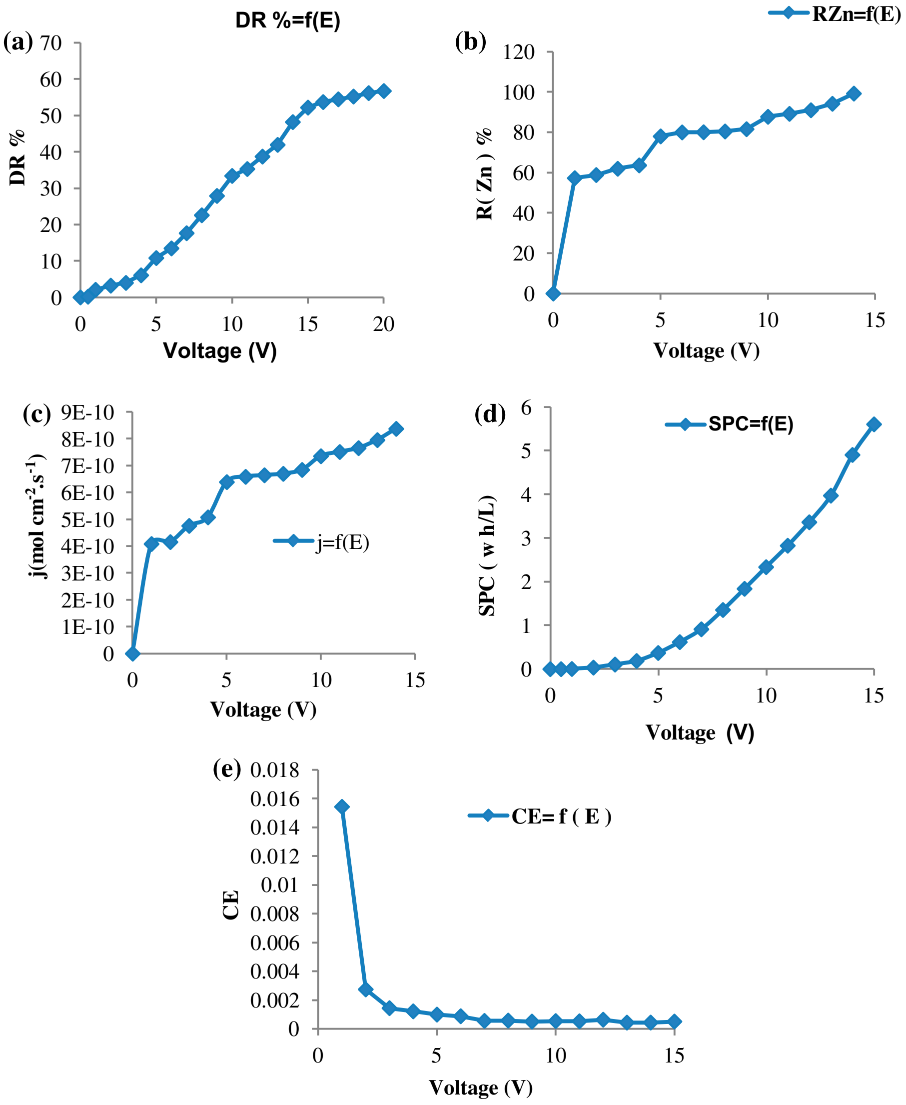

Fig. 4. Effect of applied voltage on: (a) DR, (b) zinc removal *R* (Zn), (c) zinc flux *J* (Zn), (d) SPC, and (e) CE. (Ionic strength 0.05 M, pH 3, flow rate 10L/h).

of boundary layers adjacent to the membrane surfaces with increasing solution velocity.

The results also show that at high flow rates (or low residence times), separation almost stopped. This is because when the feed velocity is high, ions do not have enough time to be separated. As illustrated in Fig. 5(d), the SPC depends also on this parameter and SPC is higher for low flow rate. Thus, medium flow rates are recommended to get better separation and power consumption. Fig. 5(e) shows that the CE increases with an increase in the feed flow rates. The induced current is used for the transport of zinc ions.

3.4. Effect of pH

The zinc removal rate and SPC were studied at different pH values, ranging from 2.81 to 10.95 keeping ionic strength, initial zinc concentration, and flow rate, constant. From Fig. 6(a) zinc retention rate is almost constant in the pH range between 2 and 8 and thereafter increases. This is mainly due to the change of Zn speciation with pH value. Quantitatively at low pH, Zn^{2+} is the dominant specie, while at alkaline pH Zn is essentially in a precipitate form $Zn(OH)_2$. The increase in Zn removal observed is related to the elimination of a quantity of Zn by precipitation. An accumulation of zinc hydroxides at the surface of

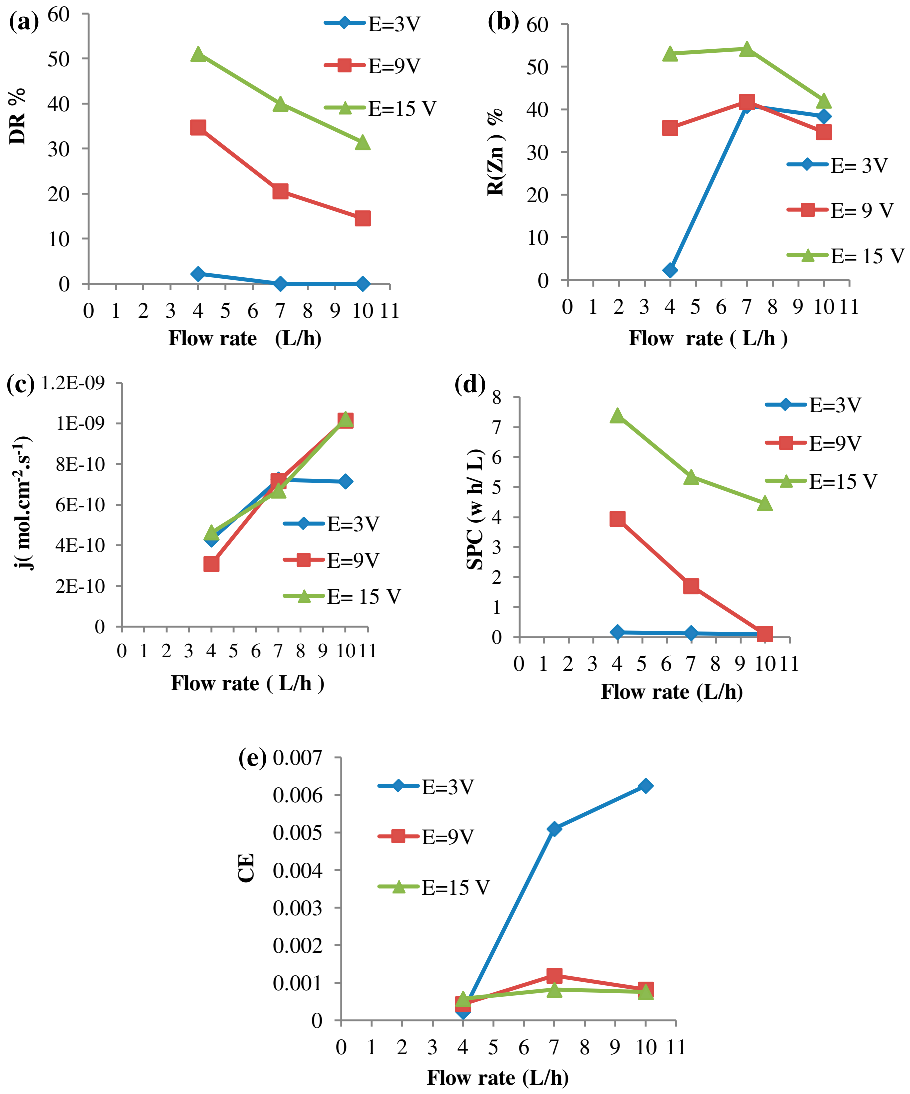

Fig. 5. Effect of the flow rate on: (a) DR, (b) the zinc removal *R* (Zn), (c) zinc flux *J* (Zn), (d) SPC, and (e) CE. (Ionic strength 0.05 M, pH 3, zinc concentration = 5 mg/L).

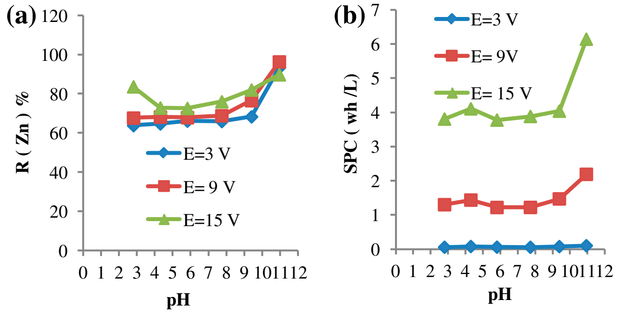

Fig. 6. Effect of the pH of the feed solution on: (a) zinc removal rate and (b) SPC. (Ionic strength 0.05 M, zinc concentration = 5 mg/L, flow rate 10 L/h).

membrane may occur which affects the process efficiency and increases the power consumption.

3.5. Effect of ionic strength

The effect of the ionic strength on the removal of zinc was investigated by adding different amounts of NaCl salt. The initial zinc concentration, the pH, and the flow rate of feed solution were fixed at 5 mg/L, 3, and 10 L/h, respectively. Three voltages 3, 9, and 15 V were applied across the entire assembly.

According to Fig. 7(a), for the two voltages 3 and 9 V, the zinc retention rate increases with the increase in NaCl concentration up to 2 g/L above

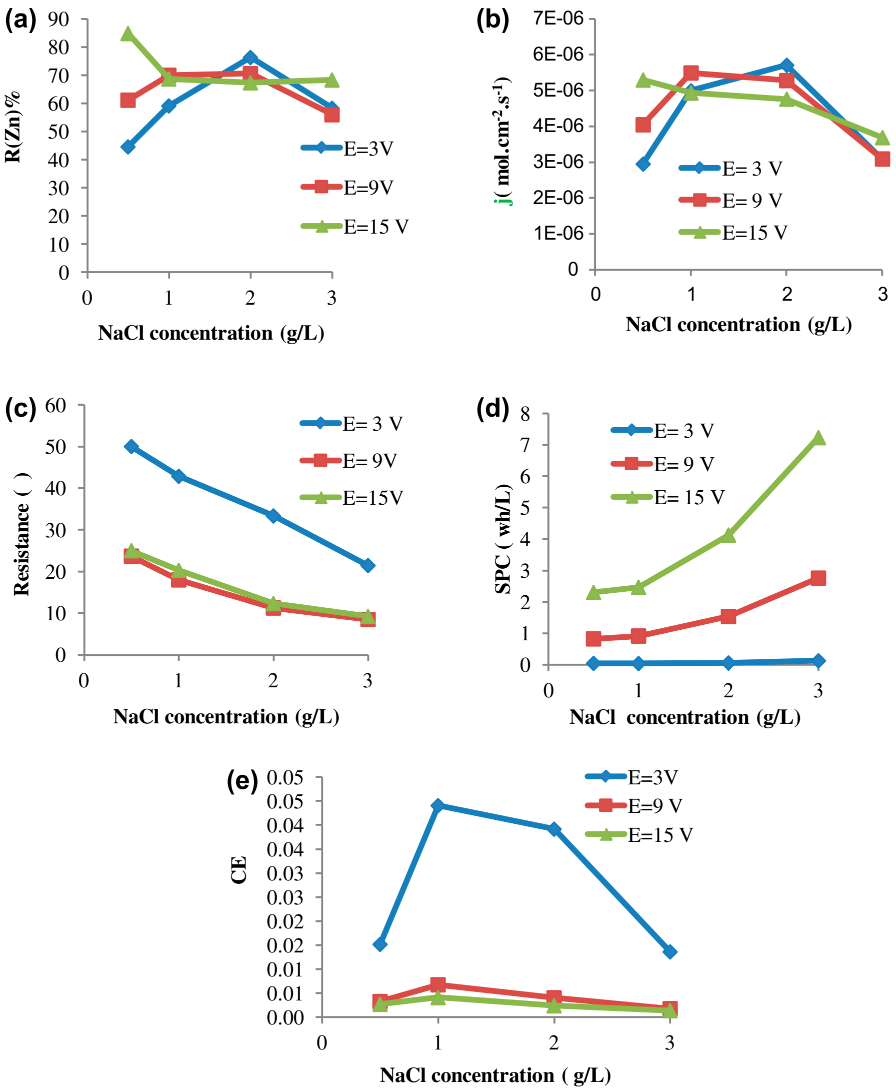

Fig. 7. Effect of the feed solution ionic strength on: (a) the zinc removal, (b) the resistance *R*, (c) zinc flux *J* (Zn), (d) SPC, and (e) CE. (pH 3, initial zinc concentration = 5 mg/L, flow rate 10L/h).

which it decreases sharply when ionic strength exceeds 3.5 g/L. When the applied potential is 15 V, retention rate decreases first and then remains constant. This can be related to the variation of the resistance of electrodialysis stack ($R = E/I$) as a function of the applied voltage and the current (Fig. 7(c)). The evolution of flux of Zn with ionic strength follows almost the same trend as *R* (Zn). As shown in Fig. 7(d), the SPC is also strongly dependant on ionic strength. In fact, the increase in ionic strength leads to an increase in the conductivity of the solution. As a consequence, the electric current and then the SPC increased. The CE shown in Fig. 7(e) decreases with an increase in the ionic strength. This can be related to the decrease in the amount of zinc transferred to the concentrated compartment. At the same time, the current quantity supplied to the system increases with an increase in the conductivity.

4. Conclusion

In the present work, separation of low concentrations of zinc ions from a model salted water solution was investigated using a laboratory-scale ED cell. Demineralization, zinc retention rate, CE, and SPC were examined as a function of key operating parameters. It was found that the applied voltage, the feed flow rate, the pH, the initial zinc concentration, and ionic strength have a significant effect on the process efficiency and mainly on the zinc transfer from the dilute to the concentrate compartment. As a result, higher voltage and lower flow rates were recommended to modify the performance of ED cell. In addition, the results confirmed that an increase in the initial concentration leads to the increase in the zinc removal and the maximum zinc removal was obtained for 7.5 mg/L.

The SPC parameter decreases with an increase in the feed flow rates and depending on ionic strength, the increase in ionic strength leads to an increase in the solution conductivity. As consequence, the electric current induced and then the SPC is higher. In a pH range of 2–8, the zinc removal rate and the SPC were constant and increased sharply when the pH exceeded 8.

Symbols

EC_0 — conductivity of the dilute before treatment, (expressed in μS/cm)
EC_t — conductivity of the dilute after treatment, (expressed in μS/cm)
DR — demineralization rate
C_0 — initial concentration of zinc in the feed phase (mol/L)
R (Zn) — removal rate of zinc
V — volume of receiver phase (L)
A — effective membrane area (cm^2)
ΔC — transported amount of zinc at a time (mol/L)
Δt — period time (s)
J (Zn) — zinc transport flux
SPC — specific power consumptions
CE — current efficiency
E — applied potential
I — applied current
z — charge of ion
F — Faraday constant (96,485 A s/mol)
Q_f — dilute flow rate (m^3/s)
N — number of cell pairs (2 in this study) and I is the current (A)

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