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Improvement of cadmium ion electrochemical removal from dilute aqueous solutions by application of multi-stage electrolysis

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Abstract Improvement of cadmium ion electrochemical removal from dilute aqueous solutions in a spouted bed reactor was investigated. Enlargement of cathode surface area from 1,000 to 1,500 cm² resulted in a decrease of nearly 30 % in both of the process time and the specific energy consumption. Application of a three-stage electrolysis process for a solution containing initial concentration of 270 ppm cadmium ion, resulted in the removal of 99.9 % cadmium ion in 135 min with the specific energy consumption of 2.29 kWh/kg, 23 % less than the value of a single-stage process. For a solution with cadmium ion initial concentration of 180 ppm, 99.9 % of cadmium ion was removed in 135.5 min by application of a two-stage electrolysis process, while the specific energy consumption was 2.82 kWh/kg, 30 % less than that of a single-stage process. For a solution with cadmium ion initial concentration of 90 ppm, 99.5 % of cadmium ion was removed in 100.2 min with the specific energy consumption of 3.78 kWh/kg in a single-stage electrolysis process.

Keywords Spouted bed electrode · Multi-stage electrolysis · Cadmium ion · Dilute aqueous solutions

Introduction

Metal ions are one of the most toxic and non-biodegradable hazardous species released into water bodies (Abdel-Salam 2013; Gupta et al. 2010). Therefore, the efficient treatment of wastewater containing metal ions is crucial as it can cause serious environmental problems that will affect the natural ecosystems. Exposure to heavy metal ions such as cadmium, lead, copper, and zinc, even at very low levels, is believed to pose a risk to living organisms (Singh et al. 2013). There are various techniques currently used for the efficient removal of heavy metal ions from wastewater, such as adsorption (Gupta et al. 2011; Ossman and Mansour 2013), chemical precipitation (Fu et al. 2012), membrane filtration (Hofman and Pietrzak 2013), ion exchange (Ismail et al. 2013), chemical reduction (Naggar et al. 2012) and electrochemical technologies (Liu et al. 2013; Segundo et al. 2012).

Electrochemical treatment of wastewater containing metal ions is a relatively simple and clean methodology that is attractive due to little sludge production, high selectivity exhibition and low operating costs (Su et al. 2009); hence, it has been an interest for several years, and many researchers have tried to overcome the limitations of the process (Dutra et al. 2008; Körbahti et al. 2011; Melnyk and Goncharuk 2009). This process is limited by several steps (Scott 1995):

- Metal ion mass transfer to the electrode surface.
- Charge transfer to the electrode surface.
- Electrochemical reaction over the electrode surface.

In order to improve the electrochemical removal process, it is necessary to enhance mass and charge transfer rates as well as electrochemical reaction rate. Since the electrochemical reaction occurs over the electrode surface, increase in the electrode surface area can also improve the process.

Three-dimensional electrodes were introduced in order to increase the electrode surface area. Improvement of mass transfer in these electrodes has been studied by several researchers (Hwang and Chun 1999; Shvab et al. 2000a, b). Mass transport phenomenon in three-



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dimensional electrodes is influenced by reactor configuration and hydrodynamics involving fluid superficial velocity, bed porosity, bed height and particles diameter (Pak et al. 2001; Shirvanian et al. 2006).

Increase in liquid superficial velocity causes to increase the mass transfer coefficient in a packed bed state, but excess increase in liquid velocity results in a change in the bed state from the packed bed to a fluidized bed. In the fluidized bed, a rise in the superficial fluid velocity results in the expansion of the bed, i.e., reduction in the concentration of the particles which contributes to reduce the mass transfer coefficient; hence, the highest mass transfer coefficient is approximately achieved in the minimum fluidization velocity (Amin 2011). A spouted bed electrode is an intermediate between the fluidized and the packed bed of particles. In such a bed, only a fraction of the bed particles are in vigorous motion and the rest undergo a slow movement until they find their way to the spout. This arrangement not only provides a high mass transfer rate, but also satisfies a suitable potential distribution (Salas-Morales et al. 1997). For raising the inner particles and forming a stream of them passing through a central core that is assembled within the bed, the jet velocity must be higher than a minimum spouting velocity (Verma et al. 1997). If the jet velocity increases significantly, the bed porosity of central core increases and consequently the mass transfer coefficient decreases; therefore, the highest mass transfer coefficient is achieved approximately in the minimum spouting velocity. Since the minimum spouting velocity is a specified value for a special bed configuration, central duct position, bed height and particles diameter, the mass transfer coefficient can be improved only by optimization of the reactor configuration especially the central duct position for a specified bed height and particles diameter (Baghban and Mehrabani-Zeinabad 2012; Makibar et al. 2012).

Charge transfer to three-dimensional electrode surfaces has simultaneously been improved by the use of the spouted bed electrodes in which a suitable contact of electrode particles and current feeder has been obtained by providing a packed bed zone (Jiricny et al. 2002a, b; Shirvanian and Calo 2005). This process has also been enhanced by Vatistas and Bartolozzi (1990) and Yen and Yao (1991) by the use of three-dimensional current feeders.

Increase in applied electrical current can also intensify the rate of charge transfer to the electrode surface and consequently the electrochemical reaction rate over the electrode surface. But increasing the applied electrical current to more than a limiting value causes the reaction to be controlled by mass transfer phenomenon and the specific energy consumption to increase. In order to avoid a high energy consumption and a low deposition rate, the electrolysis should be exerted at a controlled potential in which the applied electrical current is instantaneously



justified in accordance with the instantaneous limiting current; however, it is not suggested due to unacceptable capital investment of potentiostats and significant decrease in reaction rate for the small amounts of dissolved metals. Application of multi-stage electrolysis, in which the current of each stage is adjusted near but below the instantaneous limiting current, is a simple way to maximize the performance of the reactor (Panizza et al. 2008).

Upon enhancement of charge and metal ion transfer rates to the electrode surface, electrochemical reaction rate must also be improved. Electrochemical reaction over the electrode surface is influenced by the operational parameters including electrolyte concentration, electrolyte initial pH, metal ion initial concentration and applied electrical current density which have been studied or optimized by several researchers (Grimshaw et al. 2011; Kaminari et al. 2007; Rana et al. 2004).

It must be emphasized that the effective hydrodynamic parameters of the designed and constructed spouted bed reactor have been optimized in a published paper in order to minimize the minimum spouting velocity in which the maximum mass transfer coefficient is achieved (Baghban and Mehrabani-Zeinabad 2012). The effective operational parameters which influence the cadmium ion electrochemical removal rate have also been studied and optimized via response surface methodology in the relevant studies. In this paper, the effect of enlargement of the cathode surface area on the improvement of cadmium ion removal process in the spouted bed reactor has been studied. The multi-stage electrolysis process has also been investigated in order to increase the cadmium ion final removal efficiency and decrease the specific energy consumption. This research has been carried out in the chemical engineering department of Isfahan university of Technology (Isfahan, Iran), in 2013.

Materials and methods

The theory of single and multi-stage electrolysis

Single-stage electrolysis

Limiting current is the current in which all of the passing charges through the electrode are consumed for the desired electrochemical reaction. It can be calculated by Eq. 1 which has been derived based on the definition of limiting current and with respect to the material balance over the electrode surface:

$$i_{\rm lim}(t) = -nFAk'_mC(t) \tag{1}$$

in which n, F, A and C(t) are the number of electrons per ion, Faraday constant, electrode surface area and metal ion concentration in the bulk solution, respectively. The coefficient of $k'_{\rm m}$ is the corrected mass transfer coefficient and is obtained by Eq. 2:

$$k'_{\rm m} = \frac{k_{\rm m}}{1 + k_{\rm m}/k_{\rm r}} \tag{2}$$

where $k_{\rm m}$ is the mass transfer coefficient and $k_{\rm r}$ is the reaction rate constant.

Based on similar studies for the electrochemical removal of organic pollutants (Panizza et al. 2008) and the results obtained during analysis of the experimental data for the electrochemical removal of cadmium ion, the following operating regimes are identified for the electrochemical removal of metal ions under galvanostatic conditions:

- $i < i_{\text{lim}}$: The electrolysis is under the current control, and all of the passing charges are consumed for metal ion removal; hence, the instantaneous current efficiency (ICE) is expected to be 100 %, and the metal ion concentration decreases linearly with time. This behavior persists until a critical time (t_{cr}) or to a critical conversion (X_{cr}), corresponding to the time, or conversion, at which the applied current is equal to the limiting current.
- $i > i_{\text{lim}}$: Mass transport and electrochemical reaction control the electrolysis, and metal ion reduction occurs as well as the secondary reactions which results in a decrease in the current efficiency. Under these conditions, the metal ion concentration follows an exponential trend.

For the electrochemical removal of cadmium ion from dilute aqueous solutions in the low initial pH, the hydrogen ions are in intensive competition with cadmium ions; hence, the instantaneous current efficiency of cadmium ion removal is extremely low at the beginning of the test and rapidly increases to 100 % upon the increase in pH. The rapid change in current efficiency is transient and has no significant importance on the overall process; therefore, the variation of current efficiency in this transient time is not investigated. The transient time (t_t) can be estimated based on the intensive variation of catholyte pH which is in accordance with the rapid change in instantaneous current efficiency.

The variation of metal ion concentration in transient time is negligible and can be neglected. The maximum relative error of this assumption for cadmium ion concentration, calculated based on the variation of catholyte pH in transient time, is 2 %.

After transient time, hydrogen ion concentration is extremely low; hence, all of the passing charges are consumed for the electrochemical removal of cadmium ions, and the instantaneous current efficiency remains 100 % until the critical time:

$$ICE = 100 \% \quad t_t < t < t_{cr} \tag{3}$$

Since the instantaneous current efficiency is constant before the critical time, the average current efficiency defined by Eq. 4 is also 100 % in the time interval of $t_{\rm t}$ to $t_{\rm cr}$:

$$CE = mnF/q \tag{4}$$

In Eq. 4, m and q are the moles of deposited metal and total amount of passing charges, respectively (Scott 1995):

The critical time can then be obtained based on the definition of current efficiency in the time interval of t_t to t_{cr} :

$$100\% = \frac{VnF}{i} \frac{C(t_{\rm t}) - C(t_{\rm cr})}{t_{\rm cr} - t_{\rm t}}$$
(5)

in which $C(t_{cr})$ and $C(t_t)$ represent the cadmium ion critical and transient concentrations and can be substituted by the relevant limiting currents from Eq. 1; hence:

$$t_{\rm cr} = t_{\rm t} + \frac{V}{Ak'_m} \frac{i_{\rm lim}(t_{\rm t}) - i_{\rm lim}(t_{\rm cr})}{i}.$$
(6)

Since $C(t_t)$ is assumed to be the same as C(0), $i_{lim}(t_t)$ is also replaced by $i_{lim}(0)$, but a correction factor of k_c is introduced to compensate the effect of the relevant assumptions. Based on the equality of limiting and applied currents at critical time:

$$t_{\rm cr} = t_{\rm t} + k_{\rm c} \frac{V}{Ak'_{\rm m}} \frac{1 - \alpha}{\alpha} \tag{7}$$

where the parameter of α is defined as the ratio of the applied current to the initial limiting current:

$$\alpha = \frac{i}{i_{\lim}^0} \tag{8}$$

Critical conversion is defined as:

$$X_{\rm cr} = 1 - \frac{C(t_{\rm cr})}{C(0)}$$
 (9)

Hence, it can be obtained by substituting $C(t_{cr})$ and C(0) from Eq. 1 and with respect to the equality of limiting and applied currents at critical time:

$$X_{\rm cr} = 1 - \alpha \tag{10}$$

The linear correlation of cadmium ion concentration with time between the transient and the critical time can be described by Eq. 11:

$$C(t) = C_0 \left(1 - \frac{1}{k_c} \frac{\alpha A k'_m}{V} (t - t_t) \right) \quad (t_t < t < t_{cr})$$
(11)

The time in which metal ion conversion exceeds the special value of *X* can also be derived:

$$\tau = t_{\rm t} + k_{\rm c} \frac{XV}{\alpha A k_{\rm m}'} \tag{12}$$



The mass balance over the entire system dictates the equality of the rate of mass dissipation in the overall process and mass consumption during the electrochemical reaction over the electrode surface, i.e.:

$$-V\frac{\mathrm{d}C}{\mathrm{d}t} = k_{\mathrm{r}}AC_{\mathrm{S}}(t) \tag{13}$$

with respect to the mass balance over the electrode surface:

$$-\frac{\mathrm{d}C}{C} = \frac{A}{V}k'_{\mathrm{m}}\mathrm{d}t\tag{14}$$

by integrating this equation in the time interval of t_{cr} to t:

$$C(t) = C_{\rm cr} \exp\left(-\frac{Ak'_{\rm m}}{V}(t - t_{\rm cr})\right)$$
(15)

The time in which the specific conversion of X can be achieved is derived based on Eq. 15:

$$\tau = t_{\rm cr} - \frac{V}{Ak'_{\rm m}} \ln\left(\frac{1-X}{\alpha}\right) \tag{16}$$

Instantaneous current efficiency can be derived by rearranging Eq. 4 for cadmium ion removal in the time interval of Δt and approaching Δt to zero:

$$ICE = -\frac{VnF}{i}\frac{dC(t)}{dt}$$
(17)

Therefore, the instantaneous current efficiency after critical time can be estimated as an exponential function of time:

$$ICE = \exp\left(-\frac{Ak'_{\rm m}}{V}(t - t_{\rm cr})\right)$$
(18)

Multi-stage electrolysis

Multi-stage electrolysis must be applied in such a way that the current remains near but below the instantaneous limiting current, except for the low concentrations of metal ions. In order to apply n current steps, with $i_1 < i_{lim}^0$, the equations obtained for single-stage electrolysis, Eqs. 7 and 10, can be adapted to calculate the required time for each stage to obtain fast electrochemical removal and restricted energy consumption.

For multi-stage electrolysis, the critical time and critical conversion of each stage can be correlated as explained by Eqs. 19 and 20:

$$t_i^{\rm cr} = t_i^t + k_{\rm c,i} \frac{V}{Ak_{\rm m,i}'} \frac{1 - \alpha_i}{\alpha_i}$$
(19)

$$X_i^{\rm cr} = 1 - \prod_{j=1}^i \alpha_j \tag{20}$$

in which $k'_{m,i}$ and $k_{c,i}$ are the corrected mass transfer coefficient and correction factor of each stage. The factor

of $k_{c,i}$ is equal to 1 except for the first stage and is obtained for this stage by fitting the linear part of the model with the experimental data. The parameter of t_i^t is the transient time which is determined for the first stage with respect to the intensive variation of the catholyte pH and is equal to zero for the other stages. The parameter of α_i is also defined as:

$$\alpha_i = \frac{i_i}{i_{\rm lim}^{i-1}} \tag{21}$$

where i_{lim}^{i-1} and i_i are the initial limiting current and applied current of the *i*th stage, respectively. The parameter of i_{lim}^{i-1} is also described by Eq. 22:

$$i_{\rm lim}^{i-1} = nFk'_{m,i}AC_0\left(\prod_{j=1}^{i-1}\alpha_j\right)$$
(22)

The linear correlation of cadmium ion concentration with time is derived for $T_{i-1}^{cr} < t < T_i^{cr}$ based on the derived correlation for single-stage electrolysis:

$$C(t) = C_0 \left(\prod_{j=1}^{i-1} \alpha_j\right) \left(1 - \frac{1}{k_{c,i}} \frac{\alpha_i A k'_{m,i}}{V} (t - T_{i-1}^{cr})\right)$$
(23)

where T_{i-1}^{cr} represents the total time in which the critical conversion of (i - 1)th stage, i.e. X_{i-1}^{cr} , is achieved and can be calculated for i > 1 as follows:

$$T_{i-1}^{\rm cr} = \sum_{j=1}^{i-1} t_j^{\rm cr} = t_1^{\rm tr} + \sum_{j=1}^{i-1} \left[k_{c,i} \frac{V}{Ak'_{\rm m,j}} \frac{1-\alpha_j}{\alpha_j} \right]$$
(24)

and is replaced by t_1^t for the first stage.

The time in which the special conversion of $X_{i-1}^{cr} < X < X_i^{cr}$ is achieved can also be calculated:

$$\tau = T_{i-1}^{\rm cr} + k_{c,i} \frac{V}{Ak'_{\rm m,i}} \left[\frac{X - 1 + \prod_{j=1}^{i-1} \alpha_j}{\prod_{j=1}^{i} \alpha_j} \right]$$
(25)

For $t > T_n^{cr}$ or $X > X_n^{cr}$, the exponential dependence of cadmium ion concentration and instantaneous current efficiency with time can be explained by Eqs. 26 and 27:

$$C(t) = C_0 \left(\prod_{j=1}^n \alpha_j\right) \exp\left[-\frac{Ak'_{\mathrm{m,n}}}{V} \left(t - T_n^{\mathrm{cr}}\right)\right]$$
(26)

$$ICE = \exp\left[-\frac{Ak'_{m,n}}{V}\left(t - T_n^{cr}\right)\right]$$
(27)

The time in which the special conversion of $X > X_n^{cr}$ is achieved can also be calculated by Eq. 28:

$$\tau = T_n^{\rm cr} - \frac{V}{Ak'_{\rm m,n}} \left[\ln \left(\frac{1-X}{\prod_{j=1}^n \alpha_j} \right) \right]$$
(28)





Fig. 1 a Schematic diagram of the system used for the electrochemical removal of cadmium ion, b diagram of the spouted bed reactor (All of the dimensions are in millimeter)

Experimental conditions

Experimental set-up

A set of laboratory-scale tests was carried out in a designed and constructed batch recycled spouted bed reactor system, including a reservoir and a circulating pump for each of the catholyte and anolyte solutions. A schematic diagram of this system is shown in Fig. 1a.

The cell was made of Plexiglas. The effective hydrodynamic parameters of the cell (Fig. 1b), involving catholyte inlet nozzle diameter and central duct height, weight and position were determined based on the values optimized during the previous hydrodynamic studies (Baghban and Mehrabani-Zeinabad 2012). Cut wires of copper, 92.8 % mesh 16-20 and 7.2 % mesh 20-30 were used as cathodic particles, while an aluminum plate containing a draft tube was applied as a current feeder. The applied dimensionally stable anode was a reticulated plate made of ruthenium mixed iridium oxide-coated titanium, a product of Suzhou Borui Industrial Material Science and Technology Company, LTD. The cathodic and anodic compartments were separated by a strong base anion exchange membrane made by Yichi Biotech and Chemical Company, LTD, with a contact area of 138 cm^2 . The membrane was covered by a polypropylene cloth to be maintained from the physical contact of the cathodic particles. The catholyte flow rate was adjusted to 50 cm³/s according to the minimum spouting flow determined through performed hydrodynamic studies. The catholyte circulation allowed continuous feeding of the cathodic compartment with fresh electrolyte as well as maintaining the bed in the spouted state. The total volume of the catholyte was $1,000 \text{ cm}^3$. The anolyte was also circulated in order to not only feed the anodic compartment by fresh electrolyte, but also remove produced oxygen from the anodic compartment. The total anolyte volume was 400 cm³, and the anolyte circulation rate was set to $0.3 \text{ cm}^3/\text{s}$.

The tests were performed in a batch recirculation mode. A DC power supply was used in order to apply constant electrical current during each test.

Procedures

Required solutions were prepared by the use of octahydrate cadmium sulfate (Hopkins Williams Company, with the purity of 98 %), anhydrous sodium sulfate (Sigma-Aldrich company, with the purity of greater than 99.0 %) and distillated water.

Solutions with 90, 180 and 270 ppm of cadmium ion in 0.3 M sodium sulfate with a pH of 4.4 were prepared. The bulk pH of the catholyte was adjusted by the use of sodium hydroxide and sulfuric acid. A solution of 0.5 M sodium sulfate was used as the anolyte in all of the tests.

The constant electrical current density of each stage was applied by adjusting the cell voltage in each test.



In all of the tests, cadmium ion concentration was periodically monitored by the use of an atomic absorption spectrophotometer of Buck Scientific Company (VGP System, model 210). A theoretical model fitted with the experimental cadmium ion concentration data was also determined. Instantaneous current efficiency was also monitored with time based on the adjusted theoretical model.

Specific energy consumption was determined as indicated by Eq. 29 in which M is the molecular mass and E_{cell} is the cell potential (Scott 1995).

SEC =
$$\frac{E_{\text{cell}} \text{it}}{3600M(C_t - C_0)V}$$
 (kWh kg⁻¹) (29)

For multi-stage electrolysis, this correlation was rearranged as explained by Eq. 30.

$$SEC = \frac{\sum_{i} (E_{cell,i} i_{i} t_{i})}{3600M(C_{t} - C_{0})V} \quad (kWh kg^{-1})$$
(30)

Extension of cathode surface

Electrochemical removal of cadmium ion from a solution containing 180 ppm of cadmium ion was studied for the cathodic surface area of 1,000 cm² by applying the electrical current of 130 mA. In order to investigate the effect of cathodic surface area on the cadmium ion electrochemical removal, the cathode surface area was increased from 1,000 to 1,500 cm^2 and the results were compared.

Since the positive effect of increasing the electrode surface area was theoretically predictable, multi-stage electrolysis was applied for the cathodic particles with the total surface area of 1,500 cm².

Application of multi-stage electrolysis

In order to obtain fast electrochemical removal with minimum energy consumption for the solutions with different initial concentrations of cadmium ion, multi-stage electrolysis was theoretically analyzed by investigating the various scenarios of stages number and applied electrical currents. The time and final conversion of each stage, final process time and specific energy consumption were predicted in each scenario based on the developed correlations. Then the best scenario was selected and experienced with respect to the predicted process time and specific energy consumption.

For analysis of the multi-stage electrolysis by the previously described theoretical model, it was necessary to determine the corrected mass transfer coefficient and cell voltage of each stage and also the first stage transient time and correction factor. The corrected mass transfer coefficient of each stage was experimentally obtained by the adjustment of the exponential part of the model with the experimental data for the relevant single-stage process. The cell voltage of each stage was also obtained experimentally based on the results of the single-stage electrolysis. The first stage correction factor was determined by fitting the linear part of the model with the experimental data. The first stage transient time was estimated to be 1 min based on the initial variation of catholyte pH.

The final process time and specific energy consumption of several investigated scenarios were compared for the solution with the cadmium ion initial concentration of 270 ppm. Then the best scenario with three-stage was selected in order to minimize both of the process time and the specific energy consumption simultaneously. The predicted results of the selected scenario are shown in Table 1.

Based on the predicted results, in order to investigate the three-stage electrolysis for the electrochemical treatment of the solution with 270 ppm cadmium ion, the electrical current of 200 mA was applied for 24 min and then the electrical current was adjusted to 130 mA for 6 min, and finally it was reduced to 80 mA.

For the solution with the initial concentration of 180 ppm cadmium ion, a variety of scenarios with different stages number and applied electrical currents were theoretically investigated. Finally, a two-stage scenario was selected. Indeed, application of the three-stage process for this solution was theoretically predicted that it did not significantly affect the specific energy consumption and final process time in comparison with the two-stage process; hence, the scenario with less number of stages was suggested which is more convenient in performance. The predicted results are shown in Table 2. In order to experience these results, an electrical current of 130 mA was applied for 22.5 min and then the electrical current was reduced to 80 mA.

The single-stage electrolysis was predicted to minimize both of the process time and the specific energy consumption simultaneously for the solution with the initial concentration of 90 ppm cadmium ion. The predicted results of this process are shown in Table 3. The singlestage electrolysis for the electrochemical treatment of this solution was experimentally applied by the adjustment of the electrical current to 80 mA.

Application of the two-stage or three-stage electrolysis for the solution with cadmium ion initial concentration of 90 ppm was predicted to decrease the specific energy consumption. However, decrease in the applied electrical current to less than 80 mA in the other stages caused to decrease the reaction rate of the process and increase the process time; hence, the two-stage or three-stage processes were not recommended.



Table 1 Predicted results of three-stage electrolysis for the solution with cadmium ion initial concentration of 270 ppm

j (–)	i_j (mA)	$k'_{\mathrm{m},j}A/V~(\mathrm{min}^{-1})$	$i_{\lim,j}^0$ (mA)	α _j (-)	$X_j^{\rm cr}$ (–)	$C_j^{\rm cr}$ (ppm)	$t_j^{\rm cr}$ (min)	$E_{\text{cell},j}$ (V)	SEC (kWh/kg)
1	200	0.066	509.9	0.392	0.608	105.8	24.0	3.0	
2	130	0.057	172.6	0.753	0.705	79.7	5.8	2.6	
3	80	0.055	125.4	0.638	0.812	50.8	10.3	2.53	
Final	-	_	-	_	0.999	0.27	135.3	-	2.330

Table 2 Predicted results of two-stage electrolysis for the solution with cadmium ion initial concentration of 180 ppm

j (–)	i_j (mA)	$k'_{\mathrm{m},j}A/V~(\mathrm{min}^{-1})$	$i_{\lim,j}^0$ (mA)	α _j (–)	X_j^{cr} (-)	$C_j^{\rm cr}$ (ppm)	$t_j^{\rm cr}$ (min)	$E_{\text{cell},j}$ (V)	SEC (kWh/kg)
1	130	0.057	293.5	0.443	0.557	79.7	22.5	2.6	-
2	80	0.055	125.4	0.638	0.717	50.8	10.3	2.53	
Final	-	-	-	-	0.999	0.18	135.4	-	2.823

Table 3 Predicted results of single-stage electrolysis for the solution with cadmium ion initial concentration of 90 ppm

j (–)	i_j (mA)	$k'_{\mathrm{m},j}A/V~(\mathrm{min}^{-1})$	$i_{\lim,j}^0$ (mA)	α_j (-)	$X_j^{ m cr}$ (–)	$C_j^{\rm cr}$ (ppm)	$t_j^{\rm cr}$ (min)	$E_{\text{cell},j}$ (V)	SEC (kWh/kg)
1	80	0.055	141.6	0.565	0.435	50.9	14.3	2.53	
Final	-	_	-	-	0.995	0.45	100.2	-	3.775



Fig. 2 The effect of increasing the cathode surface area on the electrochemical removal of cadmium ion

Results and discussion

The effect of cathode surface area

The effect of cathodic surface area on the electrochemical removal of cadmium ion from dilute aqueous solutions was investigated by the use of copper cathodic particles with the total surface areas of 1,000 and 1,500 cm². Cadmium ion concentration and instantaneous current efficiency were monitored in each test as shown in Figs. 2, 3. Analysis of the experimental data showed that a rise in the cathode



Fig. 3 The effect of increasing the cathode surface area on the instantaneous current efficiency

surface area did not influence the rate of cadmium ion electrochemical removal before critical time, while resulted in the significant increase in the removal rate after critical time.

Increase in cathode surface area results in an increase in the initial limiting current and consequently a decrease in the parameter of α ; hence, the critical conversion increases as described by Eq. 9. This also causes to enhance the exponential growth constant of cadmium ion concentration and instantaneous current efficiency as explained by Eqs. 15 and 18; but it does not affect the slope of the linear



Table 4 The effect of extension of cathode surface area on the electrochemical removal of cadmium ion

A	i ⁰ _{lim}	$C_{t_{\rm cr}}$	<i>t</i> cr	Ecell	$\frac{k'_m A/V}{(\min^{-1})}$	τ _{99 %}	SEC
(cm ²)	(mA)	(ppm)	(min)	(V)		(min)	(kWh/kg)
1,000	191	122.5	13	2.56	0.037	127	3.953
1,500	289	81	22	2.56	0.056	90	2.801



Fig. 4 Variation of cadmium ion concentration and instantaneous current efficiency with time in the three-stage electrolysis

function of cadmium ion concentration with time, because the parameter of αA appeared in the related equation (Eq. 11) is independent of the electrode surface area.

Extension of the cathode surface also results in an increase in the critical time. Although a rise in the electrode surface area does not influence the parameter of αA , but increases the parameter of $(1 - \alpha)$ which causes to increase the critical time as described by Eq. 7.

Enlargement of the cathode surface area from 1,000 to $1,500 \text{ cm}^2$ resulted in a decrease of approximately 30 % not only in the process time to remove 99 % of cadmium ions, but also in the specific energy consumption, as shown in Table 4.

Multi-stage electrolysis process

The three-stage electrolysis process was applied for the electrochemical removal of cadmium ion from the dilute aqueous solution containing 270 ppm of cadmium ion. Cadmium ion concentration and instantaneous current efficiency were monitored with time, Fig. 4.

Cadmium ion final conversion efficiency of 99.9 % was achieved in only 135 min with the specific energy consumption of 2.29 kWh/kg. This specific energy consumption is about 23 % less than that of the single-stage process applied by the electrical current of 130 mA, i. e., 2.99 kWh/kg for the cadmium ion conversion of 99.9 % in 143 min.





Fig. 5 Variation of cadmium ion concentration and instantaneous current efficiency with time in the two-stage electrolysis



Fig. 6 Variation of cadmium ion concentration and instantaneous current efficiency with time in the single-stage electrolysis

Comparison of the experimental results with the predicted ones confirms the validity of the model generalized for the multi-stage electrolysis of metal ions.

The two-stage electrolysis process was performed for the electrochemical removal of cadmium ion from the solution with the initial concentration of 180 ppm cadmium ion. Cadmium ion concentration and instantaneous current efficiency were monitored with time as shown in Fig. 5.

The experimental results are in good agreement with the theoretical ones obtained based on the developed model. It is also observed that 99.9 % of cadmium ion was removed in only 135.5 min with the specific energy consumption of 2.82 kWh/kg. This specific energy consumption is about 30 % less than the value obtained in the single-stage process by applying the electrical current of 130 mA, i. e., 4.07 kWh/kg for the cadmium ion conversion of 99.9 % in 130 min.

The single-stage electrolysis process was predicted to provide better results for the solution containing 90 ppm of cadmium ion. Cadmium ion concentration and instantaneous current efficiency in this process were monitored as shown in Fig. 6.

Cadmium ion final conversion efficiency of 99.5 % was achieved in 100.2 min, with the specific energy consumption of 3.78 kWh/kg. These results are in good agreement with the predicted theoretical ones shown in Table 3.

Conclusion

Electrochemical removal of cadmium ion from the dilute aqueous solutions was improved by increase in the cathode surface area and application of the multi-stage electrolysis process.

Extension of the cathode surface area caused to increase the cadmium ion electrochemical removal rate and decrease the specific energy consumption. Enlargement of the cathode surface area from 1,000 to 1,500 cm² resulted in the decrease of nearly 30 % in both of the process time and the specific energy consumption.

The three-stage electrolysis process resulted in high cadmium ion removal rate and restricted energy consumption for the solution with the cadmium ion initial concentration of 270 ppm. 99.9 % of cadmium ion was removed in only 135 min, while the specific energy consumption was 2.29 kWh/kg, i.e., significantly lower than the result obtained for the single-stage electrolysis.

Cadmium ion conversion efficiency of 99.9 % was achieved in 135.5 min for the two-stage electrolysis of the solution with the cadmium ion initial concentration of 180 ppm. The specific energy consumption of the process was 2.82 kWh/kg that is significantly lower than the value of the single-stage electrolysis.

The single-stage electrolysis was preferred for the solution with the cadmium ion initial concentration of 90 ppm. The single-stage electrolysis resulted in the removal of 99.5 % of cadmium ion in 100.2 min with the specific energy consumption of 3.78 kWh/kg.

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List of symbols

Variables

Α	Area of electrode (m^2)
С	Reactant concentration in the bulk
	solution (mol/m ³)
Cs	Reactant concentration on electrode
	surface (mol/m ³)
C _{cr}	Critical reactant concentration (mol/m ³)
CE	Current efficiency or current yield (%)
$E_{\rm cell}$	Cell voltage (V)

ent	k _c	Correction factor (–)
	k _m	Mass transfer coefficient (m/min)
	$k'_{\rm m}$	Corrected mass transfer coefficient
		(m/min)
	<i>k</i> _r	Reaction rate constant (m/min)
	т	Moles of deposited metals (moles)
ute	М	Molecular mass (kg/moles)
ode	n	Number of electrons (-)
vsis	q	Total amount of charges passed (C)
	SEC	Specific energy consumption (kWh/kg)
ase	t	Time (min)
and	t _{cr}	Critical time (min)
of	t _t	Transient time (min)
ted	Т	Total time (min)
me	V	Electrolyte volume (m ³)
	X	Conversion percent (%)
igh	$X_{\rm cr}$	Critical conversion percent (%)
		• • • •

Greek symbols

F

i

 $i_{\rm lim}$

ICE

α	The ratio of applied to initial limiting
	current (–)
v	Stoichiometric coefficient (-)
τ	The time of specified conversion (min)

Faraday constant (C/g equiv)

Instantaneous current efficiency (%)

Electrical current (A)

Limiting current (A)

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