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Development and optimization of Cu-Zr/Ti cathode for removing copper from contaminated water using electrochemical reduction

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ABSTRACT

Consumption of copper contaminated water may lead to adverse health effects, and therefore, it is of utmost importance to remove copper from contaminated streams. More specifically, removing copper from industrial streams, before they enter surface water bodies can reduce anthropogenic copper contamination to a larger extend. This research therefore targeted at optimizing a cathode material and testing the same for employing it in electrochemical copper reduction technology. A Cu-Zr composite coating was developed and optimized on Ti substrate, using electrochemical deposition technique. Coating conditions, including coating current densities and coating durations, were thoroughly investigated. It was found that the best cathode (in terms of electrochemically active surface and stability) can be obtained at copper coating current density of 50 mA/cm^2, copper coating duration of 0.5 h, zirconium coating current density of 75 mA/cm^2, and zirconium coating duration of 1.5 h. A cathode developed with earlier parameters was evaluated using scanning electron microscope coupled with energy dispersive X-ray spectroscopy. The final cathode was successfully employed in removing copper from contaminated water, indicating the ability of using electrochemical reduction technology in removing copper from contaminated streams. About 92% removal of copper from contaminated synthetic wastewater was achieved after 6 h of reaction duration at 10 mA/cm^2 of current density.

Keywords: Cathode; Composite coating; Copper; Electro-deposition; Electrochemical reduction

1. Introduction

Heavy metal pollution has been identified as one of the major water quality issues. Copper is one such heavy metal which is often identified in natural water sources. Industrial wastewaters containing copper (e.g., material processing industry and petroleum refineries), and pesticides with copper as the active ingredient are among the major copper pollution sources. In addition, copper is naturally available in earth's crust, approximately 60 mg/kg [1,2]. Therefore, copper can be present in excess values in water due to natural copper deposits as well. Consumption of copper contaminated water may lead to chronic health problems such as hepatic cirrhosis and kidney defects. Acute effects such as skin and eye irritations and enlarged liver may occur as well [3,4]. National primary drinking water regulations of the United States Environmental Protection Agency (USEPA) suggest maximum contaminant level goal for copper as 1.3 mg/L [5].

Above factors reveal the necessity of removing copper from contaminated water, preferably before entering the drinking water sources such as rivers and irrigation reservoirs. It is worth noting that the traditional water treatment

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process virtually has no capacity to remove copper. Therefore, it is of eternal importance to develop a reliable technology which is capable of removing copper from wastewater at the source of generation itself. Technologies such as chemical precipitation, adsorption, ion exchange, and membrane filtration have been researched to remove copper from water [6–8]. Difficulty in sludge handling, cost of regeneration and disposal of sorbents, resin and membranes, and high energy requirement are the disadvantages related to above technologies. In addition, some technologies are not efficient at treating wastewater with low copper concentrations [7].

Compared with the other technologies, electrochemical technologies to remove copper from contaminated water have distinct advantages. For example, electrochemical reactors are often compact, robust, easy to control, and low cost compared with other technologies [9]. However, sufficient conductivity is a key factor in reducing the cost of energy consumption. In actual wastewater streams, conductivity is high since the total dissolved solids content is generally high in such water. In some parts of Sri Lanka, even the drinking water sources have sufficient conductivity to apply electrochemical water treatment technologies [10].

Electrocoagulation and electrochemical reduction are the two major electrochemical technologies reported in literature for removing copper from contaminated water. Electrochemical coagulation uses in-situ generated coagulants through oxidation of Al or Fe based anodes. Above 97% removal of copper has been reported in literature [11,12]. While the electrocoagulation is effective in removing copper, it generates sludge which is contaminated with copper. In contrast, electrochemical reduction removes copper through reducing the copper ions onto the cathode of the electrochemical reactor cell. In this technology, sludge generation cannot be seen.

Heavy metal removal by using electrochemical reduction has been researched and reported in literature. Heavy metals such as lead [13] and copper [14,15] are among the metals investigated. However, in these studies, little attention has been paid toward the development of new materials and specific properties of cathode material pertaining to the efficient heavy metal removal. In addition, no reported work has been found on optimization of cathode material for removing heavy metals from wastewater.

The objective of this work was to optimize a laboratory developed novel cathode material for removing copper from contaminated wastewater using electrochemical reduction technology. In our previous research, a copper/ zirconium composite coating was successfully developed on titanium substrate [16] and in this study, the developed coating was further optimized. While copper coating provides an excellent environment to reduce copper in wastewater solution, corrosion and wear resistant property of zirconium provides the stability to the cathode. Stability is important since the developed cathode has to be regenerated later by using it as the anode in the same cell. Efficiency of optimized cathode in removing copper from contaminated water has been researched using a laboratory scale electrochemical batch reactor.

2. Materials and methods

2.1. Materials

Ti sheets (technical grade) were purchased from a local supplier. Chemicals including $Cu(NO_3)_2.3H_2O$, $ZrOCl_2.8H_2O$, HCl, oxalic acid, H_2SO_4, Na_2SO_4, and $NaClO_4$ were purchased from Fluka (Switzerland), Merck (Germany), or BDH (UK). All chemicals were of reagent grade.

2.2. Methods

2.2.1. Statistical design of experiments for optimization of coating parameters

In order to evaluate the optimum conditions for electrode coating, electrodes were prepared varying both copper and zirconium plating current density and plating duration. The ranges of parameters to investigate for this study were selected based on preliminary experiments. Table 1 shows the selected minimum and maximum values of four study parameters. Those values were fed in to MINITAB 16 software. Box–Behnken method was selected to obtain the experimental design. Table 2 shows the software-generated experimental design. According to the design, 27 different electrodes were prepared using separate electrolyte baths containing 0.3 M, $Cu(NO_3)_2{\cdot}3H_2O$ and 0.3 M, $ZrOCl_2{\cdot}8H_2O$ while varying the deposition current density and duration.

2.2.2. Coating of Ti substrates for preparing cathodes

A 10 × 10 × 2 mm test piece was cut out from a titanium plate to serve as the cathode substrate. The substrate surface was mechanically cleaned with No 220 silicon carbide paper and then boiled in 5% oxalic acid for 10 min. Subsequently, the substrate was again boiled in 37% HCl for 10 min. Sample was ultrasonically washed in distilled water and dried until obtaining a constant weight. A 1 mm diameter Pt wire was employed as the counter electrode in electrodeposition reactor. Separate electrolyte baths were prepared with aqueous solutions containing Cu and Zr salts for the electrodeposition of Cu and Zr, respectively (details are in Section 2.2.1). Galvanostatic electrodeposition was carried out for the preparation of coatings using potentiostat-galvanostat

Table 1
Levels (maximum and minimum values of parameters) used in the experimental design

Level	Copper plating current density (mA/cm^2)	Copper plating duration (h)	Zirconium plating current density (mA/cm^2)	Zirconium plating duration (h)
Low(−1)	10	0.5	25	0.5
High(+1)	50	3	75	1.5

Table 2
Experimental design

Exp #	Level of factors			
	Cu plating duration (h)	Cu plating current density (mA/cm^2)	Zr plating duration (h)	Zr plating current density (mA/cm^2)
1	3.00	30	1.0	75
2	3.00	10	1.0	50
3	1.75	30	1.0	50
4	0.50	30	0.5	50
5	0.50	30	1.0	75
6	3.00	30	0.5	50
7	3.00	30	1.5	50
8	1.75	50	1.0	75
9	3.00	30	1.0	25
10	0.50	50	1.0	50
11	1.75	10	1.0	75
12	1.75	30	1.0	50
13	1.75	10	1.5	50
14	1.75	50	0.5	50
15	0.50	30	1.0	25
16	1.75	30	1.5	75
17	1.75	50	1.5	50
18	3.00	50	1.0	50
19	0.50	10	1.0	50
20	1.75	10	0.5	50
21	1.75	10	1.0	25
22	0.50	30	1.5	50
23	1.75	30	1.5	25
24	1.75	50	1.0	25
25	1.75	30	1.0	50
26	1.75	30	0.5	25
27	1.75	30	0.5	75

(Metrohm Autolab PGSTAT 128N) equipment. Copper coatings were prepared by electrodepositing copper on titanium substrate at selected current densities for selected durations, based on Table 2. Subsequently, zirconium electrodeposition was done on these surfaces at selected current densities for selected durations according to Table 2. The specimen was then removed from the cell and surface was ultrasonically cleaned in distilled water.

2.2.3. Electrochemical characterization

Accelerated lifetime test and determination of anodic charge of developed electrodes were carried out using Potentiostat-Galvanostat (Metrohm Autolab PGSTAT 128N). Accelerated lifetime of electrode provides a platform for compare the stability of electrode life while anodic charge is an indication of the electrochemically active surface area of electrode. Accelerated lifetime experiments were performed in three electrode cell using 0.5 M H_2SO_4 as electrolyte and 0.25 A/cm^2 as current density. Anodic charge was determined from cyclic voltammetry (CV) data. CV experiments were carried in three electrode system using 0.5 M Na_2SO_4 as the electrolyte (scan rate: 0.01 V/s; range of scan voltage for cathode and anode materials were 0.8 to −0.8 V and 2 to −2 V, respectively). Standard Ag/AgCl electrode was used as the reference electrode and Pt wire was used as the counter electrode. Electrode under investigation was used as the working electrode.

2.2.4. Scanning electron microscopy

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy of the optimized electrode were obtained using SEM/EDX instrument (Zeiss Evo LS15).

2.2.5. Copper removal experiments

A two electrode batch reactor cell with a cell volume of 50 mL was used to conduct the copper removal experiments. In the cell, 1 mm diameter Pt wire was used as the anode, and optimized Cu-Zr/Ti electrode was used as the cathode. A 10 ppm Cu^{2+} solution in 0.025 M $NaClO_4$ was used as the electrolyte. Initial solution pH was adjusted to 7 ± 0.1. Copper removal reactions were carried out at a current density of 5 mA/cm^2 and 10 mA/cm^2 for a reaction period of 6 h. Copper concentrations of the initial and final solutions were measured using Atomic Absorption Spectrophotometer (AAS - GBC 933AA).

3. Results and discussion

3.1. Cathode optimization

The main criterion for efficient removal of copper from contaminated water using electrochemical reduction technology is active surface area of the cathode. High active surface area of the electrode leads to higher removal of metal ions from the solution due to the availability of high amount of active sites on the electrode surface. In addition to the availability of active sites, stability of the electrode is another crucial factor in the recovery of deposited metal. In the recovery process the polarity of the electrodes has to be shifted, thus, cathode of the reactor cell becomes the anode and prone to corrosion. Considering these two important factors, optimization process was carried out to obtain optimized conditions for the development of electrode with the highest removal efficiency as well as highest stability. Our previous studies showed that the plating conditions, that is, the plating duration and reaction time, play a major role in cathode properties [16]. Therefore, the effect of plating current and duration was used as the factors in optimization process while electrochemically active surface area (which is indirectly measured through anodic charge) and stability (which is measured through accelerated lifetime test) were kept as responses.

Based on the matrix generated (presented in Table 2), 27 different electrodes were prepared by coating Cu followed by Zr on Ti (i.e., Cu-Zr/Ti cathodes), under different coating conditions. The prepared Cu-Zr/Ti cathodes were analyzed for obtaining the two different responses which were mentioned earlier.

Eq. (1) shows the obtained relationship between anodic charge and coating conditions:

$$C5 = -0.177 + 0.385\,C1 - 0.0012\,C2 + 0.568\,C3 + 0.0040\,C4 - 0.0053\,C1 \times C1 + 0.000126\,C2 \times C2 + 0.126\,C3 \times C3 + 0.000115\,C4 \times C4 + 0.00378\,C1 \times C2 - 0.334\,C1 \times C3 - 0.00317\,C1 \times C4 - 0.00238\,C2 \times C3 - 0.000215\,C2 \times C4 - 0.00697\,C3 \times C4 \tag{1}$$

where C1 = copper coating duration, h; C2 = copper coating current density, mA/cm^2; C3 = zirconium coating duration, h; C4 = zirconium coating current density, mA/cm^2; and C5 = anodic charge, C.

The regression coefficient (R^2) of the model is 73.80% showing a fair fit of data. Figs. 1(a) and (b) show the modeled anodic charge versus observed anodic charge and residual plot, respectively. Two-tailed, heteroscedastic *t*-test, considering a significance level (α) of 0.05, showed a p value of 0.98, suggesting that the variations between observed and modeled anodic charges are not statistically significant. In addition, the random scatter plot obtained for residuals shows that the obtained model, that is, Eq. (1), represents the data well.

Eq. (2) shows the obtained relationship between accelerated lifetime and coating conditions:

$$C6 = 2789 - 803\,C1 - 1.8\,C2 - 966\,C3 - 44.4\,C4 - 32\,C1 \times C1 - 0.212\,C2 \times C2 + 691\,C3 \times C3 + 0.287\,C4 \times C4 - 3.13\,C1 \times C2 + 270\,C1 \times C3 + 16.09\,C1 \times C4 + 7.3\,C2 \times C3 + 0.409\,C2 \times C4 - 27.5\,C3 \times C4 \tag{2}$$

where C6 = accelerated lifetime, s.

The regression coefficient (R^2) of the model is 60.24% showing moderate fit of data. However, as can be seen in Fig. 2(a), high deviation is observed at large accelerated

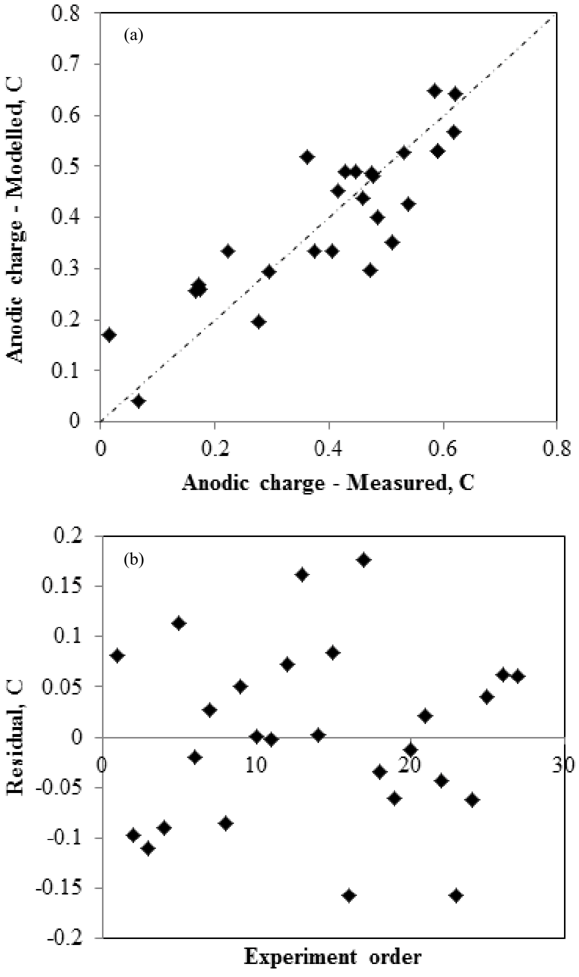


Fig. 1. (a) Modeled and measured anodic charge and (b) Residual plot for anodic charge modeling.

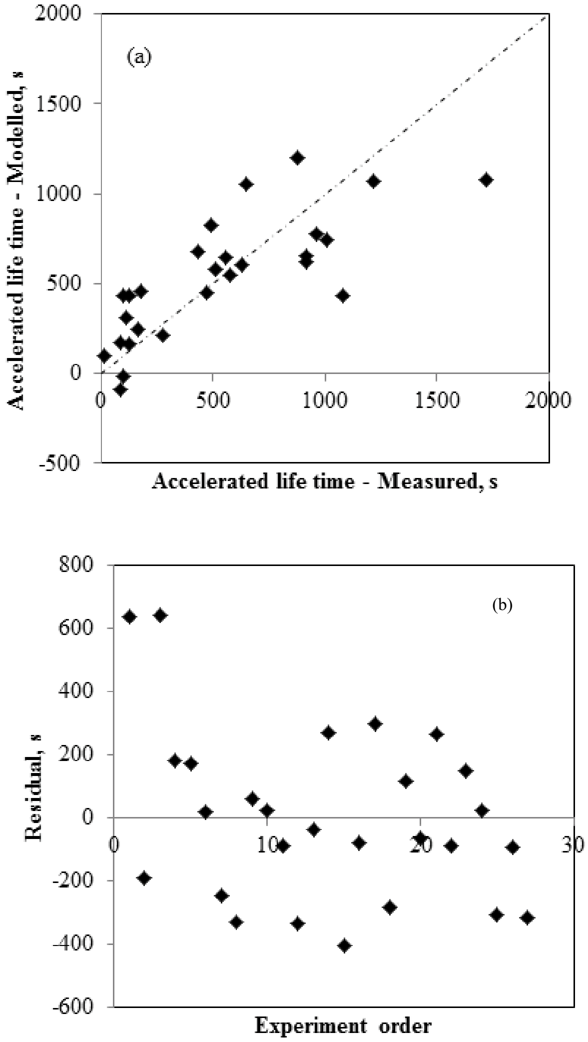


Fig. 2. (a) Modeled and measured accelerated lifetimes and (b) Residual plot for accelerated lifetime modeling.

lifetimes (e.g., lifetime > 1,500 s), while for lower lifetimes, the model does not show significant variation. Two-tailed, heteroscedastic *t*-test, considering a significance level (α) of 0.05, showed a p value of 0.99, suggesting that the variations between observed and modeled accelerated lifetimes are not statistically significant. Random scatter of residuals shown in Fig. 2(b) suggests that the obtained model, that is, Eq. (2), represents the data well.

Therefore, the obtained relationships were further analyzed to identify the optimum coating conditions for developing cathode material.

Fig. 3(a) shows the contour plot of anodic charge versus Cu plating current and Cu plating duration. The highest anodic charge of 0.618 C was obtained from the electrodes plated under 50 mA/cm^2 current density and 0.5 h plating duration. At high current densities, the mass transfer rate of Cu^{2+} ion from bulk solution to the liquid-substrate interface is high and this increases the population density at the liquid/substrate interface. The smallest nuclei can be expected at high population densities increasing the active surface area [17]. Although the maximum anodic charge was obtained at the highest current density under investigation, the current density cannot be further increased due to the formation of copper oxide. Formation of an oxidized layer at cathode (where reduction occurs) at high current densities is worth further scientific investigations. At this juncture, the speculation is as follows. At high current densities, Cu nuclei formed on the surface of the electrode are tending to be large. Therefore, the deposition layer may contain high amount of pores. Electrolyte solution may leach in to the pores and as a result individual microelectrochemical cells may occur within the deposition layer. Oxidation of Cu atoms at the anodic sites may lead to the formation of Cu_2O depositions within the deposited Cu layer. Therefore, no effort was taken to further increase the applied current density. In addition, increasing plating duration may produce a compacted deposition, reducing the active surface area of electrode.

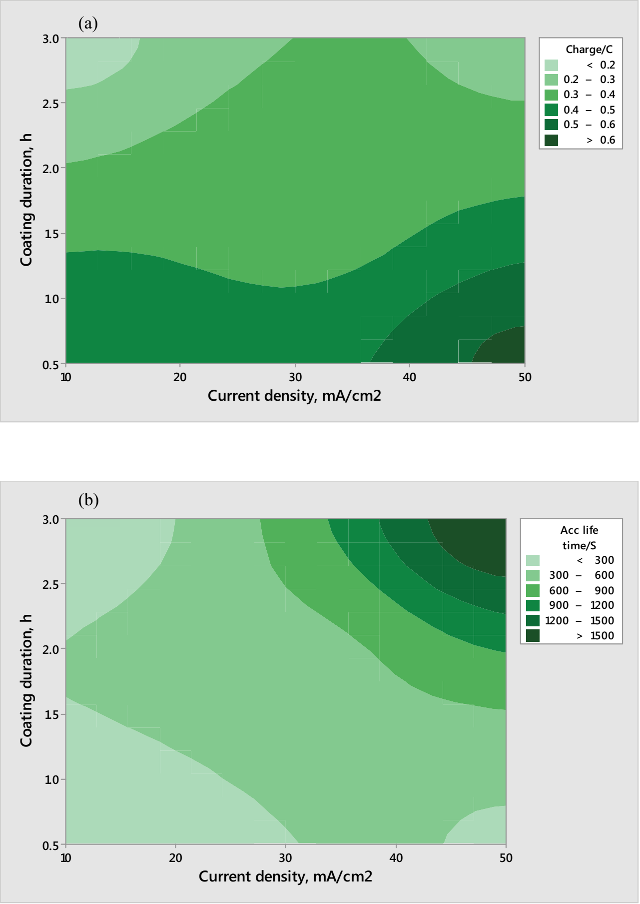


Fig. 3. (a) Contour plot of the variation of anodic charge with the Cu plating duration and current density and (b) Contour plot of the variation of accelerated lifetime with the Cu plating duration and current density.

Fig. 3(b) shows the contour plot of accelerated lifetime of developed anodes versus Cu plating current and Cu plating duration. Fig. 3(b) indicates that 50 mA/cm^2 of Cu plating current density and 3 h of Cu plating duration give the highest accelerated lifetime of 1,720 s. According to the results obtained, highest Cu plating current gave highest anodic charge as well as highest accelerated lifetime. When considering the Cu plating duration, lowest Cu plating duration gave the highest anodic charge while highest Cu plating duration gave the highest accelerated lifetime.

However, higher anodic charge reflects higher surface area and higher surface area may leads to higher corrosion rate. Also, it should be noted that high pore density in coating layers deposited at high currents leads to high active surface area and due to the same reason stability can be lower. In that sense, showing both higher anodic charge and stability at high currents is controversial. When further analyzing this finding, the mediation of Zr layer on previously deposited Cu layer should be considered. Since the electrodes were tested electrochemically after depositing both materials, effect of both materials should be considered in evaluating the findings. It can be speculated that during Cu deposition at high current densities porous structure can be created. Then, Zr layer was deposited on that already deposited Cu layer. Due to porous nature of previously deposited Cu layer, Zr may have migrated successfully to the coating structure and increased the accelerated lifetime of electrode. At long Cu coating durations, as suggested previously, denser layers may have deposited adding more stability to the electrode compared with the short Cu plating durations.

Variation of anodic charge of the electrodes with respect to the Zr plating current density and duration is given in Fig. 4(a). Fig. 4(a) indicates that 75 mA/cm^2 Zr plating current density and 1.5 h of Zr plating duration gave the highest anodic charge of 0.623 C, hence highest surface area. Zr deposition time and current density cannot be further increased due to the voltage overload at higher currents and durations. As explained previously for Cu deposition, high mass transfer rate at high deposition currents may have contributed to the high anodic charge. Unlike Cu deposition, the highest anodic charge is associated with longest Zr coating durations. This phenomenon can be explained as follows. Zr was deposited on top of the Cu layer. When Zr is deposited for a longer duration, during initial period, Zr may have migrated to the Cu layer providing lower anodic charges. When the deposition time is increased, layer-by-layer deposition of

Zr may have occurred and improved the electrochemically active surface area.

Variation of accelerated lifetime with Zr plating current density and duration is presented in Fig. 4(b). Fig. 4(b) indicates that highest accelerated lifetime was obtained for the electrode with 75 mA/cm^2 Zr plating current density and 1.5 h zirconium plating duration. This high corrosion resistant can be due to the high mass transfer of Zr at high currents and migration of Zr into deposited Cu matrix at high plating durations.

Based on earlier analysis, it is clear that highest anodic charge and accelerated lifetime were given when Zr coating current density and duration were 75 mA/cm^2 and 1.5 h, respectively. However, when it comes to Cu coating current and duration, best anodic charge and accelerated lifetime were achieved under two different conditions. Since the effect of copper coating conditions on corrosion resistance is lower compared with that of Zr (note that Zr improve the corrosion resistance of the layer), it is speculated that improvement in anodic charge is more important in selecting coating parameters for copper. Therefore, it is decided to proceed with coating conditions shown in Table 3 for removal experiments.

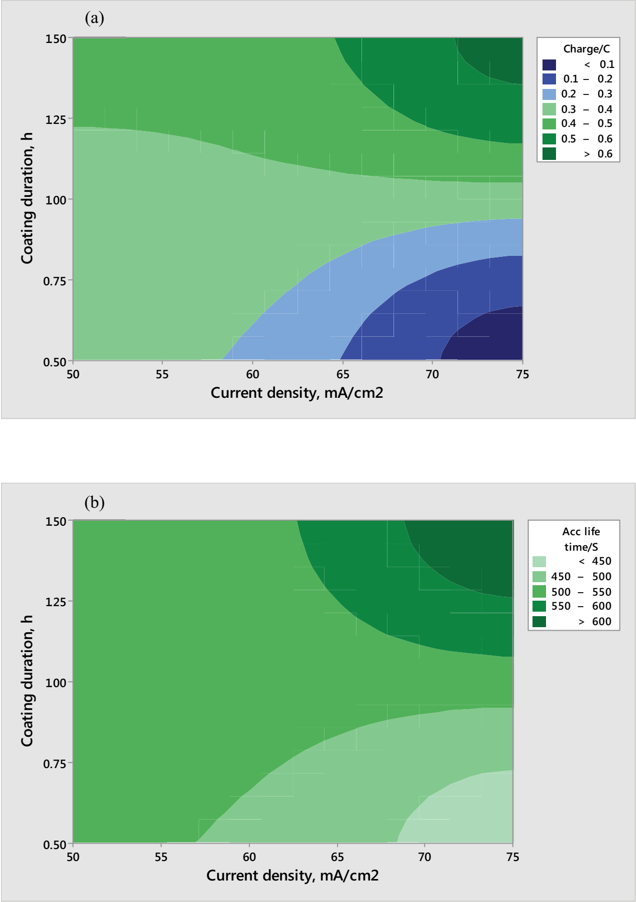


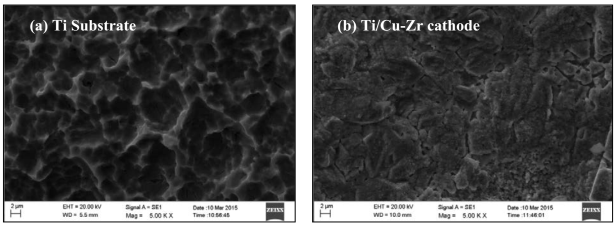
Fig. 4. (a) Contour plot of the variation of anodic charge with the Zr plating duration and current density. (b) Contour plot of the variation of accelerated lifetime with the Zr plating duration and current density.

3.2. SEM/EDX analysis

A Cu-Zr/Ti cathode was prepared at coating conditions which are shown in Table 3. The optimized Cu-Zr/Ti cathode and the substrate material (Ti) were analyzed using SEM/EDX and results are shown in Fig. 5.

As shown in Fig. 5, surface morphology of the optimized cathode is significantly different compared with that of the Ti substrate material, indicating successful coating on the substrate. Anodic charge of uncoated Ti substrate was found through cyclic voltammetric studies as 0.105 C, indicating a very low electrochemically active surface area. The anodic charge of optimized Cu-Zr/Ti cathode was found as 0.605 C. It is interesting to see that, although in Fig. 5(a) the Ti substrate shows highly porous structure (physically), the electrochemically active surface area is extremely low compared with that of the optimized electrode.

Fig. 5(a) shows that atomic percentage of Ti on substrate material surface is 96.24%. Little amounts of Cl and Fe can be due to impurities on the Ti substrate. Fig. 5(b) indicates a considerable atomic percentage of Cu (53.94%) on the coated cathode. However, no Zr can be seen on the surface, although Zr was coated on the substrate. However, a very clear increment in accelerated lifetime can be seen due to the application of Zr. Similar findings were reported previously [16]. Since



Element	Weight %	Atomic %
Cl	0.68	0.92
Ti	96.02	96.24
Fe	3.30	2.84

Element	Weight %	Atomic %
C	8.42	28.41
O	6.97	17.65
Cu	84.60	53.94

Fig. 5. SEM/EDX results obtained for (a) Ti substrate and (b) optimized Ti/Cu-Zr cathode.

Table 3
Coating parameters used in developing final cathode (Ti/Cu-Zr) coating layer

Coating parameter	Cu		Zr	
	Coating current density (mA/cm^2)	Coating duration (h)	Coating current density (mA/cm^2)	Coating duration (h)
Value	50	0.5	75	1.5

Zr is deposited after depositing the Cu later on Ti, Zr may have penetrated through the Cu layer. It has been further reported that, when the Zr deposition duration is increased, Zr can be found on the surface of the coating. Deposition of Zr in the layers of Cu may have contributed to the high stability of the coating, compared with a cathode without any Zr deposited [16].

3.3. Copper removal efficiency of optimized cathode

Fig. 6 shows the copper removal efficiency at two different current densities versus reaction time. Irrespective of the applied current density, copper removal efficiency was very low during initial 2–3 h of reaction. When the electrolysis time was further increased, a remarkable increase in removal efficiency was observed. This may be due to the time taken to stabilize the interface between electrode (solid) and solution (electrolyte with dissolved copper). It is important to note that the initial concentration of copper ions in solution was around 10 ppm and therefore, mass transfer limitations may exist. In addition, the electrochemical reduction occurs at cathode surface and not in the bulk solution. Indirect electrochemical reactions do not support the reduction of copper, which must occur on the cathode surface. Therefore, the initial stabilization period is crucial in removing copper using electrochemical reduction. Moreover, it can be seen that under both current densities, efficiencies at extended reaction durations does not improve drastically. However, after 5 h of reaction, the availability of copper in solution is limited. At a current density of 5 mA/cm^2, the availability of copper in solution was 2.32 ppm and under 10 mA/cm^2, it was only 1.7 ppm. The lower copper concentrations would have limit the mass transfer from bulk solution to cathode surface. At the end of 6 h reaction period, 82.3% and 91.86% removal of copper was reached at 5 mA/cm^2 and 10 mA/cm^2 current densities, respectively.

However, in literature, copper removal efficiencies as high as 97% are reported, employing electrocoagulation, instead of electrochemical reduction [11,12,18]. In electrocoagulation, reactions mainly occurred at bulk solution and thus, the mass transfer between pollutant (in this case, copper) and coagulant would be easy. In contrast, migration of pollutants from bulk solution to electrode surface for reduction would be difficult. Therefore, the efficiencies are higher in electrocoagulation compared with that of electrochemical reduction. However, in electrochemical reduction, there is no sludge generation and thus, no residual disposal is required. In addition, the metal can be regenerated by reversing the polarity of the reactor cell. Possibility of easy reclamation of copper from polluted water is an advantage of proposed electrochemical reduction reactor.

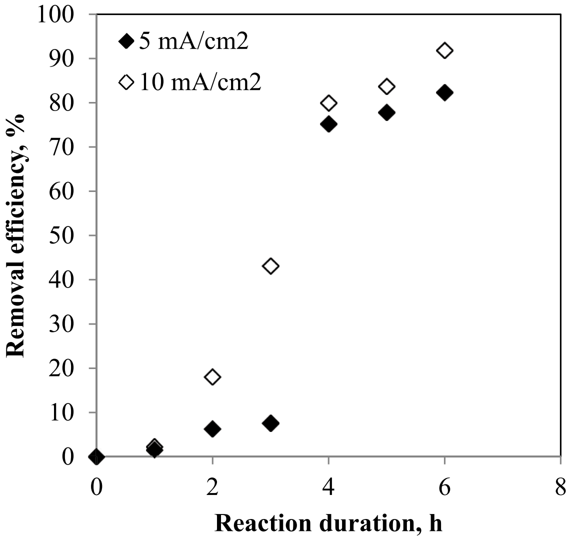


Fig. 6. Copper removal efficiency using the optimized cathode.

4. Conclusions

This research focused on optimizing a previously developed Ti/Cu-Zr composite coating for removing copper from contaminated wastewater using electrochemical reduction. Coating conditions, including coating current density and duration at which Cu and Zr are to be deposited, were examined for obtaining the best electrochemical activity and stability. It was found that the coating conditions pay a major role in controlling the properties of the electrodes.

The best anodic charge was related to the highest copper deposition current density which was studied, which was an interesting finding, questioning "whether further increments enhance the anodic charge?" However, it was observed that, a further increment in current density was not possible due to formation of oxides on the coating. It is concluded that this may be due to the formation of anodic sites between deposited layers of copper. Further studies are essential to clarify this phenomenon. Extended plating durations were not preferable in increasing anodic charge of the electrodes. It can be due to formation of compacted layers, reducing the porosity of coating. The best stability was found at high copper coating current densities and longer plating durations. This may be due to the intervention of Zr on cracked copper coating, rather than based on the properties of copper layer itself. Analysis of Zr coating conditions showed that both highest anodic charge and stability occurred at high plating current densities and longer plating durations. It is concluded that this can be due to the high mass transfer rates and migration of Zr into copper layer during initial coating periods. Final optimized coating conditions were decided based on high effect of copper on electrochemical activity (i.e., anodic charge) and high effect of Zr on stability of cathode. Optimum copper coating current density, copper coating duration, zirconium coating current density, and zirconium coating duration were selected as 50 mA/cm^2, 0.5 h, 75 mA/cm^2, and 1.5 h, respectively.

The cathode developed based on selected conditions showed an efficiency of about 92% in removing copper from contaminated water in 6 h reaction duration at a current density of 10 mA/cm^2.

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