

Removal of Trace Amounts of Copper from Concentrated Hydrochloric Acid Solutions

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Pickling process is recognized as one of the strongest acid consuming processes in the steel industry. A pickling solution that contains hydrochloric acid (HCl) is used for the metal surface treatment of steel plants. The same acid can be used for a long period of time by means of a regeneration process, in which iron concentration of the acid is decreased to insignificant concentrations. However, regenerated pickling solutions contain copper, especially when scrap is used to produce steel. Furthermore, copper deposits on the metal in the following pickling processes when its concentration exceeds a certain critical value. This study describes an electrochemical treatment process for collecting copper from regenerated pickling solutions of steel plants. Copper concentration, electrolysis time, and current density were selected as the operation variables and pH and conductivity of the acid together with the amount and morphology of the deposition were considered as the response variables for optimization. Graphite was used as the anode due to its high conductivity and stability and copper or stainless steel was used as the cathode in this study. The results showed that electrochemical treatment process decreased copper concentration to about 80 from 127 ppm using stainless steel cathode under the optimum constant current density of 2.0 A/dm² and electrolysis time of 4 hours, without any acid loss, which was verified by pH, conductivity and acidity measurements.

Keywords: Copper electrodeposition; Copper recovery; Pickling solution; Current density

1. INTRODUCTION

Pickling is a metal surface treatment technique that is used to get rid of the oxide layer, rust

scale, inorganic contaminants or other impurities that are formed on the metal surface [1]. The process is the reaction between the pickling solution and the surface impurities together with the base metal [2]. It is one of the critical steps in surface preparation. Hydrochloric acid, one of the strongest acids, is used for pickling [1].

During the pickling process, a large amount of acid is spent [1]. The spent pickling acid contains varying concentrations of dissolved and waste heavy metals such as iron, chromium, copper, nickel, and zinc which are also economically valuable [3]. The dissolved and waste metals depend on the treated metal [4]. In other words, the source of these metals is the pickled metal itself [1]. It is not possible to use the spent pickling solution when it reaches saturation [5]. The efficiency of pickling solution decreases with increasing dissolved metal content and the spent pickling solution should be discarded when the efficiency decreases [1]. A regeneration process is usually carried out to delay the disposal. During the regeneration process, most of the impurities are removed except the copper ions. When the copper ion concentration in the solution increases and exceeds the level of about 100 ppm [6], copper begins plating out onto the steel strip randomly with varying severity in the following pickling processes.

The copper deposition depends on the displacement reaction between copper and iron ions. Reaction (1) shows the dissolution of iron into the acid. Dissolved iron releases two electrons to form soluble metal cation of Fe^{+2} . These electrons are exchanged with Cu^{+2} in the solution. Reaction (2) shows the electrochemical copper plating back onto the steel strip [6].



In addition to the regeneration process, several treatment methods have been developed for metal recovery operations. These methods include; chemical precipitation [7-11], ion exchange [11-14], solvent extraction [15-20], membrane technology [4, 20], acid swapping and cementation [21], adsorption [20, 22] and electrochemical treatment [23-27]. For a cost-effective and environmental solution, electrodeposition method is a promising technique for recovery of some metals from waste solutions using insoluble anodes [21].

Electrodeposition is the process of depositing a material onto a conducting surface from a solution containing ions by passing a current through an electrochemical cell from an external source. In the case of electrodeposition, it is possible to use large tanks as electrolytic cells [28]. Recovery of metal ions from different industrial effluents by electrodeposition is an attractive method [29].

Electrolytic copper extraction from dilute solutions was reported previously [30]. However, the method is less effective for copper extraction when the contents of non-ferrous metal ions are much higher [31]. During the copper electrowinning from dilute solutions, the deposition morphology differs in the presence of other metals [32]. Studies also showed that current efficiency during the copper electrowinning decreases proportionally with the ferric ion concentration in the solution [33, 34]. For this reason, working on regenerated pickling solution instead of spent pickling solution is more efficient. Although ferric ion concentration diminishes the current efficiency, hydrogen evolution

reaction (HER) on the cathode surface is the major interfering reaction during the electrodeposition process [35]. Increasing current density triggers the undesired side reactions. Therefore, current density is one of the most important factors affecting the current efficiency [36].

In the potentiostatic operation, too high voltages result in Cl_2 evolution at the anode and too low voltages yield in only H_2 evolution at the cathode [37]. The hydrogen evolution reaction effects the crystal and physical structure of the coating [38]. Therefore, the electrochemical cell should operate at an optimum voltage, which will enable copper reduction without too much H_2 and Cl_2 evolution.

The purpose of this study is to develop an environmentally-friendly and economical process for keeping the copper level of regenerated pickling solution below 100 ppm using electrodeposition method. As mentioned previously, there are studies for either copper removal from pickling solutions or electrolytic recovery of copper from acidic solutions. However, to the best of our knowledge, electrolytic copper recovery from pickling solutions (HCl) for such low concentrations has not been studied yet. By this way, it was aimed to reduce acid consumption in pickling and utilize the recovered copper.

2. EXPERIMENTAL DETAILS

2.1. Materials and Equipment

Regenerated pickling acid solution was collected from Borçelik steel plant located in Bursa, Türkiye. The characteristics of the effluent were determined by pH, conductivity and acidity measurements and inductively coupled plasma-mass spectrometry (ICP-MS). The characteristics are given in Table 1.

Thermo Scientific Orion Star A215 was used for pH and conductivity measurements. Agilent 7700x ICP-MS equipment was used for ICP-MS analysis. The electrolysis experiments in the direct current mode were performed using an Agilent B2901A type power supply. The ICP-MS equipment, a precision scale (Precisa 152A) and an XRF analyzer (Fischerscope X-Ray XDV-SDD 604-447) were used to determine removed and therefore collected copper amounts. A hot plate (Mtops HSD 180), employing a contact thermometer and a magnetic stirrer was used to maintain the homogeneity of the temperature and composition of the system.

Table 1. Characteristics of regenerated pickling solution

Characteristics of effluents	Values
pH	-0.5
Conductivity (mS/cm)	800
Acidity (g/L)	185

Color	Yellow
Odor	Pungent. Irritating (Strong)

ICP-MS analyses of the solution and XRF analyses of the deposits were evaluated during the selection of electrode materials. Linear sweep voltammetry (LSV) was carried out by a Gamry Instruments Reference 3000 Potentiostat for the determination of the current density range to be studied. In addition, the amount of copper collected and the morphology of the deposits were taken into consideration for the selection of anode and cathode materials.

2.2. Experimental Setup

The experimental setup used in this study is mainly consisted of a 500 ml beaker used as a batch reactor to hold 300 ml solution. The beaker was covered by a Teflon lid to keep the solution volume constant during the experiments. The electrodes were cylindrical graphite anode and a thin foil of copper or a plate of stainless steel cathode.

The desired current density was maintained constant during the experiments. The electrodes were cleaned with a sodium hydroxide solution (0.5 M) and a nitric acid solution (%50 V/V) before each experimental run. All of the experiments were performed at 60°C, which simulated the temperature of the acid used in the steel plant. After each experiment, the electrodes were dried and cathode was examined. The solution samples were transferred to a leak-proof plastic container after each run to perform ICP-MS analyses.

Since the foils are very light, the weight gain could be determined by a precision scale when copper foils were used as cathode. However, the weight gains of stainless steel cathodes were examined by measuring the plating thickness using X-Ray Fluorescence (XRF) because a very small weight change on a relatively heavy stainless steel plate could not be measured precisely by weighing. The weights of copper deposited on copper cathodes were determined from the difference between the initial and the final weights. The deposited copper amounts on the stainless steel cathode were calculated according to formula (3), where m is the mass of the deposited copper, t is the thickness of the deposition determined by XRF measurements, A is the deposition area and ρ is the density of copper.

$$m = t \times A \times \rho \quad (3)$$

The amount of copper removal from the regenerated pickling solution was determined in terms of the copper concentrations by equation (4):

$$\%removal = \frac{(C_i - C_f)}{C_i} \times 100 \quad (4)$$

where C_i and C_f are the initial and final concentrations in ppm, respectively. The concentration data were obtained by the ICP-MS analyses.

2.3. Experimental Design

Among the possible anode materials, graphite was chosen for being inert in the solution after performing electrolysis using different anode materials.

Utilization of collected copper will be an important issue in industrial application. Therefore, copper cathode was chosen for an easier operation because in this case, separation of collected copper from the cathode material is not necessary. However, it was found that working with copper cathodes needs close attention because the hot acid can dissolve copper at a very fast rate when it is not cathodically protected. In order not to incorporate a new copper source into the solution from outside, stainless steel cathode was also studied as an alternative material. Stainless steel had a much better resistance to the electrolyte when compared to copper and collected copper could easily be peeled off from the passive surface of this material.

The range of applied current density was determined by linear sweep voltammetry (LSV). LSV was performed using a two-electrode setup. The working electrode was a copper foil and a graphite rod was used as the counter and the reference electrode. From the LSV result, it was deduced that the potential must remain between 0.5 V and 1.5 V. The corresponding current densities to these voltages were between 0.5 and 2.0 A/dm². The anode and cathode surface areas were equal to 0.05 dm².

The independent variables and their levels for treatment of regenerated pickling acid solution are given in Table 2.

Table 2. Independent variables and their levels

Independent Variables	Level 1	Level 2	Level 3
Current density (A/dm ²)	0.5	1.0	2.0
Electrolysis time (h)	2	4	6
Copper concentration (ppm)	85	127	154

3. RESULTS AND DISCUSSION

3.1. Voltammetric Analysis

Linear sweep voltammetry analysis was performed on copper containing pickling solution of the steel plant and corresponding blank solution. Figure 1 shows the linear sweep voltammogram of both of the solutions. From the examination of the figure, potentials and corresponding current densities for the electrode reactions could be picked up. As can be seen in Figure 1, there was an

anodic current before the voltage was applied because of the dissolution of copper into the electrolyte in this extremely corrosive environment. At around -0.5 V vs. graphite electrode, the first cathodic reaction started and gave a clear reduction peak at about -0.7 V. This peak was attributed to the reduction of Cu^{+2} to Cu^+ . When the cathodic potential was further increased, a second reduction peak was obtained at around -1.5 V, which was thought to be originated from the reduction of Cu^+ to solid Cu [37]. Potentials more negative than -1.5 V resulted in too much H_2 evolution at the working electrode. Furthermore, it was observed that higher current densities resulted in a fast and discontinuous powder deposition [39]. Therefore, it was decided to operate the electrochemical cell between -0.5 and -1.5 V to include both electrode reactions. These voltages corresponded to a current density range from 0.5 to 2.0 A/dm^2 . At this range, the cell reactions were considered as follows:

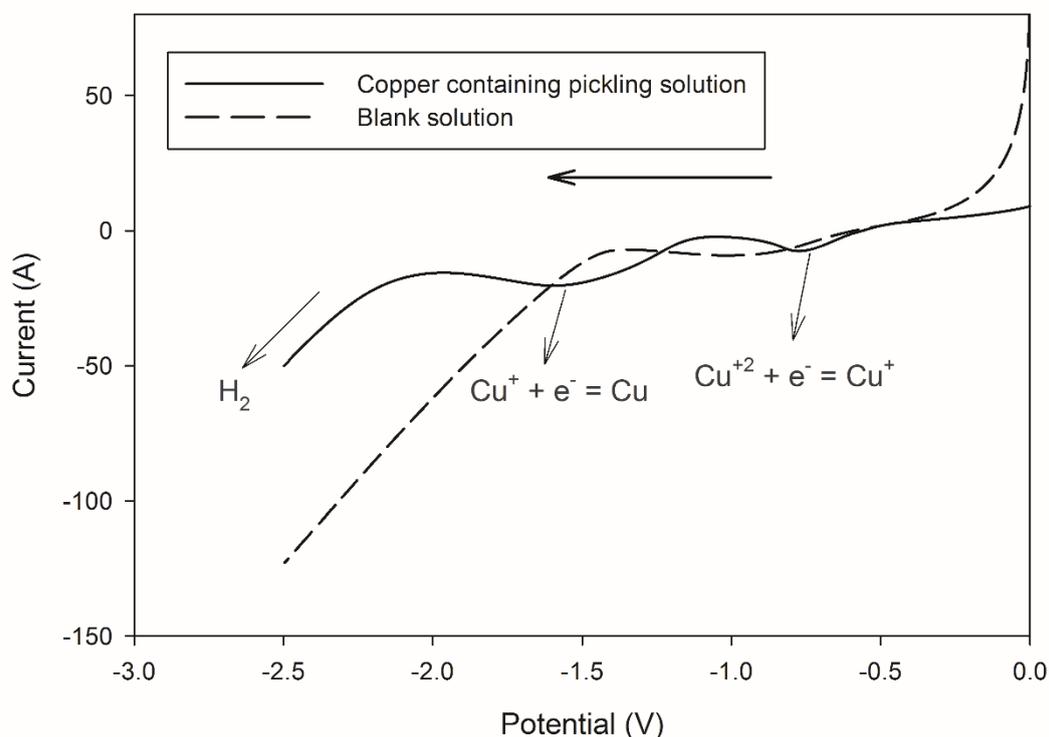


Figure 1. Linear sweep voltammetry of copper containing pickling solution and corresponding blank solution at a scan rate of 25 mV/s. The arrow at the top indicates the scan direction.

3.2. Material Choice

3.2.1. Anode Choice

Titanium, lead and graphite were tested as the anode candidates. Constant current electrolysis experiments were conducted and deposited samples together with the electrolytes were characterized. Each experiment was done at 1.0 A/dm^2 current density and for 4 hours of electrolysis time. The regenerated pickling solution contained 145 ppm copper and the cathode material was stainless steel. From the visual examination of the cathodes and measurements of thickness of deposited copper by XRF, it was seen that brighter surfaces and more copper removal were obtained from the experiments employing titanium anode. Measured thicknesses by XRF were 1.345, 1.096 and $0.857 \mu\text{m}$ for titanium, lead and graphite anodes, respectively. The thickness results were given by taking the average of randomly selected 16 points from all over the cathode surface.

From the analysis of ICP-MS results, the anode materials were sorted in terms of copper removal from more to less as titanium, lead and graphite. The level of copper was reduced to 93, 103 and 104 ppm when titanium, lead and graphite anodes were used, respectively. However, it was observed that titanium and lead anodes released large amounts of titanium and lead ions into the solution. The levels of titanium and lead increased from almost 0 to 716 and 2600 ppm when they were used as anodes in the corresponding experiments. These results were in accordance with the studies which reported corrosion of lead [40] and titanium [40-42] in concentrated HCl solutions at room temperature. The corrosion rates were even higher in this study because these materials were used as the anode of an electrochemical cell and their potentials were further increased. Graphite was chosen as the best anode material in the electrochemical treatment of copper from regenerated pickling solutions based on no detectable anode dissolution.

3.2.2. Cathode Choice

The choice of cathode material is important for effective copper removal and its utilization. The effects of the parameters given in Table 2 were investigated using mainly copper as the cathode material. The copper cathode was chosen for an easier copper utilization because there is no need for scrapping off the deposit from the electrode. When the electrodes are loaded to a certain level, they can be melted together with the deposited copper.

Copper is prone to oxidation by hot acid and its vapor, so it was hard to manage the copper cathode assembly [43]. It was previously reported that soluble cuprous complexes like CuCl , CuCl^{-2} , CuCl_3^{-2} and CuCl_4^{-3} are formed at high HCl concentrations [44]. However, as being the cathode of the electrochemical cell, copper was protected to an extent by the applied potential difference in this study. A constant voltage between the electrodes was provided while immersing them into the solution to prevent any rapid attack of HCl to copper. After the cathode was completely immersed in the solution, the selected constant current was applied. It was observed that copper electrodes were severely corroded especially above the electrolyte level by HCl gas in 6 hours long experiments.

For the above mentioned problems of copper cathode, some selected experiments were repeated using stainless steel as the cathode material because it possesses higher corrosion resistance due to formation of a protective film on its surface. Although this film was reported to corrode in HCl [45], the presence of electrical current (cathodic protection) provided extra resistance to corrosion in

this study. The thin chromium oxide layer at the stainless steel surface provided adequate adhesion between the deposit and the electrode which kept the deposit on the electrode under the influence of the applied potential but prevented very good adhesion. Therefore, the deposit could easily be peeled off from the electrode when it was taken out of the electrolyte.

It was easier to manage stainless steel cathode at the beginning of the electrolysis. After some time of electrolysis, the stainless steel cathode was covered with copper and the rest of the electrolysis can be considered as copper plating onto copper. Therefore, the rest of the electrolysis experiments were the same as those with copper cathodes. However, there was no copper above the electrolyte level in contact with HCl vapor. Utilization of the collected copper required a secondary process to separate the copper from the stainless steel cathode. When the deposit was separated from the surface, the stainless steel cathode could be used again.

3.3. Investigations of the Effects of Experimental Parameters on Copper Removal from Regenerated Pickling Solution

The effects of initial copper concentration, electrolysis time and current density on copper removal were investigated by a full-factorial experiment design using a graphite anode and a copper cathode. The figures in the following sections, showing the main effects, were drawn by taking into consideration of all possible combinations of all the input factors in three levels as given in Table 2. This choice of presentation was made to derive statistical conclusions from small amount of copper collected from strong acidic solution containing very low copper concentrations. Average of 9 experiments were used for each point and all 27 results were used in the construction of each line/curve of the plots. In the experiments with stainless steel cathode, the three current densities and electrolysis times given in Table 2 were studied. However, only one initial copper concentration, 127 ppm, was used. As a result, in the construction of the figures showing the results of experiments with stainless steel cathode, 3 data were involved in each point and 9 data were involved in each line/curve of the plots. The error bars in the following figures were used to indicate the uncertainty in ICP-MS measurements.

3.3.1. Effect of Initial Copper Concentration on Copper Removal

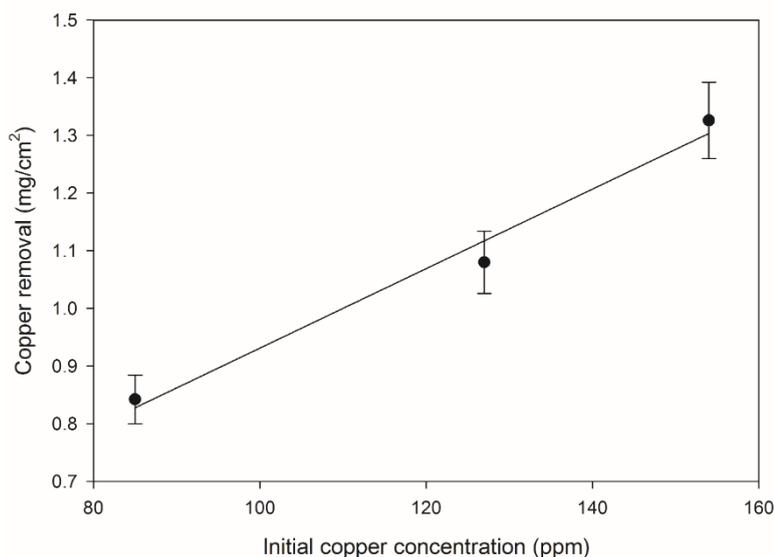


Figure 2. Main effect of initial copper concentration on copper removal by a copper cathode at 60 °C. The points are the averages of 9 experiments conducted at all the possible current density-electrolysis time combinations according to Table 2.

The effect of three different initial copper concentrations (85, 127, 154 ppm) on copper removal was examined at the same electrolysis times and current densities at 60°C using a graphite anode and a copper cathode. The main effect of initial copper concentration, which was calculated by taking the averages of the results of the experiments conducted at three levels of electrolysis times and current densities, on copper removal is shown in Figure 2. As can be seen in this figure, copper removal increased with increasing initial copper concentration of the solution [36] due to the increase of copper ion activity in the solution. Removal of 1 mg/cm² of copper corresponds to a decrease of approximately 14 ppm in copper concentration of the pickling solution when the area of the cathode and the volume (total weight) of the acid used in this study were considered.

3.3.2. Effect of Electrolysis Time on Copper Removal

The effect of three different electrolysis times (2, 4 and 6 hours) on copper removal was examined under the same experimental conditions. The main effect of electrolysis time on copper removal by copper and stainless steel cathodes are given in Figure 3(a) and Figure 3(b), respectively. As can be seen in these figures, a greater amount of copper was removed as a result of increasing electrolysis time.

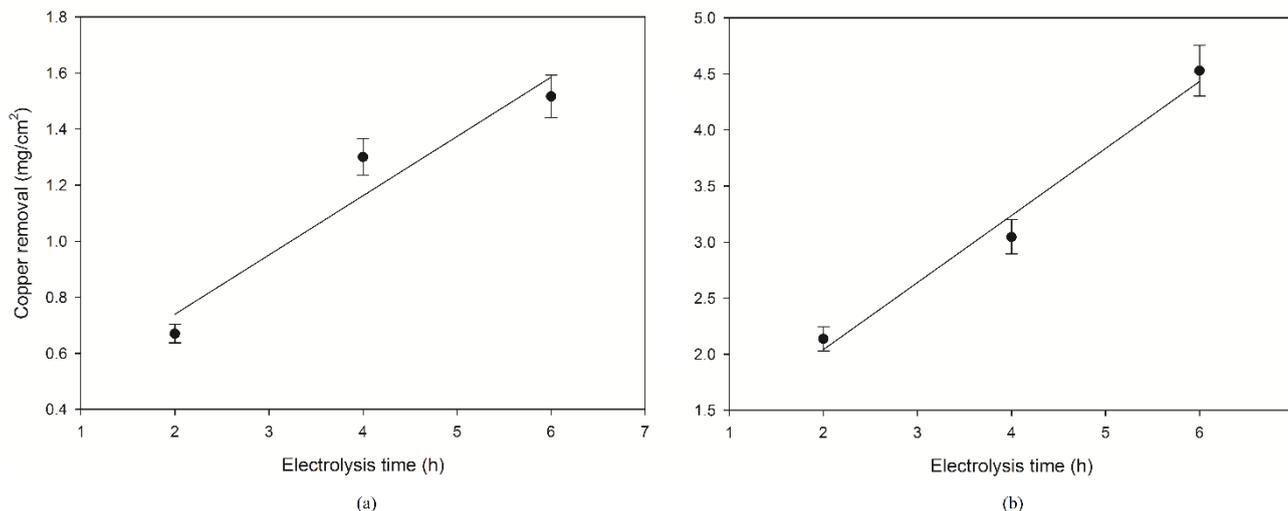


Figure 3. Main effect of electrolysis time on copper removal by (a) copper and (b) stainless steel cathodes at 60 °C, using a graphite anode. For (a), the points are the averages of 9 experiments conducted at all the possible current density-copper concentration combinations according to Table 2. For (b), the points are the averages of 3 experiments conducted at different current densities according to Table 2, with 127 ppm initial copper concentration.

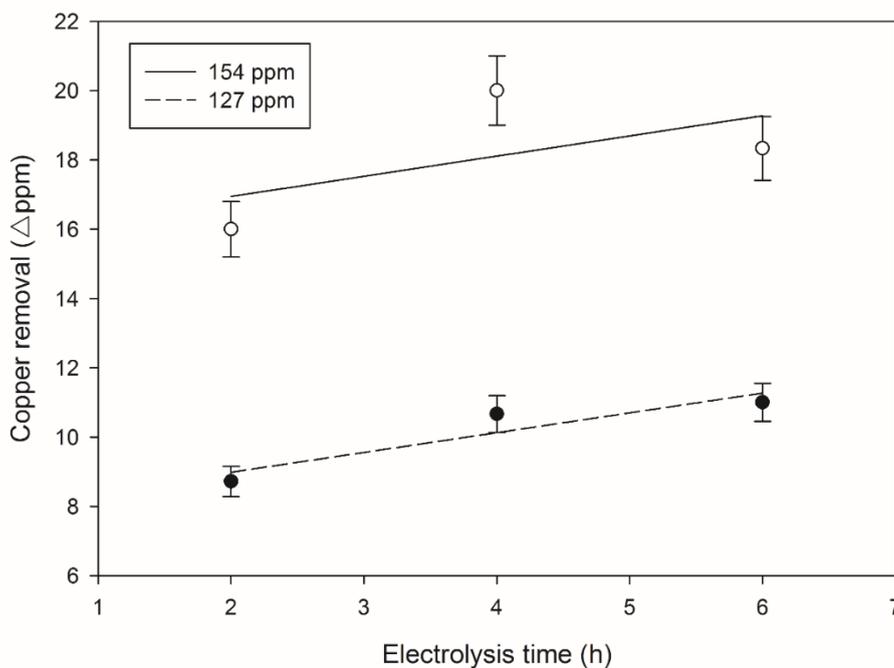


Figure 4. Interaction of electrolysis time and copper removal on initial copper concentration for the copper cathode at 60 °C using a graphite anode. The points are the averages of 3 experiments conducted at different current densities according to Table 2.

The efficiency of copper cathode was lower when compared to stainless steel as displayed in Figure 3. Maintaining the stability and repeatability in the experiments were much more difficult with the copper cathode due to the interaction of copper with the HCl and its vapor. Figure 4 shows the

interaction between electrolysis time and copper removal for two different initial copper concentrations for the copper cathode. As seen from the positions of data points in this figure, copper removing tendency diminished with increasing electrolysis time from 4 to 6 hours. However, it should be noted that the results and measurements were very challenging because copper was very reactive in this extremely corrosive environment. Therefore, stainless steel was found to be a better option especially for experiments covering longer durations.

3.3.3. Effect of Current Density on Copper Removal

The effect of three different current densities on copper removal was examined under the same experimental conditions. The main effect of current density on copper removal by copper and stainless steel cathodes were shown in Figure 5(a) and Figure 5(b), respectively. As it can be deduced from these figures, copper removal increased with increasing current density [46]. Conductivity and pH measurements indicated that the potential ranges and electrolysis times covered in this study did not cause a remarkable shift in the properties of the acid. The acidity measurements indicated an increase in all of the experiments due to the anodic reaction of water electrolysis which released H^+ ions into the solution. However, higher potentials carry the risk of decreasing the efficiency of the acid due to the inevitable H_2 evolution at the cathode and the Cl_2 evolution at the anode. In addition, longer electrolysis times cause irregular and discontinuous powder deposition, which does not adhere strongly but only remains hanging on the cathode as long as the voltage is applied.

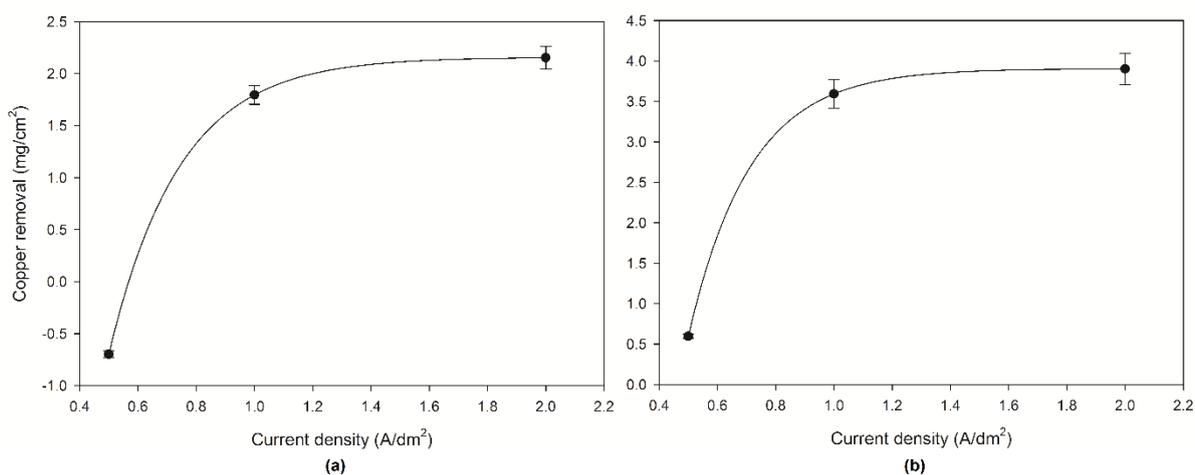


Figure 5. The main effect of current density on copper removal by (a) copper and (b) stainless steel cathodes at 60 °C. For (a), the points are the averages of 9 experiments conducted at all the possible electrolysis time-copper concentration combinations according to Table 2. For (b), the points are the averages of 3 experiments conducted at different electrolysis times according to Table 2, with 127 ppm initial copper concentration.

4. CONCLUSIONS

An electrochemical batch reactor was developed to recover copper from the regenerated pickling solution of a steel plant. A current density range of 0.5 to 2 A/dm² was selected from the examination of linear sweep voltammetry analysis. Higher current densities were avoided because of too much H₂ evolution at the cathode, the possibility of Cl₂ evolution at the anode and irregular copper deposition.

Graphite was chosen as the anode material, because it provided the best stability in hot HCl. Although copper recovery was higher with titanium anode, ICP-MS analyses revealed that this material released titanium ions into the electrolyte which can cause problems in long-term use of the acid.

Copper and stainless steel were preferred as the candidate cathode materials for easier utilization of the collected copper. The results showed that copper could be electrodeposited to both of the cathode materials. However, it was seen that copper was very reactive with the acid and its vapor and any interruption in the current (i.e. if it is not cathodically protected) at any stage, could cause introduction of large amounts of copper into the solution. It was observed that the efficiency of the copper cathode was very low, especially for longer durations. Therefore, stainless steel was decided to be a better option because it has much more resistance to the hot acid and its vapor and it does not possess the risk of incorporating any extra copper into the solution. Furthermore, it had a better copper collecting efficiency and collected copper was easily peeled off from the stainless steel surface after the experiments.

It was found that copper removal increased with increasing the initial copper concentration, current density, and electrolysis time. It was seen that there was no significant change in the properties of the acid as tracked by pH and conductivity measurements within the ranges of the parameters covered in this study. Furthermore, the acidity measurements revealed an increase due to the anodic reaction of water electrolysis.

The best operational conditions for copper removal and copper evaluation were attained at the current density of 2.0 A/dm² with a stainless steel cathode and graphite anode. The optimization was done by considering the amount and surface morphology of deposited copper together with the conditions of the electrolyte and electrode materials.

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