Recovery of Copper Ions from Industrial Wastewater by Electrodeposition

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Electrodeposition is an attractive method used for the recovery and removal of metal ions from metal coatings, metal processing and electronic industry wastes. In this study, copper was both removed and recovered from industrial wastewater containing copper by using the electrodeposition method. Two series of experiments were conducted by using copper and stainless steel as cathodes. In both experiments, the effects of current, pH, conductivity and initial copper concentration on the electrodeposition efficiency were investigated, and optimum values were obtained. With this method, the amount of copper removed from industrial wastewater under optimum conditions was 66% in the experiments conducted with the copper cathode and 80% in the experiments conducted with the stainless steel cathode. It was also observed as a result of the experiments that the copper removed from the wastewater was deposited on the cathode. In addition, reaction kinetics suitable for the experimental conditions were investigated and generally found to be compatible with a second-order kinetic model.

1 Introduction

The majority of industrial wastewaters contain undesirable rates of heavy metal ions according to wastewater discharge standards [1,2]. High concentrations of heavy metals coming from pollutants or natural sources into various environments such as water and air can be harmful; in air, animals and humans may absorb the pollution through breathing, whereas in water, the pollutants move to the soil, into plants and then to animals and humans through the food chain [3,4]. The toxic effects of heavy metals vary based on the properties of each metal and when they enter into a living body, they can cause severe disease and death. Therefore, the removal of heavy metals, which are extremely harmful in the ecosystem, from water and wastewaters is of great importance.

In the treatment of wastewaters containing heavy metals, physicochemical methods such as chemical precipitation, coagulation, electrochemical treatment, ion exchange, and recovery by

evaporation are used [5-9]. Since these methods are not commercially economic and easily applicable, the problem of disposing the mud obtained after treatment in most of them has led to the need for new reliable treatment methods. In particular, the treatment and/or recovery of wastewater containing low metal concentrations are an important problem for industries in terms of ecological and economic perspectives. An absence of by-products that may cause pollution, easy application and inexpensive cost have increased the interest in electrochemical treatment techniques. With its high chemical removal an electrochemical deposition technique that requires simple equipment and operating conditions has become an attractive treatment technique in literature.

The removal of heavy metals via electrodeposition is based on the removal of metal ions from a water environment using a porous cell and redox reactions. In the system, in an aqueous medium containing metal ions is the electrolyte, and the process occurs in an electrolytic cell consisting of a metal anode and a porous cathode.

Positively charged metal ions in the medium are reduced on the porous cathode by an electric current provided from outside of the cell so that they become an atom and form a layer on the surface of the porous structure. The very high surface area of these electrodes and the formation of a turbulent current during passing of the electrolyte solution through the electrodes cause a significant mass transfer to the electrode surface. The electrochemical reactions occurring in the electrolytic cell where the metal ions are stored are shown in Equations 1, 2 and 3.

cathodic reactions

$$M^{n+}(aq) + 2e^- \rightarrow M^0(s) \qquad \text{Eq-1}$$
$$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad \text{Eq-2}$$

anodic reactions

$$4OH^-(aq) \rightarrow O_2(g) + 2H_2O + 4e^- \quad \text{Eq-3}$$
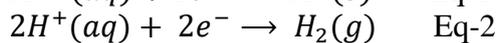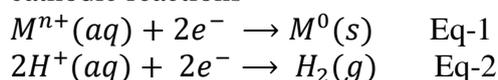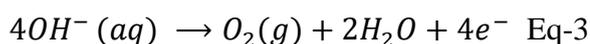
There are several competitive reactions in the cathode, and the most common reaction is the reduction of H^+ ions to hydrogen gas. Although the metal to be recovered will be deposited at the cathode, the anode must be carefully selected to ensure that it is effective in the electrolyte. A common reaction in the anode is shown in Equation 3.

Apart from the recovery of metals in their metallic forms, the electrochemical treatment of metal ion pollutants has several advantages: does not require extra chemical reagents, no sludge production, high selectivity, low operating cost and disinfects waste water. However, it also has disadvantages: the deposition rate and, in some cases, the composition of the solution can lead to the production of dendrites and loose or spongy deposits, and the interference resulting from the hydrogen evolution reaction or the dioxygen reduction must be minimized [10].

With this method, it can economically achieve a recovery of even very low concentrations of heavy metals and perform a successful treatment of metal ions from industrial wastewater [11-17]. Da Silva et al. [18] conducted a study on the recovery of metals in electronic waste. In the article, the aim was to recover tin from waste computer printed circuit boards (PCBs) using the electrodeposition method. By using a copper electrode, the tin, copper and lead in the printed circuit boards were recovered at a rate close to 100% [18]. In a study conducted by Guimaraes et al. [19], copper, tin and lead were recovered from printed circuit boards (PCBs) containing 48% copper, 40% other metals and 12% non-metal compounds. A result of 96% copper recovery was achieved with an agitation speed of 415 rpm at

25 °C and an electrolysis time of 15 hour [19]. In a study conducted by Jang et al. [20], the aim was to recover uranium by electrochemical deposition. The results showed that U/Transuranic recovery from a LiCl-KCl salt may be possible using a liquid Zn cathode [20]. Gezer et al. [21], used a carbonaceous porous material as an electrode material. Issabayeva et al. [22] developed an electrode material with good electrochemical properties by using activated carbon from palm shells, one of the solid wastes of the palm oil industry in Malaysia. In the electrodeposition study using this cathode, they obtained a removal efficiency of 60% for copper and 90% for lead [22].

The aim of this study is to recover and remove copper from industrial wastewater by electrodeposition reactors using copper and stainless steel (SS) cathodes. As the process variables, the effects of current, pH, conductivity, and concentration were investigated, and the reaction kinetics of the removal and recovery process were examined by obtaining optimum operating conditions.

2. EXPERIMENTAL

2.1 Chemicals and Analytical Methods

In this study, wastewater from an industry producing pure copper from scrap copper was used. This wastewater was an electrolysis liquid used in the electrolysis stage conducted to separate copper from other metals and impurities. This wastewater was at an initial concentration of 30 mg/L and was diluted 5 times before being used in the experiments. The wastewater had a pH of approximately 5 and a conductivity of approximately 1 mS/cm.

Chemicals used in this studiy were of high purity and were used as received. The pH measurements were conducted with a Sartorius pH meter, the conductivity measurements were performed with a Jenway conductivity meter. The copper was measured using an atomic absorption spectrophotometer (Solar Unicam-929 AA Spectrophotometer). GW Dual Tracking with a 5 V Fixed GPGC 3060 D was used as the power source.

2.2 Experimental Set-up and Procedure

For the removal of copper from wastewater and its recovery over the electrode by the electrodeposition method, an experimental setup composed of an electrochemical cell and a direct current power supply was established (Figure 1). The electrochemical cell had a diameter of 5 cm and a length of 10 cm and the top port of the cell was open to the atmosphere. Graphite with an 8 mm diameter and an 8 cm length was used as the anode, while copper and stainless steel (SS) with an 8 mm diameter and an 8 cm length were separately used as the cathode. Experiments were conducted first on parameters such as current, pH, and conductivity to obtain optimum electrochemical deposition efficiency for each electrolyte concentration containing approximately 6 mg/L copper with the copper and stainless steel cathodes.   The set of experiments is described in the Table 1. Before and after the experiments, the weight of the cathode was measured, and the weight increase in the electrode was calculated.
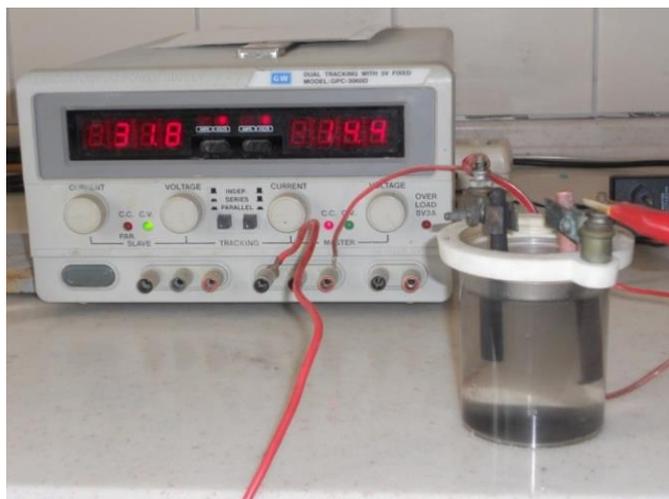
Figure 1. Experimental apparatus used in electrodeposition studies.

Table 1. Trial sets performed in the study.

Set	Process Parameters	Electrode Materials
1	Different current (0.25; 0.5; 0.75; 1 A) t: 10, 20, 30, 45, 60 min, pH: 3, EC: 10 mS/cm	Anode: Graphite Cathode: Copper, SS
2	Different pH values (2, 3, 4, 5) I: 0.75 A, t: 10, 20, 30, 45, 60 min, EC:10 mS/cm	Anode: Graphite Cathode: Copper, SS
3	Different conductivity values (5, 10, 15, 20 mS/cm) I: 0.75 A, t: 10, 20, 30, 45, 60 min	Anode: Graphite Cathode: Copper, SS
4	Different initial concentrations (10, 20, 30, 40, 50 mg/L) t: 10, 20, 30, 45, 60 min, pH: 3, EC: 10 mS/cm	Anode: Graphite Cathode: Copper, SS
Reaction Kinetics	Zero order (Eq- 4)	$\dfrac{dC}{dt} = k_0$
	First order (Eq- 5)	$\dfrac{dC}{dt} = k_1 C$
	Second order (Eq- 6)	$\dfrac{dC}{dt} = k_2 C^2$

3. RESULTS AND DISCUSSION

3.1 Effect of the Current

In the experiments conducted by using copper and stainless steel cathodes, the effect of current on electrodeposition was first investigated. Fig. 2a and b show the time-dependent change in copper concentration in the solution for different current values. The weights of the copper and stainless steel cathode were measured before and after the experiment. The weight in the electrodes increased as the current value increased. An increase in temperature at high current values caused the graphite electrode to dissolve therefore, the optimum current value was selected as 0.75 A for both electrodes although the removal efficiency increased with increasing current. In the experiments conducted by using 0.75 A

current for 60 min, the removal of copper ions from the solution was determined to be 60% for the copper cathode and 80% for the stainless steel cathode.

(a)   (b)
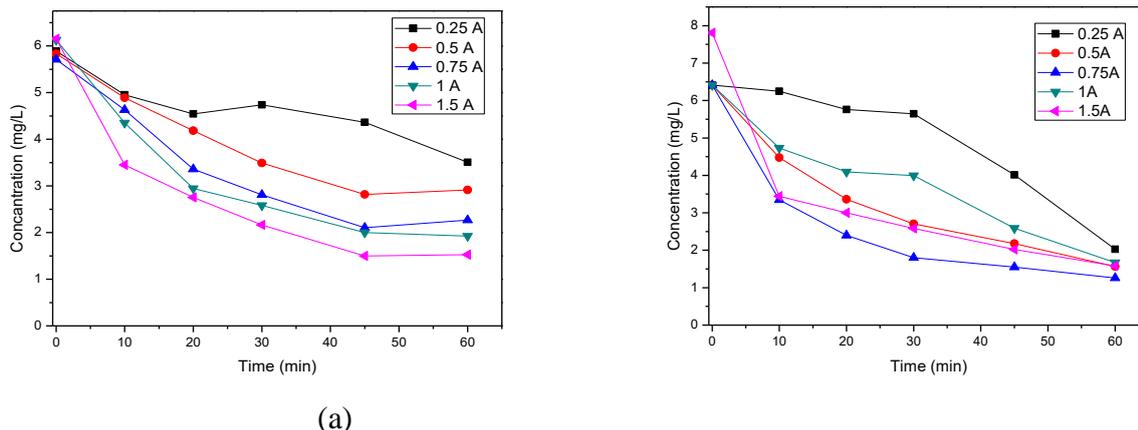
Figure 2. Time-dependent change of copper concentration in wastewater for the current experiments conducted with copper (a) and stainless steel (b) cathodes (pH 3; conductivity 10 mS/cm).

Table 2. Zero order, first- and second-order rate constants (k_0, k_1, k_2) and R^2 values for the different current experiments conducted with the copper and stainless steel (SS) cathode.

Current (A)	Copper Cathode		SS Cathode	
	Reaction rate (k_0)	R^2	Reaction rate (k_0)	R^2
0,25	0,0324	0,859	0,0718	0,894
0,5	0,0501	0,889	0,0740	0,876
0,75	0,0586	0,843	0,0725	0,709
1	0,0654	0,800	0,0725	0,951
1,5	0,0679	0,751	0,0821	0,658
Current (A)	**Copper Cathode**		**SS Cathode**	
	Reaction rate (k_1)	R^2	Reaction rate (k_1)	R^2
0,25	0,0071	0,871	0,0180	0,816
0,5	0,0125	0,918	0,0224	0,976
0,75	0,0167	0,888	0,0250	0,880
1	0,0193	0,894	0,0209	0,962
1,5	0,0227	0,887	0,0228	0,853
Current (A)	**Copper Cathode**		**SS Cathode**	
	Reaction rate (k_2)	R^2	Reaction rate (k_2)	R^2
0,25	0,0016	0,865	0,0050	0,725
0,5	0,0032	0,927	0,0078	0,986
0,75	0,0051	0,901	0,0104	0,982
1	0,0062	0,954	0,0068	0,894
1,5	0,0088	0,943	0,0077	0,972

The concentration changes against time obtained from the experiments conducted at different current values were transformed into a graph to determine the reaction order. The reaction rate constants were calculated from the lines obtained from zero order, first order and second order equations (equations are given in Table 1). Table 2 shows the calculated reaction rate constants. As the current value increased, the reaction rates also increased in the experiments conducted with the copper and steel cathodes. Although the correlation coefficient was appropriate for all kinetic models, the second-order kinetics is a better fit for both cathode materials.

3.2 Effect of initial pH

In electrochemical processes such as electrodeposition, pH is expected to be a key parameter because pH affects the balance between the cations and the electrode materials used to capture them [23].

To investigate the pH effect, different tests were conducted at pH values varied between 2 and 5 at a conductivity of 10 mS/cm and a current of 0.75 A, which are the optimum current conditions obtained previously. The reason for maintaining pH in this range is the precipitation risk of metal in wastewater at pH values > 6 and dissolution of the electrode at pH values ≤ 2 [1]. Figure 3 shows the changes in copper concentration for the copper and steel cathodes during these experiments. The highest removal efficiency for the copper and stainless steel electrodes was determined at the pH values of 4 and 3, respectively. For the copper electrode, at pH 2, the weight of the cathode decreased due to dissolution of the cathode. In the next step of the experiment, the wastewater was adjusted to pH 3. The copper ion removal for 60 min at pH 3 was 66% with the copper cathode and 80% with the stainless steel cathode.
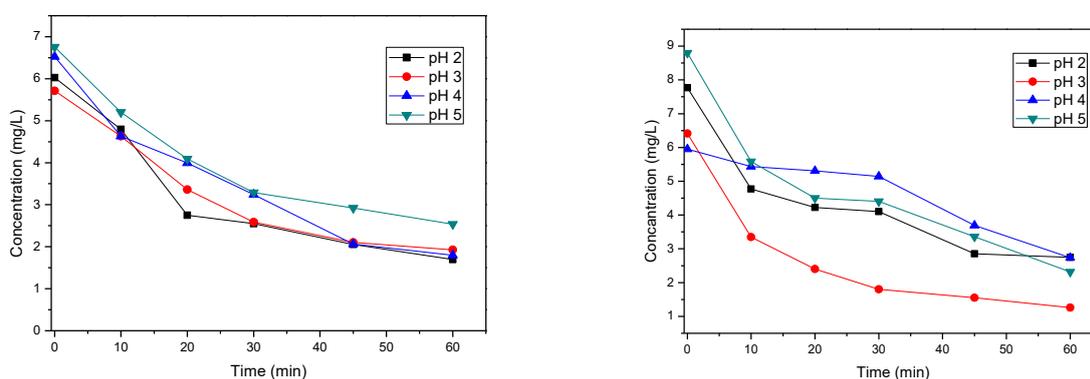
Figure 3. Time-dependent change of copper concentration in wastewater for the different initial pH experiments conducted with the copper (a) and stainless steel (b) cathodes (current 0.75 A; conductivity 10 mS/cm).

Table 3. Zero order, first- and second-order rate constants (k_0, k_1, k_2) and R^2 values for the different initial pH experiments conducted with the copper and stainless steel cathodes.

pH	Copper Cathode		SS Cathode	
	Reaction rate (k_0)	R^2	Reaction rate (k_0)	R^2
2	0,0695	0,819	0,0721	0,773
3	0,0633	0,876	0,0725	0,701
4	0,0755	0,918	0,0531	0,931
5	0,0667	0,866	0,0918	0,836
pH	Copper Cathode		SS Cathode	
	Reaction rate (k_1)	R^2	Reaction rate (k_1)	R^2
2	0,0210	0,909	0,0160	0,881
3	0,0190	0,940	0,0250	0,880
4	0,0218	0,978	0,0127	0,899
5	0,0161	0,939	0,0197	0,944
pH	Copper Cathode		SS Cathode	
	Reaction rate (k_2)	R^2	Reaction rate (k_2)	R^2
2	0,0071	0,970	0,0039	0,937
3	0,0062	0,976	0,0104	0,982
4	0,0070	0,972	0,0032	0,856
5	0,0041	0,982	0,0048	0,945

The concentration changes against time obtained from the experiments at different pH values were graphed to determine the reaction order. The reaction rate constants were calculated with the lines obtained from zero order, first order and second order equations. Table 3 shows the calculated reaction rate constants. Although there was a compatibility with all the kinetic models in the experiments conducted with the copper and stainless steel cathodes, the second-order kinetics were the best fit. In addition, it was found that the rate constants were high at low pH values.

3.3 Effect of Initial Conductivity

The pH value of the electrolyte solution at an initial concentration of approximately 6 mg/L copper was adjusted to 3. To increase the conductivity of the wastewater, NH_4Cl was used. The experiments were conducted to obtain an optimum conductivity by adjusting the conductivity of the solution to 5 mS/cm, 10 mS/cm, 15 mS/cm, and 20 mS/cm. It was observed in the experiments that the accumulation amount of metal decreased as the conductivity value increased. As seen in Figure 4, 10 mS/cm was selected as having the highest efficiency for both electrodes and occurred at the end of the 60th min (66% for the copper cathode and 80% for the stainless steel cathode).
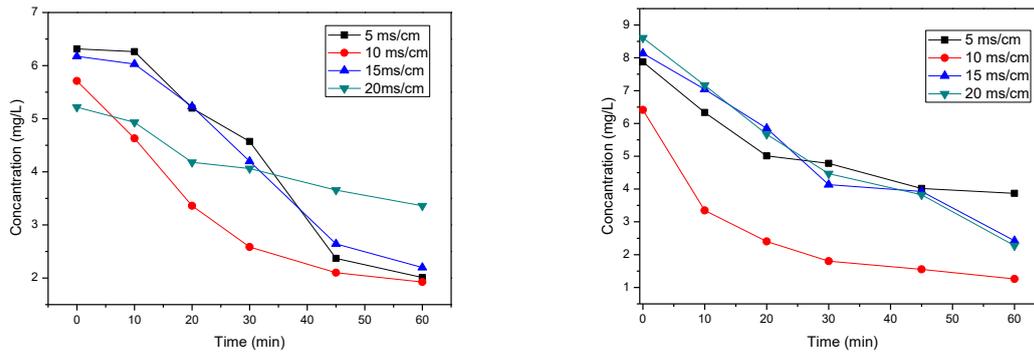
Figure 4. Time-dependent change of copper concentration in wastewater for the initial conductivity experiments conducted with the copper (a) and stainless steel (b) cathodes (pH 3; current 0.75 A).

The concentration changes against time obtained from the experiments conducted at different conductivity values were graphed to determine the reaction order. The reaction rate constants were calculated with the lines obtained from zero order, first order and second order equations. Table 4 shows the calculated reaction rate constants. It was observed in the experiments conducted with the copper and steel cathodes that there was compatibility with all the kinetic models. Furthermore, the rate constants decreased as the conductivity increased.

Table 4. Zero order, first and second-order rate constants (k_0, k_1, k_2) and R^2 values for the different initial conductivity experiments conducted with the copper and stainless steel cathodes.

Conductivity (mS/cm)	Copper Cathode		SS Cathode	
	Reaction rate (k_0)	R^2	Reaction rate (k_0)	R^2
5	0,0820	0,950	0,0643	0,843
10	0,0633	0,876	0,0725	0,709
15	0,0749	0,965	0,0937	0,954
20	0,0313	0,942	0,1015	0,965
Conductivity (mS/cm)	Copper Cathode		SS Cathode	
	Reaction rate (k_1)	R^2	Reaction rate (k_1)	R^2
5	0,0215	0,928	0,0116	0,901
10	0,0190	0,940	0,0250	0,880
15	0,0192	0,956	0,0196	0,964
20	0,0074	0,963	0,0212	0,980
Conductivity (mS/cm)	Copper Cathode		SS Cathode	
	Reaction rate (k_2)	R^2	Reaction rate (k_2)	R^2
5	0,0062	0,895	0,0022	0,944
10	0,0062	0,958	0,0104	0,982
15	0,0053	0,929	0,0046	0,911
20	0,0018	0,978	0,0050	0,906

3.4. Effect of Initial Concentration

The effect of initial copper concentrations on the electrochemical recovery of the copper was examined over a one-hour run time. The copper concentrations were between 10 and 50 mg/L. For each experiment, other operating conditions such as current density, initial pH, conductivity and electrode type were kept constant.

As shown in Fig. 5, the copper concentration in the solution decreased rapidly for both cathode materials during the first 30 min and then continued to decrease at a slowly. For example, within the first 30 min the copper concentration decreased 53% for the copper cathode and 44% for the stainless steel cathode with an initial concentration of 50 mg/L. At the end of 60 min, the final copper concentration was found to be 13.14 mg/L for the copper cathode (concentration reduction of 73%) and 18.3% mg/L for the stainless steel cathode (concentration reduction of 64%) with the initial concentration of 50 mg/L. This meant that there was a high rate of metal recovery for all studied initial concentrations. In a study conducted by Chen and Lim [10], up to 98% copper recovery was achieved at the end of 24 hours.
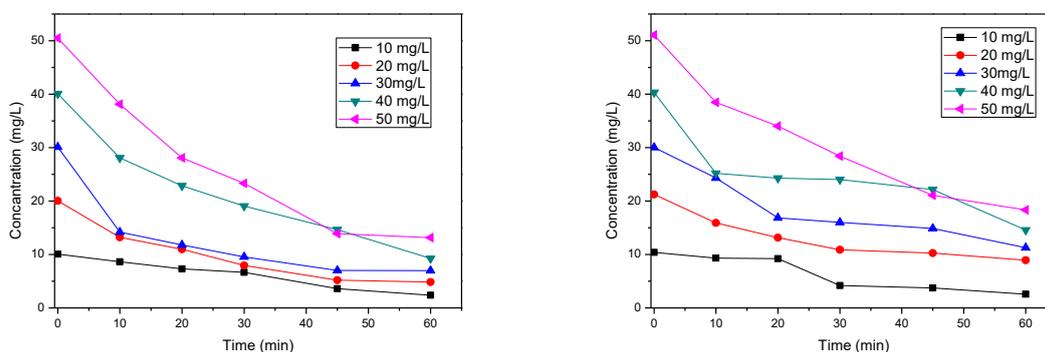
Figure 5. Time-dependent change of copper concentration in wastewater for the different initial concentration experiments conducted with the copper (a) and stainless steel (b) cathodes (pH 3; current 0.75 A; conductivity 10mS/cm).

The concentration changes against time obtained from the electrodeposition experiments performed at different initial concentrations were graphed to determine the reaction order. The reaction rate constants were calculated with the lines obtained from zero order, first order and second order equations. Table 5 shows the calculated rate constants. Although the compability to the all the kinetic models was good in the experiments conducted with the copper and stainless steel cathodes, the second-order kinetic model had the best fit for the stainless steel cathode in particular. When the initial copper concentration was higher, the electrodeposition kinetics were also observed to be faster.

Table 5. Zero order, first and second-order rate constants (k_0, k_1, k_2) and R^2 values for the different initial concentration experiments conducted with the copper and stainless steel cathodes.

Concentration (mg/L)	Copper Cathode		SS Cathode	
	Reaction rate (k_0)	R^2	Reaction rate (k_0)	R^2
10	0,1313	0,985	0,1444	0,878
20	0,2397	0,866	0,1863	0,833
30	0,3184	0,665	0,2861	0,846
40	0,4668	0,919	0,3257	0,748
50	0,6180	0,906	0,5215	0,929
Concentration (mg/L)	Copper Cathode		SS Cathode	
	Reaction rate (k_1)	R^2	Reaction rate (k_1)	R^2
10	0,0246	0,956	0,0253	0,910
20	0,0242	0,956	0,0136	0,908
30	0,0224	0,832	0,0152	0,912
40	0,0228	0,986	0,0132	0,822
50	0,0237	0,964	0,0170	0,982
Concentration (mg/L)	Copper Cathode		SS Cathode	
	Reaction rate (k_2)	R^2	Reaction rate (k_2)	R^2
10	0,0053	0,882	0,0051	0,916
20	0,0028	0,969	0,0010	0,960
30	0,0019	0,938	0,0009	0,944
40	0,0013	0,935	0,0006	0,990
50	0,0010	0,957	0,0006	0,827

4. CONCLUSIONS

In this study, the removal and recovery of copper from industrial wastewater containing copper was achieved with an electrodeposition method. By examining the effects of the operating parameters such as current, pH, conductivity and initial copper concentration, on the electrodeposition of copper, optimum conditions were obtained.

In both experiments conducted with copper and stainless steel cathode, the copper removal efficiency was observed to increase as the current values increased but the increase of temperature at high current values caused a negative effect on the electrodes. A concentration reduction of 66% for the copper cathode and 80% for the stainless steel cathode were obtained during the 60 min experiment and a 0.75 A current was determined as the optimum current. As a result of these experiments, it was found that low operating times were required at high current values.

In the experiments conducted for both cathodes at different pH values, the most appropriate pH value was selected as pH 3, where a concentration reduction of 66% was obtained for the copper cathode and 80% was obtained for the stainless steel cathode during the 60 min experiment. In the experiments performed at different pH values, the pH was kept between 2 and 6. The reason for this is to prevent

dissolution of the metal electrode at pH values of < 2 and precipitation of copper at pH values of > 6. In the experiments conducted with the copper and stainless steel cathodes, the highest efficiency was obtained with a conductivity of 10 mS/cm compared to the other values, thus, this was optimum conductivity.

In the experiments conducted with the synthetic solutions containing copper in different concentrations under optimum conditions it was observed that copper concentration did not have any effect on the electrodeposition. According to the data, it was observed that the weight increase in the copper electrode was not compatible with the copper amount removed from the wastewater. This is because copper molecules were attached to the cathode surface with weak bonds. The evidence of this was the precipitation of copper particles that were deposited on the cathode surface sinking during electrolysis to the bottom of the electrochemical cell. From the experimental results, it was observed that the compatibility of the kinetic models to all variables was high, but the second-order kinetic model was found to be more compatible than the other kinetic models.

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