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Influence of Different Sulphate Salts as Anolytes Towards the Performance of Copper(II) Recovery by using an Electrogenerative Process

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The influence of different types of sulphate salts towards the performance of copper(II) recovery via an electrogenerative process was investigated in this study. Here, the electrogenerative process was based on the use of a batch cell with reticulated vitreous carbon and zinc plate as the cathode and anode, respectively. The anolytes used in this study were ammonium sulphate, sodium sulphate and potassium sulphate. While the catholyte used was copper(II) sulphate. Results showed that ammonium sulphate with a concentration of 0.5 M was the most suitable anolyte to fully recover 100 mg L^{-1} initial copper(II) sulphate within three hours of operation. Ammonium sulphate has a higher mobility as compared to other salts. Type of electrolyte, size of ion and solubility are strongly implicated in determining its mobility. Thus, it provided a better recovery rate of copper(II) in this electrogenerative process. Finally, The recovery of copper(II) was evaluated by using atomic absorption spectroscopy (AAS).

Key words: Ammonium sulphate, copper(II) recovery, electrogenerative process, reticulated vitreous carbon, static batch cell
Kata kunci: Ammonium sulfat, perolehan semula kuprum(II), proses elektrogeneratif, karbon vitreus berongga, sel kelompok statik

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Copper is a reddish metal extensively used as a major interconnecting material in industries, such as cooking utensils production, electroplating industries, printed circuit board (PCB) manufacturing and decorative arts due to its excellent thermal and electrical conductivity properties [1]. Moreover, copper is one of the trace elements that is considered as a persistent, bioaccumulative and toxic (PBT) chemical. This chemical can remain in the environment for long periods of time and usually it is not readily destroyed and builds up in body tissues [2]. Long term exposure to copper also leads to headaches, dizziness, diarrhoea and kidney and liver damage [3]. On the basis of environmental protection, copper needs to be recovered. Therefore, serious approaches must be taken in order to limit and reduce industrial wastes that contain overloaded copper.

There are various methods that have been developed for the recovery of copper(II), such as ion exchange, reverse osmosis, adsorption, electrodialysis and precipitation [4]. One of the environmental friendly methods for the removal and recovery of copper(II) in aqueous solution is electrogenerative process which is a galvanic process. Galvanic process is an electrochemical process in which reactions that occur in a system produce an electric current without an external supply of energy due to the spontaneous chemical reactions. Hence, a good approach in the removal and recovery of metal in wastewater can be done by using a galvanic process [5].

Langer *et al.* (1986) discovered that electrogenerative processes are those in favorable thermodynamics of overall reaction ($\Delta G < 0$) where the Gibbs' free energy should be negative, with requisite kinetic and mechanistic factors in order to produce a desired chemical while generating electricity as a by-product [6]. Furthermore, second law of thermodynamics states that the entropy of the universe always increases for spontaneous processes, which means $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$. Then, at constant temperature and pressure, the change in Gibbs' free energy is defined as $\Delta G = \Delta H - T^*\Delta S$. When ΔG is negative, overall cell potential, $E°_{cell} > 0$; so the process will proceed spontaneously and it is referred as exergonic [7-15].

In an electrogenerative process, zinc is preferred as an anode rather than iron because it can give Cu^{2+}/Zn system higher $E°_{cell}$ of 1.100 V compared to Cu^{2+}/Fe system which has $E°_{cell}$ of 0.780 V [16]. In the system, the reduction process of Cu^{2+} ion to Cu metal occurs, followed by the oxidation of Zn metal to Zn^{2+} ion. The reactions involve the displacement of a more noble metal from the solution by a less noble metal. The overall reactions can be expressed by the following equations (1-3):

Anode: $Zn \rightleftharpoons Zn^{2+} + 2e^-$ $E° = 0.763$ V (1)

Cathode: $Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E° = 0.337$ V (2)

Overall: $Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$ $E°_{cell} = 1.100$ V (3)

Based on the reactions involved, the positive value indicates that the process occurs spontaneously without the supply of energy.

In an electrogenerative process, it is well known that types of catholyte and anolyte play an important role in determining the performance of the metal recovery process [17]. The selection of appropriate electrolytes (catholyte and anolyte) for each electrogenerative process is based on several factors such as type of liquors of the metal and ionic conductivity. Common electrolytes used as anolytes in an electrogenerative process are cyanide, chloride and sulphate. As cyanide solution is used as the catholyte in the recovery of gold and silver, sodium cyanide is always used as the anolyte [18-20]. The reason for the use of sodium cyanide as the anolyte is that it can be reused for the next cycle of analysis after undergoing a minimal treatment [20]. Few articles have reported the use of chloride solution as an anolyte in the recovery of copper [16], gold [17], palladium [21], cobalt [22] and lead [23], while there is only a single report on the use of sulphate solution as an anolyte in an electrogenerative process [24]. The influence of different types of anolytes, especially sulphate salts, towards the performance of an electrogenerative process is yet to be studied.

This study focused on the influence of different types of sulphate salts towards the recovery of copper(II) based on an electrogenerative process. Here the optimum conditions needed for the electrogenerative process were investigated by varying the type of sulphate salt, concentration of anolyte and initial concentration of copper(II) sulphate.

EXPERIMENTAL

1. Chemicals and materials

Ethanol, C_2H_5OH; and nitric acid, HNO_3 were obtained from ChemAR (Malaysia). While copper(II) sulphate, $CuSO_4$; ammonium sulphate, $(NH_4)_2SO_4$; sodium sulphate, Na_2SO_4; and potassium sulphate, K_2SO_4 were purchased from Merck (Malaysia). Oxygen, O_2; and nitrogen, N_2 gases were supplied by MOX (Malaysia). Electrodes used were reticulated vitreous carbon (RVC) 80 pores per inch (ppi) and pure zinc (99.0% purity), which were all procured from The Electrosynthesis Company (USA). Finally, anion exchange membrane Neosepta AM-1 was obtained from Tokuyama Corp. (Japan).

2. Static batch cell

In this study, a static batch cell comprising of cell compartments sandwiched together by six bolts and nuts with the dimension of 4.7 cm × 5.3 cm × 9.3 cm was utilized (Figure 1). In order to separate the two sides of electrolytes, an anion exchange membrane was utilized. Then, parafilm was utilized to adhere the electrodes to copper plates which functioned as current collectors. 100 mL of anolyte and catholyte were poured into the anode and cathode compartments, respectively. The cathode and anode were put at settled position in the compartments.

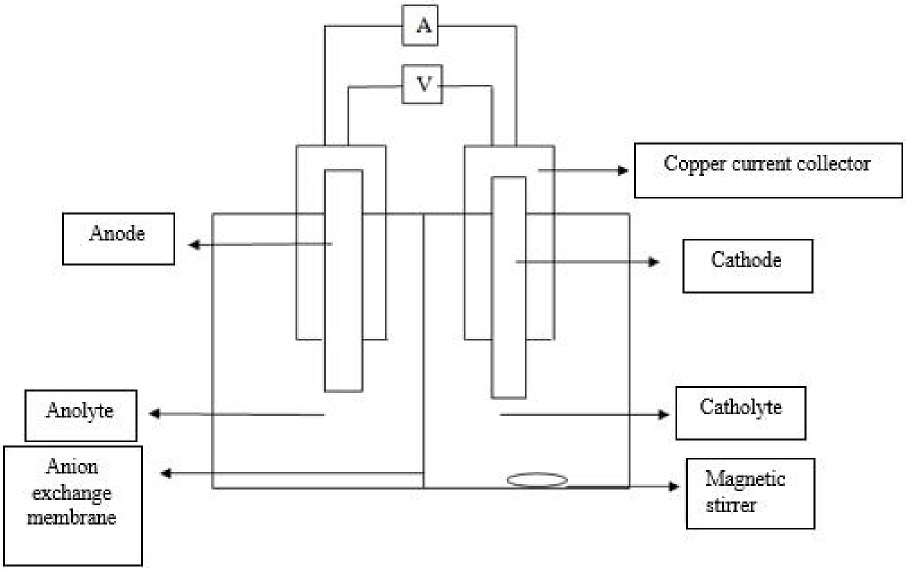

Figure 1. Schematic diagram of a static batch cell.

A magnetic stirrer with the speed of 400 rpm was utilized in the cathode in order to flutter the catholyte. The circuit was completed by connecting the current collectors to digital multimeters (Sanwa CD800A) using external conducting wires.

3. Ion exchange membrane

An anion exchange membrane (AM-1 Neosepta) was utilized in this electrogenerative process. This membrane is a semipermeable membrane that only anions could pass through.

4. Cathode and Anode

The cathode material utilized for copper(II) recovery was a carbon electrode of RVC with the porosity of 80 ppi. The cathode was activated for eight hours prior to use. There were two steps required during the activation process. Firstly, the cathode (2.0 cm × 5.5 cm × 0.07 cm) was immersed in the mixture of C_2H_5OH and distilled water with the proportion of 95:5 for four hours. The electrode was rinsed thoroughly with distilled water after four hours of immersion. Secondly, the electrode was immersed in HNO_3 for another four hours and then was rinsed again with distilled water. Finally, the activated cathode was stored in distilled water until use to maintain the surface moisture of the cathode. At the end of each experiment, the copper deposited on the cathode was stripped off by immersing the cathode in 1.0 M HNO_3 for a whole day and the cathode was rinsed thoroughly with distilled water and stored in distilled water before the next use. The anode used was pure zinc with a dimension of 2.0 cm × 5.5 cm × 0.07 cm. Sand paper was utilized to clean the zinc foil before each experiment.

5. Catholyte and Anolyte

Catholyte solutions of the concentrations of 100 mg L^{-1} and 500 mg L^{-1} were chosen for the catholyte. As for the anolyte, there were three anolyte solutions utilized in this experiment, which were $(NH_4)_2SO_4$, Na_2SO_4 and K_2SO_4. The concentrations of the anolyte solutions were 0.1 M, 0.3 M, 0.5 M and 1.0 M.

6. Procedures

A volume of 100 mL of the anolyte and catholyte were filled into the anode and cathode compartments, respectively. Then, the cathode and anode were immersed in the catholyte and anolyte in the fixed position. The catholyte was stirred by using a magnetic stirrer throughout the process.

Multimeters were connected to the cathode and anode to measure the voltage and current. The initial values of the current and voltage were recorded. Then, the values of the current and voltage were recorded for every 30 minutes. 500 µL aliquots of the catholyte were collected for every 30 minutes to measure the amount of copper recovered from the catholyte solution. The copper(II) concentration was analysed by using AAS (Perkin Elmer Analyst 200, USA) with an air acetylene flame at a wavelength of 324.8 nm. The percentage recovery of copper(II) can be calculated by using the following equation (4):

$$\text{Percentage of copper(II) recovery} = [(C_o - C_t) / (C_o)] \times 100\,\% \quad (4)$$

where C_o is the initial copper(II) concentration in mg L^{-1} and C_t is the copper(II) concentration in mg L^{-1} at a specific time.

Two digital multimeters (Sanwa CD800A) were utilized in this experiment to measure the electrical potential and the stream of electric flow during the experiment. Both readings were recorded every 30 minutes during four hours of experiment. The removal process of copper(II) from the solutions was investigated without the presence of O_2 by deaeration of the batch cell with N_2 gas. As a test of reproducibility, a particular experimental run was performed three times.

RESULTS AND DISCUSSION

1. Galvanic deposition study

The experiment of the recovery of copper(II) was conducted by using an electrogenerative system. This four-hour experiment was driven by the mechanisms of spontaneous electrochemical reactions that occur in galvanic systems. As a test of reproducibility, a particular experimental run was performed three times for each anolyte used. Initially, a layer of dark copper was deposited on the surface of the cathode, which was RVC. As the experiment progressed, an outer layer of dark copper deposits which were not infused into the pores of the cathode turned into green-blue colour. It was suspected that copper(II) oxide layer had been formed due to the exposure to oxygen. The electrode reaction was driven by mass transfer. Here the diffusion of the dissolved reactant occurred from the bulk solution to the surface of the electrode [25,26].

During the experiment, the presence of dissolved oxygen in the solution must also be taken into account. It has been reported that the recovery of copper(II) performed well in the absence of oxygen [27]. The experiment resulted with copper(II) being deposited on the electrode within a short period of time in deoxygenated state. Meanwhile, in the presence of oxygen, it took longer time for copper(II) to be recovered. Thus, during the experiment, N_2 gas was purged into the catholyte and anolyte to remove dissolved oxygen in the solutions.

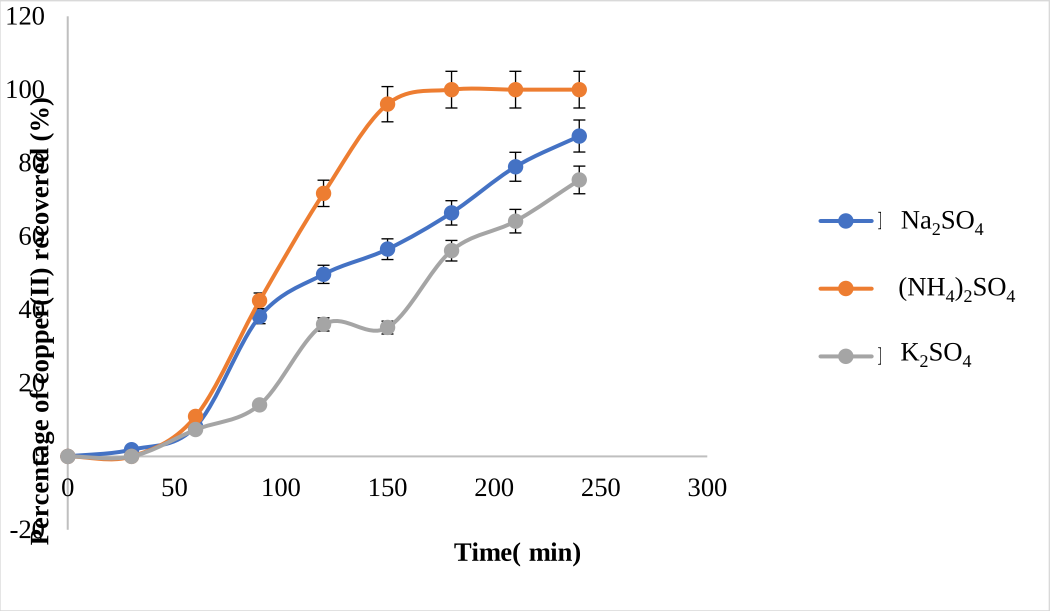

Figure 2. Graph of logarithm of normalized copper(II) concentration versus time by using $(NH_4)_2SO_4$, K_2SO_4 and Na_2SO_4 for 100 mg L^{-1} $CuSO_4$ solution.

Figure 2 shows the graph of logarithm of normalized copper(II) concentration versus time by using three different anolytes, which were $(NH_4)_2SO_4$, Na_2SO_4 and K_2SO_4. From the graph, it can be noticed that the concentration of copper(II) decreased over time in four hours. In consequence, it can be seen that $(NH_4)_2SO_4$ as the anolyte was able to recover copper(II) faster than Na_2SO_4 and K_2SO_4. Furthermore, this result (linear concentration-time relationship) also proves that the copper(II) reduction on the cathode was a mass transport-controlled process [5].

2. Influence of different anolytes

The performance of copper(II) recovery by using three different anolytes ($(NH_4)_2SO_4$, Na_2SO_4 and K_2SO_4) was quantified by using an AAS. Figure 3 shows that full recovery of copper(II) was faster with the use of $(NH_4)_2SO_4$ as the anolyte compared to Na_2SO_4 and K_2SO_4. The electrogenerative process with $(NH_4)_2SO_4$ as the anolyte only needed three hours to achieve a full recovery of copper(II) with the initial copper(II) sulphate concentration of 100 mg L^{-1}. While full recovery of copper(II) could not be achieved for the other two anolytes (Na_2SO_4 and K_2SO_4), even though the electrogenerative process was carried out for four hours.

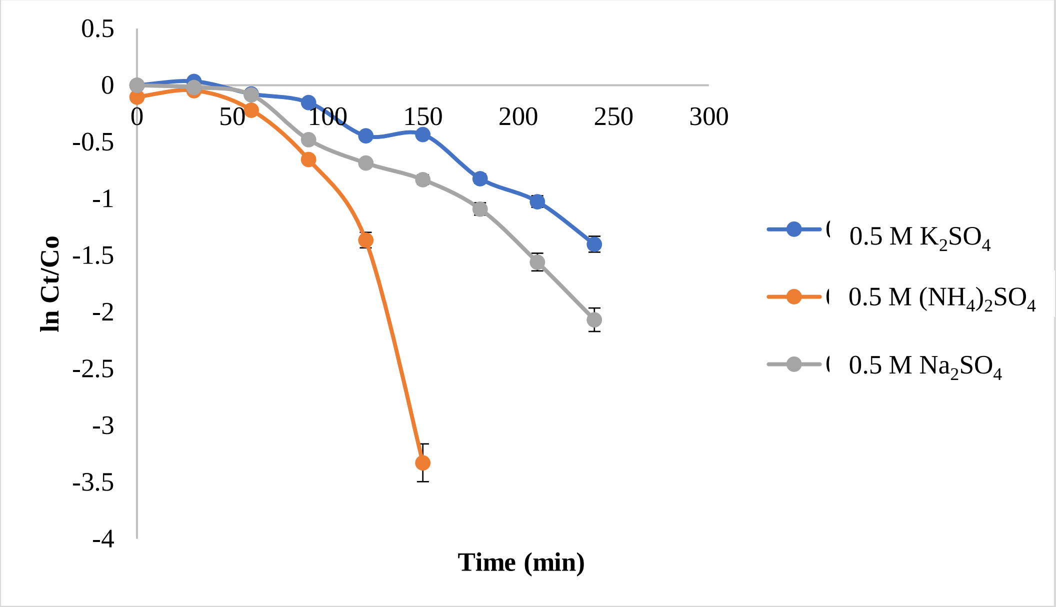

Figure 3. Graph of percentage of copper(II) recovered versus time by using 0.5 M Na_2SO_4, 0.5 M $(NH_4)_2SO_4$ and 0.5 M K_2SO_4 anolytes, and 100 mg L^{-1} $CuSO_4$ catholyte.

The explanation for this observation is that $(NH_4)_2SO_4$ is a known strong electrolyte. It has a higher electrical conductivity compared to Na_2SO_4 and K_2SO_4 at room temperature [28]. In an aqueous solution, a strong electrolyte is a good conductor of electricity. Since $(NH_4)_2SO_4$ has a higher electrical conductivity, it increases the current efficiency in an electrogenerative process. It facilitates the transfer of ions from the anode to the cathode with lower resistance. Thus, this will contribute to the faster recovery of copper(II) ions.

Size of cations also has an influence in determining the mobility of the ions [29-32]. Smaller sized cations have higher ion mobility compared to larger sized cations. Here, the size of ammonium ion (ionic radius of 175 pm) is smaller than the size of sodium (190 pm) and potassium ions (243 pm) [29]. Thus, the ammonium salt used in this study has higher mobility which later contributed to the faster movement of electrons in the electrogenerative process.

Another explanation for this observation is that $(NH_4)_2SO_4$ also has higher solubility than Na_2SO_4 and K_2SO_4. The solubility of $(NH_4)_2SO_4$, Na_2SO_4 and K_2SO_4 at room temperature are 74.4 g 100 mL^{-1}, 19.5 g 100 mL^{-1} and 11.1 g 100 mL^{-1}, respectively [28]. Here, the ionic compound of $(NH_4)_2SO_4$ dissociates into separate ions quicker and instantly solvates within the shell of water molecules. Hence, it helps the movement of electrons faster within a short period of time. As a result, a faster recovery of copper(II) was achieved by using $(NH_4)_2SO_4$ as the anolye in this electrogenerative process.

3. Influence of anolyte concentration

One of the important parameters in an electrogenerative process is the anolyte concentration. This is due to the ability of an anolyte to maintain constant ionic strength and to decrease the resistance of the solution by reducing the electromigration effect [16]. In this study, the experiment was conducted with $CuSO_4$ solution as the catholyte and $(NH_4)_2SO_4$ solution as the anolyte in order to choose the optimum anolyte concentration. It was found out that faster recovery of copper(II) was obtained with the use of 0.5 M $(NH_4)_2SO_4$ although the concentration was increased up to 1.0 M (Figure 4). The explanation for this observation is that an anolyte too concentrated with sulphate ions causes the oxidation of zinc electrode becomes slower [14]. Since the oxidation process becomes slower, the redox process also decreases. Consequently, this contributes to the slower recovery process of copper(II) by using a higher concentration of $(NH_4)_2SO_4$.

At lower concentrations of $(NH_4)_2SO_4$ (0.1 M and 0.3 M), copper(II) was not fully recovered although the experiments were conducted up to four hours. Lower concentrations of $(NH_4)_2SO_4$ decreased the conductivity of the electrochemical system due to low quantity of sulphate ions available in the anolyte. Zinc oxidation process became slower due to low quantity of sulphate ions available. Besides, lower anolyte concentrations also decreased the driving force for the movement of ammonium ions. Low driving force (mobility) of ammonium ions also contributed to low recovery of copper(II) since the movement of electrons in the electrogenerative process was slow. Therefore, it is important to use an ideal anolyte concentration to achieve higher recovery of copper(II).

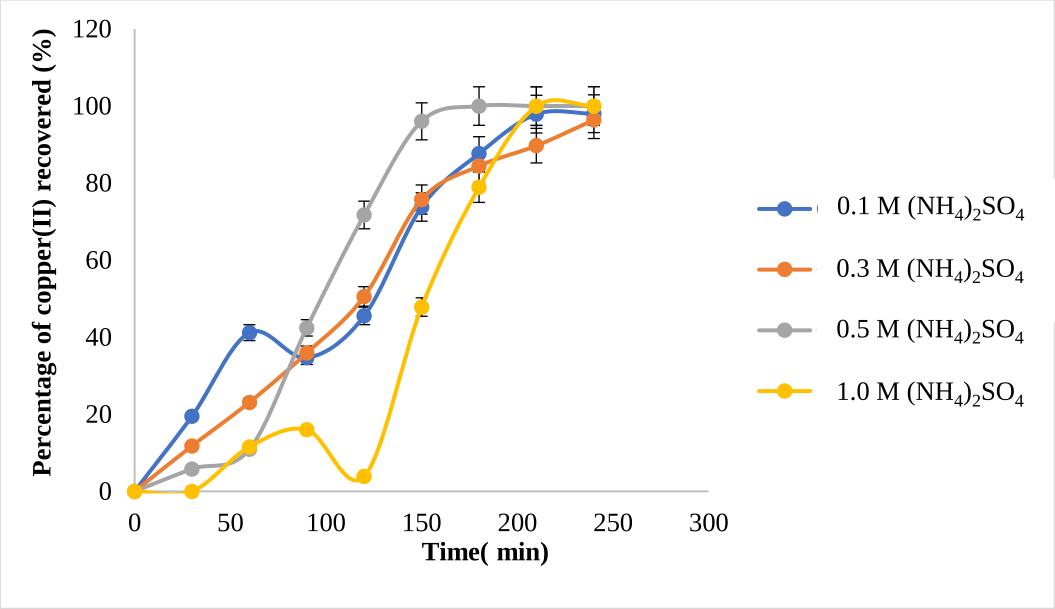

Figure 4. Percentage of copper(II) recovered versus time by using 0.1 M, 0.3 M, 0.5 M and 1.0 M $(NH_4)_2SO_4$ anolytes, and 100 mg L^{-1} $CuSO_4$ catholyte.

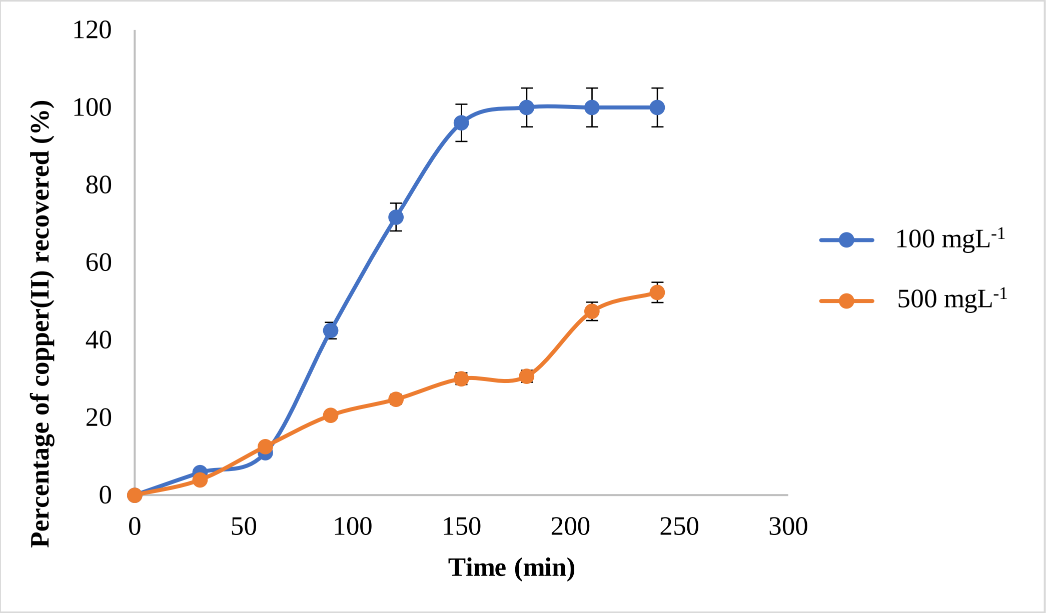

Figure 5. Percentage of copper(II) recovered versus time by using 0.5 M $(NH_4)_2SO_4$ anolyte and 100 mg L^{-1} and 500 mg L^{-1} $CuSO_4$ catholyte solutions.

4. Effect of initial catholyte concentration

The removal of copper(II) from its catholyte solution is highly dependent on the concentration. Here, two different copper(II) concentrations were studied. It was found that a longer time is needed to fully recover copper(II) from a higher initial concentration of $CuSO_4$ solution (Figure 5). This is appertaining to slow charge transfer rate in higher species of $CuSO_4$ concentrations [14]. Thus, a concentration of 100 mg L^{-1} $CuSO_4$ was utilized in this study.

CONCLUSION

The present work confirms that the recovery of copper(II) from its sulphate solution can be performed using an electrogenerative process. The recovery of copper(II) was successfully demonstrated with a variety of parameters, such as influence of oxygen, different anolytes, anolyte concentration and initial catholyte concentration. It was found that 0.50 M $(NH_4)_2SO_4$ tends to be the best anolyte because full recovery of copper(II) was achieved in three hours of operation as compared to Na_2SO_4 and K_2SO_4. The incorporation of subtle effects of type of electrolyte, size of cation and solubility of $(NH_4)_2SO_4$ are responsible for this phenomenon.

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