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Electrochemical removal of copper from synthetic wastewater using rotating cylinder electrode

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Abstract

The performance of a batch undivided electrochemical reactor with a rotating cylinder electrode of woven-wire (60 mesh size), stainless steel 316, is examined for the removal of copper from synthetic solution of o.5 M sodium chloride containing 125 ppm at pH $\approx$ 3.5. The effect of total applied current, rotation speed on the figures of merit of the reactor is analyzed. For an applied current of 300 mA at 100 rpm, the copper concentration decreased from 125 to < 0.07 mg l^{-1} after 60 min of electrolysis with a specific energy consumption of 1.75 kWh kg^{-1} and a normalized space velocity of 1.62 h^{-1}. The change in concentration was higher when the total applied currents were increased because of the turbulence-promoting action of the hydrogen evolution. The results suggest that the applied current must represent a compromise between the increase in space time yield or normalized space velocity and the increase in the specific energy consumption.

Key Words: Electrochemical effluent treatment, rotating cylinder electrode, copper removal

Introduction

Of all the natural resources, water is unarguably the most essential and precious. Life began in water and life is nurtured with water. It is a universal solvent and as a solvent, it provides the ionic balance and nutrients [1], and supports all forms of life. So that any pollution in water can be a major problem spatially when the pollutants are heavy metal ions, although heavy metals are natural components of the environment but when their concentrations increase more than normal levels they become potentially hazardous [2]. At the last decades, the problem has extended due to the increasing in industries and the wars that there effect keep on many years. Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 [3]. Copper is an essential element needed for human and other living organisms, which primarily involves several proteins and enzymes. Copper is used to make electrical wiring, pipes, valves, fittings, coins, cooking utensils and building materials. It is present in munitions, alloys (brass, bronze) and coatings. Copper compounds are used also in fungicides, algicides, insecticides and wood preservatives and in electroplating, azo dye manufacture, engraving, lithography, petroleum refining and pyrotechnics. Copper compounds, can be added to fertilizers and animal feeds as a nutrient to support plant and animal growth. Deficiency of copper causes demineralization of bones, anemia, fragility of arteries, and discoloration of skin as well as hair. High concentration of copper (above 3.0 mg/l) in water may lead to accumulation of copper in liver and lenticular nucleus of brain. Ultimately, it may cause hepatic cirrhosis and brain necrosis. Renal damage may also occur due to accumulation of copper in kidney by means of consumption of water with high copper concentration in excess of permissible limit [4].

Wastewaters from metal finishing, textile industries, electronics industry or washing effluents for remediation of soil contaminated with copper may contain up to 500 mg/L copper, which, depending on the worldwide environmental regulations and must be controlled to a permitted level before being discharged into the environment [5]. Where, the permissible limit of copper in sources of drinking water just like rivers is between 1.5 to 2 mg/L according to the EU [6].

The electricity has been used to treat water firstly in UK in 1889 [7]. Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state. Electrochemical wastewater technologies involve relatively large capital utilization. However, with the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades [8]. The applications of electrochemical technology in environmental treatment are a clean technology and the only processes have the ability to recycle materials.

Because of the rate of the electrodeposition was limited by mass-transport problems hydrodynamic electrodes are developed. Hydrodynamic electrodes are electrodes, which function in a regime of forced convection. The advantage of these electrodes is increased transport of electroactive species to the electrode, leading to higher currents and thence a greater sensitivity and reproducibility. Most of the applications of these electrodes are in steady-state conditions, i.e., constant forced convection and constant applied potential or current [9]. Electrodes have been rotated at least since 1905 to provide some quantitative control of solution conviction [10]. Recently, some authors have focused attention on the electrolytic treatment of copper; Reade et al. [11] studied the removal of cadmium and copper with a reticulated vitreous carbon rotating cylinder electrode. A decrease in cadmium concentration from 56 ppm to less than 1 ppm was reported. In a previous paper from this laboratory [12] it was reported that a packed bed rotating cylinder electrode of woven wire meshes presents mass transport coefficients three times higher than those obtained with smooth electrodes because of the turbulence-promoting action of the meshes.

The present study focused on the analysis of the behavior of an undivided electrochemical reactor with a rotating packed bed electrode of woven wire meshes for the removal of copper and the study of the process variables, such as rotation speed, total applied currents on the ‘figures of merit’ of the reactor.

Experimental Work

The experiments were performed in an undivided batch reactor, is consisted of three electrodes and placed in 2l beaker at which the electrolyte 900 ml volume has been treated. Cathode electrode was used in dimensions as 3.5, 3 cm diameter and long respectively. The lower part of the electrode was open but the upper part was joined to a Teflon sleeve in order to orientate the electrolyte flow through the mesh. A perforated Teflon disc was used on the top of the working electrode sleeve, centrally positioned, where Teflon shaft was passed through it, which is used as supporting for the electrochemical cell and to distribute the electrical connections to the electrodes. Four planer graphite anodes (10×0.7×5 cm), fixed in Teflon disc at the bottom of the anode plates and they were fixed from the top with the perforated Teflon disc, which is proved a good support. The gap between the cathode and anode plates was 1.5 cm and calomel reference. Figure 1 depicts schematically the complete experimental arrangement.

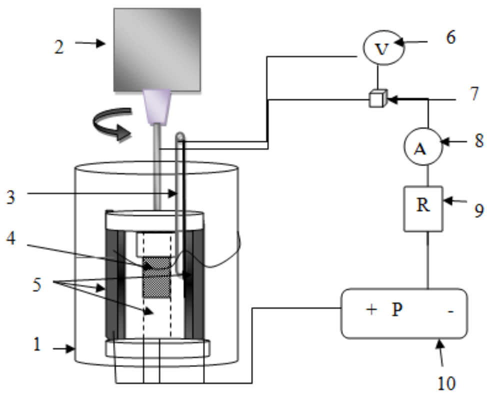

Fig. 1, General view of the reactor,(1) beaker 2l,(2) electrical mixer,(3) reference electrode,(4) counter electrode,(5) anode electrode,(6) digital voltmeter,(7) electrical connecter,(8) digital ammeter,(9) resistance box,(10) power supply.

All solutions were prepared using AnalaR grade chemicals and distilled water. Cupric ion solutions were prepared by dissolving copper chloride in an aqueous solution of 0.50 NaCl at pH 3.5.

The concentration of copper ions was monitored by atomic absorption analysis using an air–acetylene flame, in order to determine the variation of concentration with time and the differential concentration decrease. From these data the current efficiency, the space time yield, the normalized space velocity and the specific energy consumption were intended.

The anodic reaction was oxygen evolution:

$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^- \qquad ...(1)$$

The main cathodic reaction is:

$$Cu^{+2} + 2e^- \rightarrow 1/2O_2 + 2H^+ \qquad ...(2)$$

and the side reactions were the Hydrogen evolution:

$$H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad ...(3)$$

Theory

For a rotating cylinder electrode the electrolyte is assumed to be well-mixed at all times. Thus, for a batch reactor in the potential range where the tin deposition is mass-transfer controlled, the change of concentration with time is given by [13].

$$C(t) = C(0)\exp(-ka_e t) \qquad ....(4)$$

Consequently, the mass-transfer coefficient has to be evaluated in order to discuss the results obtained experimentally.

The fractional conversion and the accumulative current efficiency as a function of time are given by, [13,14]

$$x(t) = 1 - \exp(-ka_e t) \qquad ....(5)$$

and

$$\beta(t) = \frac{\nu_e F V C(0) x(t)}{M \int_0^t I(t)dt} \qquad .....(6)$$

Other ‘figures of merit’ used to compare the performance of the electrochemical reactor are the mean value of the space time yield, the normalized space velocity and the specific energy consumption, which were calculated with the following equations:

$$\rho_{mean}(t) = \frac{C(0)x(t)}{t} \qquad \text{....(7)}$$

$$s_n(t) = \frac{\ln[1-x(t)]}{t \ln 10} \qquad \text{....(8)}$$

And

$$E_s(t) = \frac{\int_0^t U(t)I(t)dt}{VC(0)x(t)} \qquad \text{....(9)}$$

Results and Discussion

Figure 2-A shows the copper concentration as a function of time at different applied current. For a given applied current, there is a pronounced decrease in concentration during the first stages of the experiments, but at longer times, the concentration approaches a constant value. A linear decay of copper concentration is observed clearly but at total applied current -250 and -300 mA, a deviation from linearity can be seen, and while at lower applied currents the decay is linear. When the concentration ramp linearly with time this means that the deposition is under mass transfer control, which is a theoretical expectation [15, 14], within the accuracy normally expected for this type of measurements. The experimental results, in general, are in close agreement with theoretical prediction mainly during the beginning of the experiments. Although the plots of normalized concentration of copper as a function of electrolysis time were apparently exponential, the expectation of linearity for the $\ln[c_{(t)}/c_{(0)}]$ against time plot was confirmed only for a portion of the curve, as shown in figure 2- B . This behavior was also observed in previous work as for copper [16], cadmium [14, 17], tin [13], and lead [18]. Where this deviation from linearity with time in the deposition of copper ions is due to the fact after half-an-hour more than 90% of copper ions had been removed then reduction in the current efficiency can be expected.

Fig. 3 shows the normalize and the linearization of normalized concentration of copper as a function of time at different rotation speeds. It may be observed from figure 3-A that the normalized concentrations of the copper remain practically slightly unchanged throughout the electrolysis with different rotation speeds. Although in general there are reductions of concentrations with time, for longer time of deposition there is also a deviation from linearity, which can be noticed as in the decay concentration curves presented in Fig. (3).

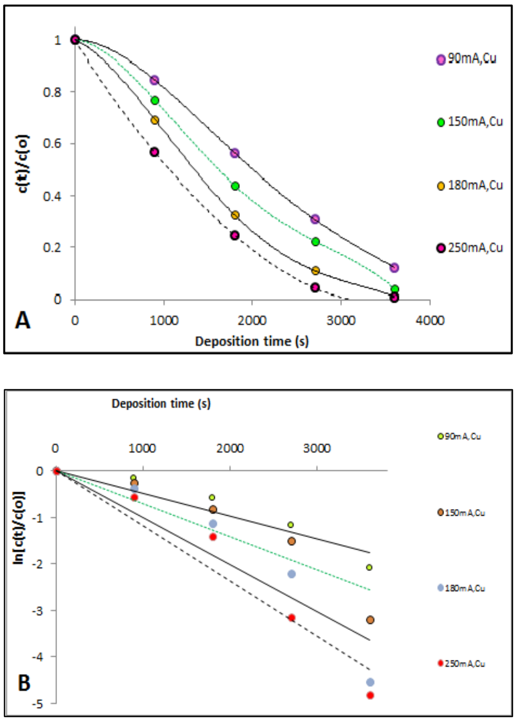

Fig. 2, (A.) Normalized concentration of copper (c(t) /co) as a function of time. (B) Linearization of normalized concentration as a function of time for different applied current

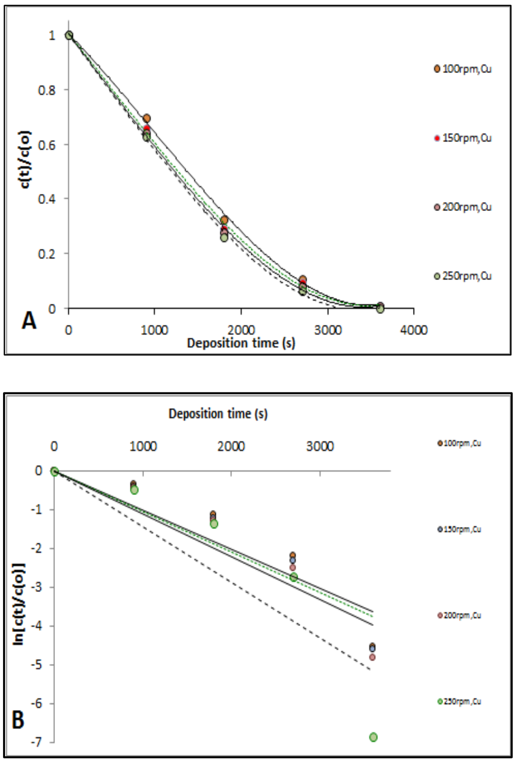

Fig. 3, (A.) Normalized concentration of copper ($c_{(t)}$ $/c_{o}$) as a function of time. (B) Linearization of normalized concentration as a function of time for different rotation speeds.

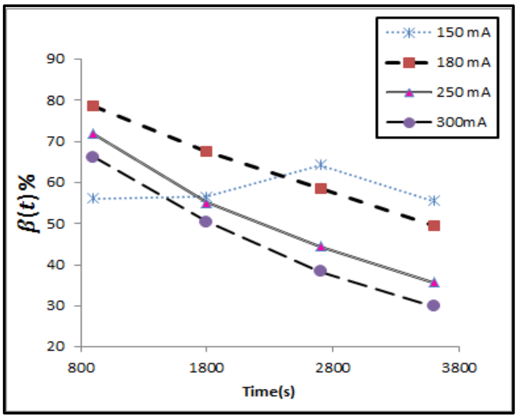

Fig. 4, Cumulative current efficiency as a function of time for different applied currents at constant rotation speed of 100 rpm

Fig. (4) shows typical curves of the accumulative current efficiency as a function of time at different total applied current. For a total applied current of 180 mA the current efficiency is close to 100% early in the experiment and decreases at higher times because the copper concentration decreases and the oxygen reduction predominates. For higher values of the total applied currents, hydrogen evolution possibly occurs as cathodic side reaction and lower values of current efficiencies are measured.

Fig. (5) and 6 show the mean value of the space time yield and the normalized space velocity as a function of the applied current where there was an increasing effect with increase in the total applied current can be noticed.

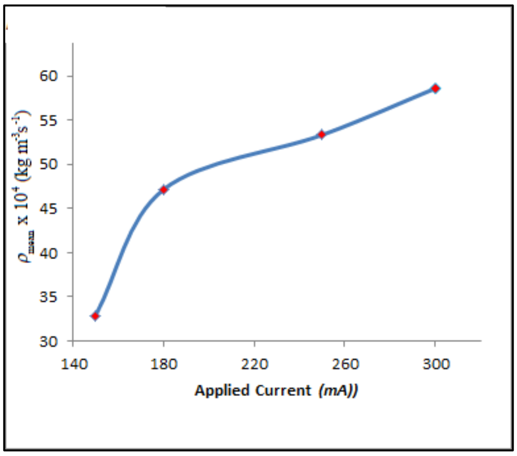

Fig. 5, Mean value of the space time yield as a function of total applied currents at constant rotation speed of 100 rpm

Fig. (7) shows the specific energy consumption as a function of time for different total applied currents. For a given applied current, as the solution becomes more dilute the current efficiency decreases and the energy consumption increases. The increase in *Es* when the total applied current increases can be attributed to a decrease in current efficiency because of the onset of hydrogen evolution. The specific energy consumption is in accordance with values previously reported [17, 19].

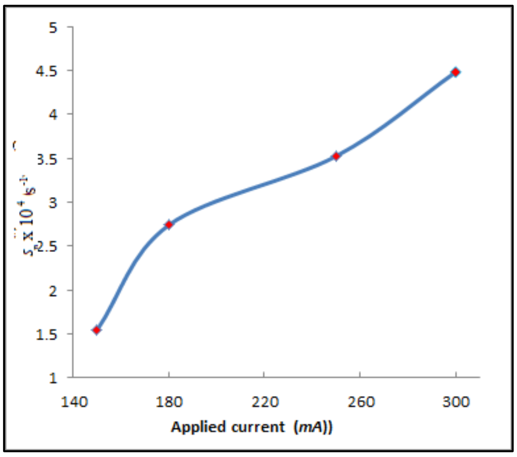

Fig. 6, Normalized space velocity as a function of total applied currents at constant rotation speed of 100 rpm

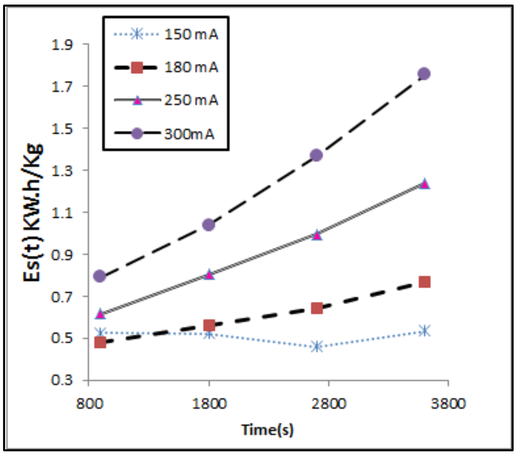

Fig. 7, Specific energy consumption as a function of time for different total applied currents at constant rotation speed of 100 rpm

Conclusions

The following conclusions may be drawn:

1. The copper removal from dilute aqueous solution can be performed efficiently in an electrochemical reactor with a three-dimensional rotating cylinder electrode of woven wire sheet. The total applied currents show an emphatic effect on the removal rate of copper and the increasing in rotation speed also increase the removal rate of copper.
2. The copper concentration follows the expected theoretical behavior during the first stages of the experiment.
3. Hydrogen evolution, as side cathodic reaction, is beneficial for tin removal because the turbulence promoting action increases the current for the main reaction and enhances the space time yield or the normalized space velocity. However, at the same time it is detrimental to the specific energy consumption because the current efficiency decreases.
4. The process shows that the removal of copper from aqueous solutions does not require addition of chemical additives, which reduces the cost and makes the process efficient and with no chemical waste or sludge.

Nomenclature

a_e	reactor specific surface area (m^{-1})
A_s	electrode specific surface area (m^{-1})
C	concentration (mg l^{-1} or kg m^{-3})
E_s	specific energy consumption (W s kg^{-1} or kWh/kg)
F	faradaic constant (C mol^{-1})= 96500 Coulomb
I	total current (A)
k	mass-transfer coefficient (m s^{-1})
M	atomic weight (g mol^{-1})
s_n	normalized space velocity (s^{-1} or h^{-1})
t	time (min or s)
U	cell voltage (V)
V	effective electrolyte volume within the reactor (m^3)
x	fractional conversion

Greek symbols

β	current efficiency (%)
ν	kinematic viscosity (m^2 s^{-1})
ν_e	charge transfer of the electrode reaction
ρ_{mean}	mean space time yield (kg m^{-3} s^{-1})

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