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Removal of copper from a copper sulphate solution using an ultrasonic-electrolysis process

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Abstract: The application of ultrasonic-electrolysis process for the removal of copper is studied. In the ultrasonic field cavitation acts as jets and agitates the solution and breaks the barrier layer between the cathode surface and the bulk of the solution. Thus increases metal deposition on the cathode surface. The results show that an ultrasonic field is successful for the removal of low copper concentrations in solution.

Keywords: ultrasonic-electrolysis; sonication; copper electrolysis

Introduction

Many metal plants discharge their wastewaters to sewerage or to open water systems without proper purification. The volume of metal-containing wastewater from these industries, while not providing new ore sources, can yield metal concentrations high enough to favour recovery or removal. Increasing and strict regulatios against release of metal containing effluent also require more effective purification methods. The adsorption, cementation, electrolysis, ion exchange, membrane separation, precipitation and solvent extraction techniques have been applied to the separation and recovery of metals from aqueous solutions (Nippon, 1986; Bin, 1986). The benefits of electroplating under the influence of ultrasonic field have been studied over the last 30 to 40 years (Prasad, 1993; Zhang, 1992; Seryanov, 1994). Ultrasound affects on electrochemical factors such as current efficiency and energy consumption. The microhardness, wear, rate of deposition, grain size, brightness, porosity, surface topography and internal stress of electrodeposits have been studied (Prasad, 1994). Here in this research work a novel technique of Ultrasound combined with an electrochemical cell has been used successively to recover copper from its dilute solutions. The work was focused on studying the effects of ultrasonic fields on the electrodeposition of copper in the following main areas: (1) effect of ultrasound on the removal of copper; (2) effect of initial concentration of copper; (3) effect of cathode type.

1 Experimental

Electrodeposition of copper with and without an ultrasonic field was carried out in a 24 cm × 11 cm × 31 cm (l × w × h) perspex reaction vessel with walls of 0.6 cm thickness. The reaction vessel was designed to be placed in an ultrasonic bath and to accommodate 5 electrodes with 12 mm spacing. The ultrasonic bath used was a Camlab Transonic Series T780/H with a volume of 12.75 dm^3 operating at a frequency of 35 kHz. Detergent was added to the ultrasonic bath solution to lower the surface tension of the water. The reaction vessel was designed in a way that all the cathodes and anodes surface areas were below the level of the water in the ultrasonic bath. Two mesh platinum coated titanium anodes, along with one mesh titanium or stainless steel plate cathode were used (Lickiss, 1996).

Different concentrations ranging from 100 mg/L – 500 mg/L Cu^{2+} were prepared from reagent grade copper sulphate ($CuSO_4 \cdot 5H_2O$) with 0.1 mol/dm^3 H_2SO_4 in distilled water. Five litres of aqueous solution were used in each experiment. The current used was 1.0 Ampere (Henglein, 1993; Cataldo, 1992). The

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tests were carried out in both the sonicated and nonsonicated fields.

The temperature and voltage during the electrolysis process in the sonicated solutions, was measured at one-hour intervals for 8 hours. In the sonicated and nonsonicated fields, voltage and temperature were constantly increased in order to maintain the same thermal conditions for nonsonicated solutions, the temperature was adjusted to match those during the sonicated process.

In order to determine the effect of cathode types, two types of cathode mesh titanium cathode or stainless steel plate cathode were used separately. The conditions of temperature, current, volume and molarity of acid were constant in every experiment and the concentrations were changed in each couple of sonicated and nonsonicated of experiments. For the detection of copper concentration in the solution, the standard method of atomic absorption is used throughout this work.

To examine and compare effectiveness of the electrolysis process, the following parameters were compared for each experiment: (a)The percentage removal, α(%); (b)the current efficiency, η(%); (c)the energy consumption, W (kWh/kg), where,

$$\alpha = \frac{\text{actual deposit(g)}}{\text{initial weight(g)}} \times 100; \quad \eta = \frac{\text{actual deposit(g)}}{\text{therotical deposit(g)}} \times 100; \quad W = \frac{\text{voltage} \times \text{current} \times \text{time}}{\text{weight deposited(g)}}.$$

2 Results and discussion

2.1 Effect of ultrasound on the removal of copper

A set of experiments was carried out to investigate the effect of sonicated field on the percentage removal of copper of 100 mg/L and 500 mg/L solutions using mesh cathode and two platinised titanium anodes. The electrolysis results are plotted as log C vs time(t) in Fig. 1.

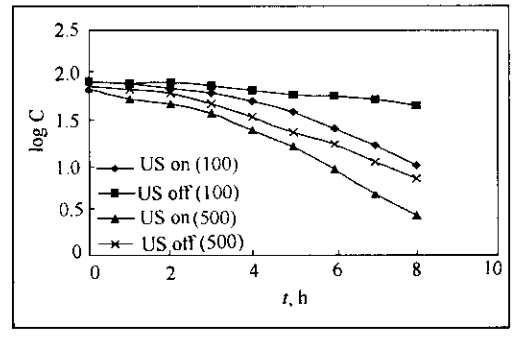

Fig. 1 Effect of ultrasound on the electrolytic removal of copper

The results of electrolysis assuming first order of the reaction kinetics, $-\frac{d[Cu^{2+}]}{dt} = K[Cu^{2+}]$ are listed in Table 1.

The electrolysis results revealed that the rate constants (K) are larger under sonicated fields than nonsonicated ones. This indicates that the electrolysis rate is higher in sonicated field. The difference of electrolysis rate constants(K) with and without ultrasonic field in both concentrations showed that the value of K in 100 mg/L solution is larger than in 500 mg/L solution. So, it is concluded that electrolysis with ultrasonic technology is more effective in lower concentrated solution than in higher concentrated solution. Talking about half-life of copper in different concentrations, the results showed that in 100 mg/L solution difference of half-life time is almost twice in nonsonicated than sonicated field. But in higher concentration (500 mg/L) the half life time is only 1/3 times more in nonsonicated field compared to sonicated one. So the function of ultrasonic technique is more suitable for lower concentrated solution.

η_{Cu} values were continuously decreased as the amount of copper ions decrease in solution in both sonicated and nonsonicated fields. After 8 hours, η_{Cu} for 100 mg/L solution decreased to 4.9% and 2.9% and for 500 mg/L, were 25.6% and 24.5% in the sonicated and nonsonicated fields respectively as presented in Fig. 2.

Table 1 Effect of ultrasound on copper removal by electrolysis

Initial concent. C_0, mg/L	Ultrasound on			Ultrasound off		
	Half life time $t_{1/2}$, min	Electrolysis constant K, min^{-1}	Correlation coefficient	Half life time $t_{1/2}$, min	Electrolysis constant K, min^{-1}	Correlation coefficient
100	240	2.19×10^{-3}	0.948	420	6.75×10^{-4}	0.986
500	120	3.38×10^{-3}	0.984	180	2.52×10^{-3}	0.989

The results indicate that the energy consumption W_{Cu} values are lower in the case of sonicated field compared to nonsonicated for both of 100 mg/L and 500 mg/L concentration. For 100 mg/L concentration, during the removal of copper, under sonicated condition, W was reduced to half compared to that in nonsoincated field as shown in Fig. 3.

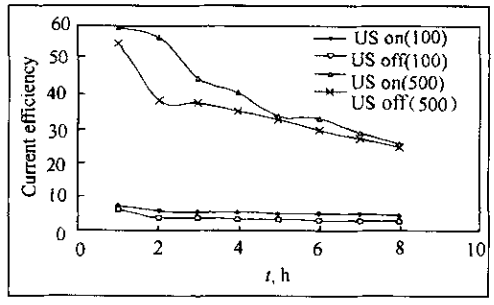

Fig.2 Effect of ultrasonic field on combination with mesh cathode on the η_{Cu} of copper from 100 and 500 mg/L solutions.

Any change in removal rate of metal deposition from dilute solution can only occur due to either a change in the diffusion layer thickness or a change in the limiting current density. The problem of thinning down the diffusion layer was solved by ultrasonically agitated bath.

The compression and rarefaction cycles in an ultrasonic system produce alternative regions of high and low pressure forming vacuum bubbles. These bubbles rapidly grow and implode generating high pressure/temperature hot spots which in turn reduce the diffusion layer thickness. Thus, the transport of the dilute metal specie of Cu^{2+} is facilitated and results in increased percentage removal rates over conventional standard electrochemical cell.

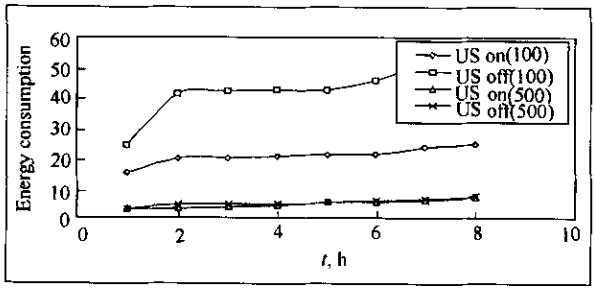

Fig.3 Effect of ultrasonic field in combination with mesh cathode on the W_{Cu} of copper from 100 and 500 mg/L solutions

2.2 Effect of copper concentration

In the nonsonicated field, the α values were increased with increasing the copper concentration as 55.1%, 63.1%, 93.0%, 93.0% and 93.1% in Cu^{2+} concentrations of 100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L and 500 mg/L, respectively, after 8 hours of electrolysis. In the sonicated field, the values were equal or greater than 95 %.

In sonicated and nonsonicated conditions, the η_{Cu} values were increased with increasing copper concentration. The η_{Cu} in sonicated solution was again more as compared to nonsonicated solutions.

The W_{Cu} in both sonicated and nonsonicated conditions were high at very low copper concentration, i.e., 100 mg/L but decreased with increasing concentration. However, this consumption is less in sonicated solution as compared to nonsonicated solution. It is shown in Table 2, for the changing α, η and W in different concentrations of Cu^{2+} in sonicated and nonsonicated fields.

The effect of ultrasonic field on the α of copper from 500 mg/L solution showed a much smaller difference in values between the sonicated and nonsonicated fields as compared to the data for the concentration of 100 mg/L. The reason is that, by increasing concentrations, number of ions were increased in solution and by applying ultrasonic field, the number of collisions with each other were

Table 2 Effect of copper concentration using mesh cathode in the presence and absence of ultrasonic field after 8 hours of electrolysis

Con., mg/L	Ultrasound on			Ultrasound off		
	α_{Cu}, %	η_{Cu}, %	W_{Cu}	α_{Cu}, %	η_{Cu}, %	W_{Cu}
100	94.6	4.9	24.5	55.1	2.9	51.49
200	95.5	10.1	11.3	63.1	6.6	18.03
300	98.3	15.5	11.5	93.0	14.7	11.47
400	97.5	20.6	8.8	93.0	18.8	10.28
500	97.3	25.6	7.1	93.1	24.5	7.05

increased too. Thus this technique for more concentrated solutions does not remain effective as for very dilute solutions.

2.3 Effect of cathode type

α_{Cu} obtained in the sonicated fields showed a steady improvement for mesh cathode as compared to plate cathode and its value increased with increasing concentration represented in Fig. 4.

η_{Cu} revealed that in the absence of ultrasonic field the mesh cathode is much better than plate cathode in different concentration of copper and by using ultrasonic field still there is a slight improvement in η_{Cu} in mesh cathode, as shown in Fig. 5.

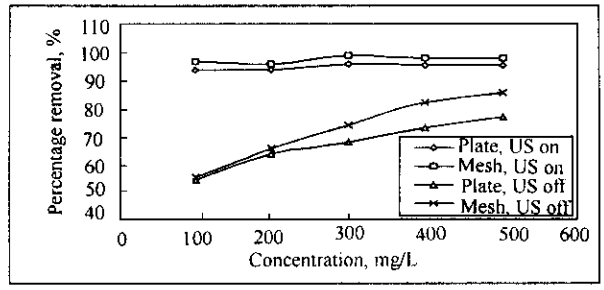

Fig.4 Comparison of cathode type(plate and mesh) in the absence and presence of ultrasonic field on the percentage removal of copper after 8hours of electrolysis

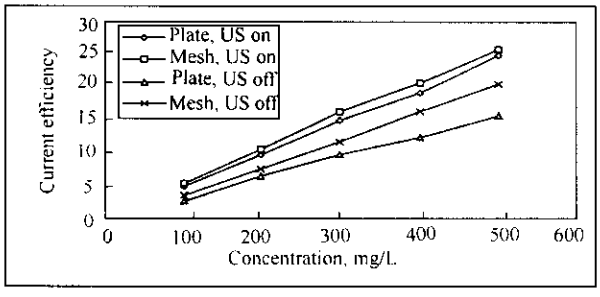

Fig.5 Comparison of cathode types(plate and mesh) in the absence and presence of ultrasonic field on the current efficiency of copper after 8 hours of electrolysis

W_{Cu} parameter expressed that plate cathodes consumed more energy throughout the experiments as compared to mesh cathodes in both sonicated and nonsonicated conditions. However, by using ultrasonic field, the amount of energy is reduced to half compared to nonsonicated field(Fig. 6).

The results on α_{Cu}, η_{Cu} and W_{Cu} in different types of cathodes showed that mesh cathode was better than plate cathode for the removal of copper from 100 – 500 mg/L solutions. It is known that the deposition of metal on the cathode surface is affected by the stirring rate. High stirring rates increase the percentage removal because of more efficient mixing of the solution during electrolysis process. This mixing breaks the diffusion layer around the cathode surface and aids movement of cations towards the surface of the cathode(Walker, 1990). This mixing rate is higher in mesh cathode compared to plate cathode, which in turn increases the percentage removal. Secondly, the higher removal rate of copper on mesh cathode because of high surface area of the metal compared to plate cathode.

3 Conclusions

The conclusion of research on the novel technology of electrolysis with an ultrasonic field is summarised as follows:

(1) An electrolytic reactor, combined with an ultrasonic field provides higher ion-transfer conditions during electrolysis by breaking up the barrier layer at the electrode, thus enabling metal to be removed efficiently from dilute solution. It was observed that the energy cost reduced to half compared to general electrolysis.

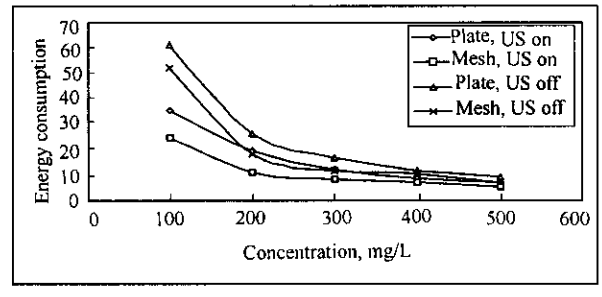

Fig.6 Comparison of cathode type(plate and mesh) in the absence and presence of ultrasonic field on the energy consumption of copper after 8 hours of electrolysis

(2) The use of sonication as an agitating medium proved much more effective for the removal of

copper at very dilute concentrations (100 mg/L), compared with less dilute concentrations (500 mg/L). The energy consumption also decreased with increasing copper concentration.

(3) The rate of copper deposition and current efficiency values for mesh cathode were higher than that for plate cathode, while mesh cathodes consumed less energy than plate cathode irrespective the presence or absence of ultrasonic field.

These results show that by applying this ultrasonic technique the beneficial effects of increased deposition rates can be achieved from dilute solutions and in this way, the stringent environmental irregularities can be overcomed.

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