

# Electrochemical Removal of Copper and Lead from Industrial Wastewater: Mass Transport Enhancement

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The effects of ultrasonic frequencies on both the mass transport process and diffusion layer were investigated during electrochemical treatment. The rates of mass transfer at a stainless steel cathode were measured for copper and lead in dilute acidified copper sulphate and lead nitrate solutions at different ultrasonic frequencies. Concentrations in bulk solution were determined by atomic absorption spectrophotometer. By increasing frequencies from 40 to 100 kHz, a high value for the mass transfer coefficient and an effective thinning of the diffusion layer were observed. Higher rates of mass transfer reduced energy consumption. Use of ultrasound with electrochemical processes can provide valuable contributions to remove metallic ions from industrial wastewater without using extra chemicals. The process has efficiently reduced the cost of energy consumption and deposition time.

**Key words:** electrochemical, ultrasound, heavy metal, mass transfer, diffusion layer

## Introduction

Wastewater from different industrial sectors (such as electroplating, photographic development, and printed circuit board production or battery technology) requires treatment to remove toxic metal ions and recycle valuable material. Due to increasingly strict regulations for the discharge of effluents, the permissible concentration of metal ions has been strongly decreased in recent years (Kreysa 1988; Kreysa et al. 1994). The removal of toxic ions from wastewater is a challenge since they are difficult to remove by biodegradation. Furthermore, some heavy metals like Pb, Cu, Hg, and Cr inhibit or prevent the oxidation of organic waste by bacteria (Bourgeois et al. 2001).

The use of an electrochemical approach to remove metal ions from wastewater can be considered a relatively simple and clean method. In many cases the technique is found to be superior to other techniques, such as chemical precipitation, ion exchange, and cementation (Genders and Weinberg 1992; Rajeshwar and Ibanez 1997; Juttner et al. 2000). But there is still a need to increase the mass transfer rate and reduce deposition time. The combination of ultrasound and electrolysis is commonly used in a wide range of subject areas such as electrode-position, electroplating, and for preventing corrosion and electrochemical dissolution (Walker 1993; Walton 1996; Compton et al. 1997a, 1997b).

Use of ultrasonic agitation for mass transfer is well known in electroplating; ultrasound accelerates the transfer processes of nickel and copper (Kobayashi et al.

2000; Kobayashi et al. 2001; Farooq et al. 2006). Each point in the liquid is subjected to alternating negative and positive pressure, which creates cavitation bubbles and subsequent implosion. This implosion creates a tiny but intense area of pressure and temperature, which reduces the diffusion layer ( $\delta$ ) of the electrochemical reaction (Richard and Joel 2002). Many of the observed effects of ultrasound in electrochemical processes can be explained by the enhancement of mass transport in diffusion-controlled processes. Sonication is believed to decrease the diffusion layer thickness thereby giving a substantial increase in the limiting current. The objective of the present study was to remove metals from model metal solutions, and to investigate the effect of ultrasound on the mass transfer rate of copper and lead.

## Materials and Methods

### Experiments

All experiments were performed with the Digital Ultrasonic Bath (Cleaner Model Utech Products, Inc.) at 40, 60, 80, and 100 kHz ultrasonic frequencies in a rectangular perspex glass vessel. Sonication was produced parallel to the liquid surface and the electrodes were hung vertically in the solution. Couples of stainless steel cathode and titanium anodes were used for the deposition of metallic ions. The surface area of the electrodes that were dipped into 1 L of solution was 102 cm<sup>2</sup>. Electrodes were connected to the DC power supply (Dazheng PS-305D) with a digital current and voltage display. The experiments were conducted for 4 hours at 10 volts.

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## Solutions

Model solutions were prepared in the lab with analytical grade salts of copper sulphate ( $\text{CuSO}_4$ ) and lead nitrate [ $\text{Pb}(\text{NO}_3)_2$ ]. The pH was adjusted by using 0.1-molar sulphuric acid.

## Measurements

Mass transfer measurements were characterized by electro-diffusional method (Touyeras et al. 2005). The mass transfer coefficient,  $K_m$ , was calculated as follows:

$$K_m = I_{\text{lim}}/nFAC_o \quad (1)$$

where  $I_{\text{lim}}$  is the limiting current (A);  $F$  is the Faraday constant (96,485);  $n$  is the number of electrons;  $A$  is the area of electrodes ( $\text{m}^2$ ); and  $C_o$  is the concentration difference of electro-active substance ( $\text{mol}/\text{m}^3$ ).

Electrical energy consumption (EC, in kWh/mg) was calculated according to equation 2:

$$\text{EC} = Pt/\text{weight deposited} \quad (2)$$

where  $P$  is the power in kWh (kilowatt hours),  $t$  is the time in hours, and deposited weight of metals is in milligrams. The concentrations of metals were determined using a PerkinElmer atomic absorption spectrophotometer.

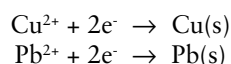
## Statistical Analyses

Data were analyzed by the two tailed  $t$ -test at  $p$ -value of 0.05.

## Results and Discussions

### Effect of Ultrasound on Mass Transfer Coefficient and Diffusion Layer

Electrochemical experiments were carried out chrono-amperometrically (the potential was maintained at a constant level and current was measured as a function of time) using aqueous solutions of 0.1-M  $\text{CuSO}_4$  and 0.1-M  $\text{Pb}(\text{NO}_3)_2$  at various ultrasonic frequencies (40, 60, 80, and 100kHz). The chemical change that takes place during the electrochemical process for copper and lead ions is:



The relationship between the limiting current ( $I_{\text{lim}}$ ) and the diffusion layer thickness can be described by the well known equation (Marken et al. 1996; Compton et al. 1997a; Gutierrez et al. 1998; Ball and Compton 1999):

$$I_{\text{lim}} = nFADC_o/\delta \quad (3)$$

where  $n$  is the number of electrons,  $F$  is the Faraday constant (96,485),  $A$  is the area of electrode in the solution ( $\text{m}^2$ ),  $D$  is the diffusion coefficient/diffusivity of the electro-active substance,  $C_o$  is bulk concentration of this electro-active substance ( $\text{mol}/\text{m}^3$ ), and  $\delta$  is diffusion layer thickness (m).

By comparing equations 1 and 3, we get that the diffusion layer thickness ( $\delta$ ) is the ratio between the diffusion constant and the mass transfer coefficient. The following equation (4) and Fig. 1a and 1b show the inverse relation between the mass transfer coefficient and diffusion layer thickness:

$$\delta = D/K_m \quad (4)$$

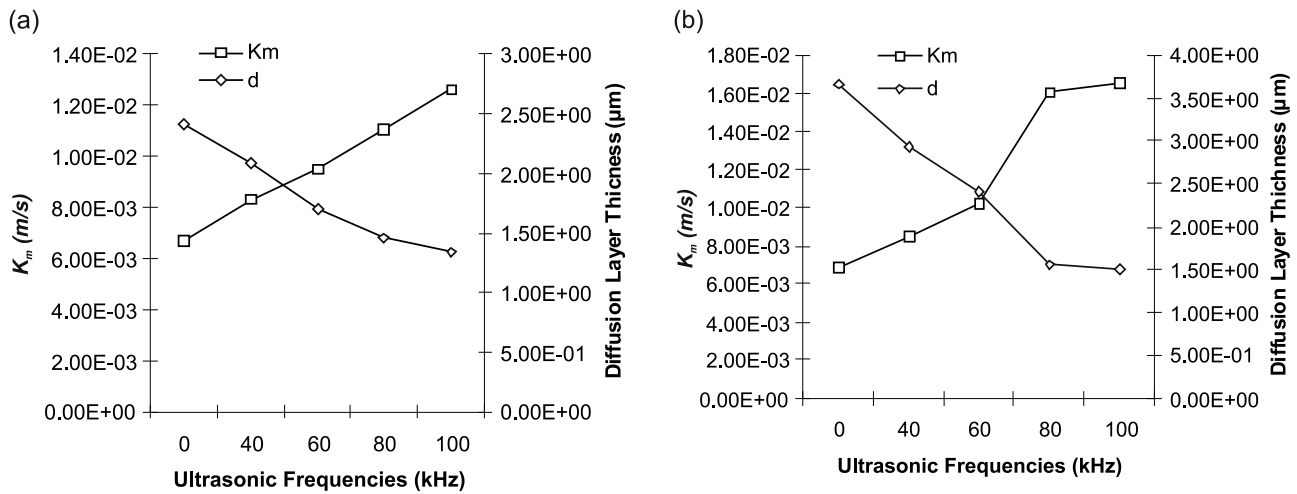
where  $D$  the diffusivity is calculated by the Cottrell equation (5) (Bard and Faulkner 2001). From the results it was found that the diffusion coefficients for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  using aqueous solutions of 0.1-M  $\text{CuSO}_4$  and 0.1-M  $\text{PbNO}_3$  were  $1.61 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-2}$  and  $2.48 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-2}$ . Bing and Ian (2004) measured an effective diffusion coefficient for  $\text{Cu}^{2+}$  using a rotating disc electrode from both the Cottrell and Levich equations. The Cottrell analysis provided a value for the effective diffusion coefficient at bulk composition and viscosity (Bing and Ian 2004).

$$I_{\text{lim}} = nFAC_o(D/\pi t)^{1/2} \quad (5)$$

Figure 1a shows an increase in the mass transfer coefficient ( $K_m$ ) for Cu as ultrasound frequency was increased to the maximum frequency of 100 kHz ( $K_m = 1.21 \times 10^{-2} \text{ m/s}$ ) from the silent condition ( $K_m = 0.67 \times 10^{-2} \text{ m/s}$ ). Similarly, in the case of Pb, Fig. 1b shows an increasing trend, and at 80 kHz a high value ( $K_m = 1.6 \times 10^{-2} \text{ m/s}$ ) was found in comparison with the silent condition ( $K_m = 0.68 \times 10^{-2} \text{ m/s}$ ).

These results can be explained as a mass transfer effect at the electrode (Walker 1993; Klima et al. 1994; Walton 1996; Compton et al. 1997b), which is due to acoustic streaming, cavitation, and/or microstreaming in the bulk solution, and has an important role in the effective thinning of the diffusion layer, as shown in Fig. 1a and 1b. Marken et al. (1995) stressed that the dominating effect of ultrasound is strongly enhanced mass transport, resulting from a very thin diffusion layer thickness. He neglected the contribution of a transient component on the limiting current. He observed that the mass transfer was enhanced near the electrode surface.

Before initiating electrolysis, the concentration of metal ions is uniform throughout the solution. The concentration of metal ions near the electrode surface becomes less than the bulk solution because, when current flows through the solution, the surface of the particles becomes charged and some ions of the opposite charge become attached to their surface. The ions are held there through electrostatic and van der Waals forces of attraction, forming a fixed layer of ions surrounded by a diffuse layer, which stops the diffusion of metallic ions towards the electrodes (Metcalf and Eddy 2003).



**Fig. 1.** Effect of ultrasonic frequencies on mass transfer coefficients and diffusion layer thickness for Cu (a) and Pb (b) during the first hour of the experiment.

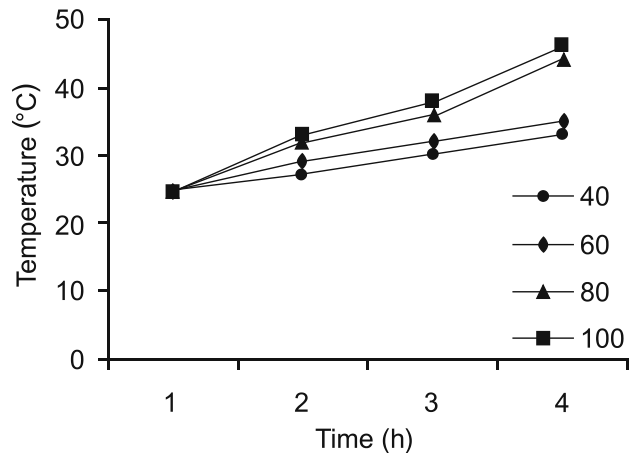
The most important mass transport processes in an electrochemical measurement are diffusion and forced convection. At low concentrations of solutions, the only way in which metallic ions can be transported across the boundary layer to the electrode is by diffusion (Farooq et al. 2006). The rate of diffusion is increased by the application of ultrasound. The direct effect of ultrasound on mass transfer can arise due to three major mechanisms: acoustic streaming, microstreaming, and microjetting. Basically, acoustic streaming arises from attenuation of the sound field within the liquid, resulting in a pressure gradient and subsequent liquid motion. Microstreaming occurs close to a forced oscillating bubble or some other vibrating body. Microjetting occurs when a cavitation bubble collapses asymmetrically next to a solid/liquid interface (Wang and Jepson 2000).

**Effect of Temperature and pH**

The temperature of the solution was adjusted at 25°C, but during the experiment, temperature was increased accordingly with the intensity of the ultrasound, as shown in Fig. 2. An increase in temperature depends upon the collapse of acoustic cavitation in the solution (Farooq et al. 2003). On collapse, a high temperature and pressure are produced. The frequency of the ultrasound also affects the creation of cavitation bubbles; more bubbles are produced at higher frequencies (Banks and Compton 2004). The temperature increase also enhanced

the deposition rate because of the degree of dissociation of the electrolyte. The viscosity of the electrolyte decreases at higher temperatures; therefore, the diffusion rate and the velocity of the copper ions and inhibitor molecules become increased.

Electrolytic removal of Cu and Pb was also studied at different pH conditions; the optimum pH range was 3 to 3.5 in the presence of ultrasound. A high concentration of hydrogen ions also increases the flow of current in the solution, which leads to an increase in the mass transport rate at the cathode, and a decrease in the diffusion layer thickness (Tables 1 and 2). However, a pH below 3 corrodes the electrode and reaction vessel.



**Fig. 2.** The effect of ultrasonic frequencies on temperature.

**TABLE 1.** Effect of different pH conditions on mass transfer coefficient ( $K_m$ ) and diffusion layer thickness ( $\delta$ ) for Cu

	pH				
	2	2.5	3	3.5	4
$K_m$ (m/s)	$1.44 \times 10^{-2}$	$1.32 \times 10^{-2}$	$1.21 \times 10^{-2}$	$1.16 \times 10^{-2}$	$0.98 \times 10^{-2}$
$\delta$ ( $\mu\text{m}$ )	1.08	1.28	1.34	1.46	1.59

TABLE 2. Effect of different pH conditions on mass transfer coefficient ( $K_m$ ) and diffusion layer thickness ( $\delta$ ) for Pb

	pH				
	2	2.5	3	3.5	4
$K_m$ (m/s)	$1.77 \times 10^{-2}$	$1.68 \times 10^{-2}$	$1.60 \times 10^{-2}$	$1.56 \times 10^{-2}$	$1.37 \times 10^{-2}$
$\delta$ ( $\mu\text{m}$ )	1.34	1.51	1.55	1.62	1.73

### Effect of Ultrasound on Removal of Metals

Figures 3 and 4 reflect the effect of different ultrasonic frequencies during electrolytic removal of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  at a steel cathode and constant voltage of 10 volts. A pH of 3 was maintained during all experiments. Temperature increased from 25 to 45°C due to the collapse of cavitation bubbles. The initial concentrations of copper and lead used were 25 and 32 mg/L, respectively.

On the basis of the test applied, it is evident that our data are significantly different from the preceding treatment ( $p < 0.05$ ). As seen from Fig. 3 and 4, the deposition of copper and lead increased rapidly in the first hour with the increase of frequency. At the frequencies of 80 and 100 kHz, 99% removal of metals in 4 hours was observed. Farooq et al. (2006) also found a high percentage of  $\text{Cu}^{2+}$  removal and a decrease in current efficiency by application of ultrasound in the electrolysis process. The deposition rate decreased with the passage of time (Fig. 3 and 4), due to the decrease in concentration gradient and the decrease in conductivity of the solution. Conductivity in wastewater is due to the presence of ions in the solution. As the electrochemical process proceeds, the ions are either converted into metallic atoms or into gases (Silberberg Chemistry 2003). The concentration of Cu at 100 kHz decreased from 25 to 8.4 ppm in 1 h, but in a simple electrolysis process, the concentration decreased from 25 to 15.1 ppm. Hence, the addition of ultrasound increased the mass transport at the electrodes. At extremely low concentrations, the rate of the mass-transport-controlled process strongly decreases (Juttner et al. 2000).

It was observed that energy consumption varied with the deposition rate. The flow of current through aqueous solutions depends upon the concentration of positive and negative ions in the solution, and the voltage applied. High concentration of ions increased the current through the solution. Since the concentration of metallic ions in the dilute solution was low, the voltage applied from the battery was 10 volts, which gave the desired current flow. High current flow and high voltage also increase the current density as well as operating costs (Walton 1996), but, by applying ultrasound, this cost can be reduced at the same current flow and voltage. Low energy consumption during the ultrasound electrolysis process was noticed.

The percentage removal of Cu in the simple electrolysis process was 67.2%, with a high electrical consumption of 0.053 kWh/mg in four hours (Table 3). However, with

the increase of frequency from 40 to 100 kHz, the rate of Cu removal was increased with a consequent decrease in energy consumption compared with the simple electrolysis process. At the frequency of 40 kHz, Cu removal was 65.8% with an energy consumption of 0.046 kWh/mg in 3 h. Similarly, 68.8% removal was found at the 60 kHz frequency after 2 h, with an electrical consumption of 0.033 kWh/mg. At 80 and 100 kHz, 67.8% Cu removal was found with an electrical consumption of 0.018 kWh/mg, which is one third of the consumption seen using the simple electrolysis process. Similar results were observed during the removal of Pb from the solution.

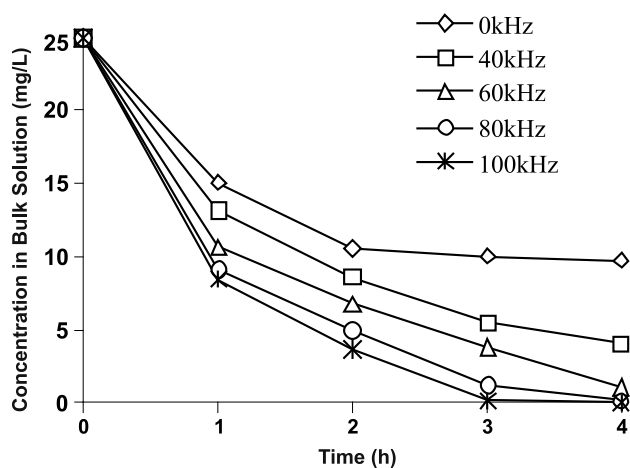


Fig. 3. Effect of ultrasonic frequencies during electrolytic removal of copper from its solution.

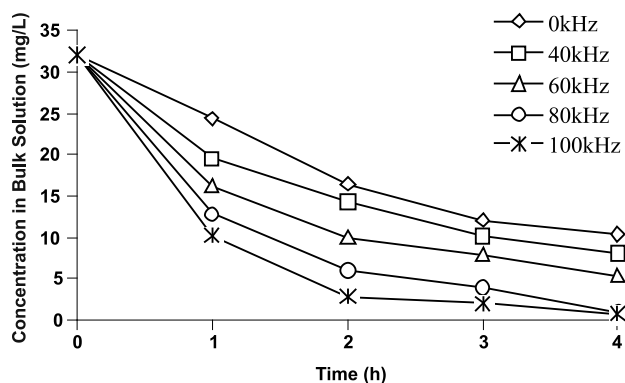


Fig. 4. Effect of ultrasonic frequencies during electrolytic removal of lead from its solution.

TABLE 3. Energy consumption of Cu and Pb at different ultrasonic frequencies

	Time (h)	0 kHz		40 kHz		60 kHz		80 kHz		100 kHz	
		EC <sup>a,b</sup>	Removal <sup>b</sup>	EC	Removal	EC	Removal	EC	Removal	EC	Removal
Cu	1	0.026	35.8	0.024	44.2	0.019	54.8	0.016	61.2	0.014	64.2
	2	0.026	55.2	0.036	60.5	0.027	71.1	0.025	78.8	0.021	83.0
	3	0.031	62.0	0.043	76.7	0.037	83.8	0.032	95.1	0.030	99.4
	4	0.037	64.0	0.051	82.6	0.047	95.7	0.039	98.6	0.038	99.9
Pb	1	0.021	24.1	0.025	39.1	0.021	49.1	0.019	59.4	0.018	67.8
	2	0.028	48.8	0.038	55.0	0.033	68.7	0.030	78.7	0.028	90.6
	3	0.041	62.1	0.046	65.8	0.042	75.3	0.038	87.5	0.036	93.7
	4	0.053	67.2	0.057	74.4	0.050	82.8	0.048	98.8	0.048	98.0

<sup>a</sup>EC = energy consumption.

<sup>b</sup>Units: EC, kWh/mg; Removal, %.

### Significance of the Study

In Pakistan, industries discharging heavy metals include the electroplating, battery, and ghee industries, as well as tanneries. Electrolytic removal of metals can be beneficial in terms of a reduction in cost of chemicals used for the precipitation (Sirajuddin et al. 2004; Farooq et al. 2006; Sirajuddin et al. 2007). Also, precious metals can be efficiently removed from their ores using electrolytic removal. Table 4 shows characteristics of the ghee and battery industries as well as tanneries. Electrolytic recovery of nickel from the solid waste of hydrogenated vegetable oil, called ghee waste, was studied by Sirajuddin et al. (2004). They found 200 ppm of nickel in the ghee waste. Sirajuddin et al. (2007) studied the electrolytic recovery of chromium from tannery effluents.

TABLE 4. Characteristics of different industrial effluents

Parameters	Effluent		
	Ghee	Battery	Tannery
Ni (ppm)	20	—	—
Pb (ppm)	—	30	—
Cu (ppm)	—	0.04	—
Cr <sup>+3</sup> (ppm)	—	—	1,000
COD (ppm)	255	—	1,760
pH	7.5–8	6	8–9
TDS (ppm)	965	300	5,260
Conductivity	1,930 $\mu$ S	605 $\mu$ S	10–12 mS

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