

# Recovery of copper from low concentration waste waters by electrowinning

Pyry-Mikko Hannula<sup>1</sup>, Muhammad Kamran Khalid<sup>1</sup>, Sami Kinnunen<sup>1</sup>,  
Petteri Halli<sup>1</sup>, Dawid Janas<sup>2</sup>, Kirsi Yliniemi<sup>1</sup>, Mari Lundström<sup>1</sup>

<sup>1</sup>*Aalto University, Department of Chemical and Metallurgical Engineering, School of Chemical Technology, Research group of hydrometallurgy and corrosion, Vuorimiehentie 2, 02150 Espoo, Finland*

<sup>2</sup>*Silesian University of Technology, Department of Chemistry, B. Krzywoustego 4, 44-100 Gliwice, Poland*

**Abstract** Metal pollution from mining operations has become a topic of concern due to the toxic nature of contaminated water. Potentially toxic metals do not degrade in the environment but accumulate in organisms while being toxic and carcinogenic. Typically, these waste waters contain low concentrations of metals which makes their recovery more difficult. In this research, the composition of waste water from various mining site and concentration plant locations were analysed. The recovery of copper from solutions by electrowinning on glassy carbon and carbon nanotube film was studied. The results show that waste water can be utilized to create novel composite structures energy efficiently.

**Key words** electrowinning, copper, carbon nanotube, waste water, low concentration

## Introduction

Rapid development of heavy industries such as mining operations has led to serious environmental issues caused by pollution. Potentially toxic metals do not degrade in the environment but accumulate in organisms while being toxic and carcinogenic. For instance, there are over 1 million abandoned mines worldwide, and an even greater number of still operational mines and neutralization ponds, that are contaminated by metals such as copper, zinc, cadmium, lead, arsenic and iron (Fields 2003). As such, there is a growing demand for the removal of these metals from different waste streams and their potential reuse as secondary raw materials. As environmental regulations become more stringent and metal prices increase the use of previously unemployed technologies may become possible for the removal and recovery of metals from different types of waste water streams.

There are many different techniques available for the recovery of low concentrations of metals from waste waters, but typically the associated costs are high. Chemical precipitation is the most widely used waste water treatment technique due to its relative simplicity, but it requires the use of large amounts of chemicals that react with metal ions to form precipitates. These precipitates are then removed by sedimentation or filtration. Other potentially toxic metals removal techniques include ion exchange, adsorption, membrane filtration, coagulation and flocculation, flotation and electrochemical treatments.

Electrochemical methods for the recovery of low concentration of copper have so far been relatively understudied due to the required high capital investment and operating costs. However, as copper is more noble than other metals typically found in waste water streams,

such as iron, nickel, lead, zinc and magnesium, it can be expected to be selectively recovered to create valuable high quality solid copper deposits. The competitive processes typically lead to some form of precipitated salts or increased concentration highlighting the potential use of electrowinning as a recovery method. The possibility of utilizing industrial waste water as a source for high quality metal deposits by electrowinning offers an exciting new way of producing new materials in circular economy. Recently, carbon nanotube (CNT) – copper composite materials by electrochemical deposition of copper onto carbon nanotube materials have been explored for various electrical applications due to promising properties, such as improved specific conductivity and ampacity (Subramaniam 2013), (Hannula 2016). However, until now these materials have been made from commercial chemicals, rather than waste waters. In addition, these synthetic solutions are free of any impurity metals that might compromise the quality of the resulting composite.

In this communication, we investigated the recovery process of high quality copper from low concentration and impure solutions by electrowinning onto carbon material. Commercial state-of-art glassy carbon and a novel carbon nanotube film were used to recover copper both from synthetic solutions as well as from an actual waste water sample collected from an industrial mine site.

## Methods

Waste waters were obtained from various locations in Sweden, Finland and Australia and their composition was analysed by ICP-OES (inductively coupled plasma, optical emission spectroscopy, Perkin Elmer Optima 7100 DV, USA). Sample 14 is process waste water composition before final neutralization and bleed out of the process.

The experimental work was carried out using a typical three electrode cell by a potentiostat (IviumStat, Netherlands) connected to a personal computer. The reference electrode was a standard calomel electrode (SCE, 0.244 V vs. SHE) by SI Analytics, Germany. Working electrode was a glassy carbon plate (GC, type 1, Alfa Aesar, America). A free-standing carbon nanotube film produced elsewhere (Janas, 2017) was also tested as the working electrode after removing an area of desired dimensions by surgical blade. The counter platinum electrode was 99.95 % purity produced by Kultakeskus, Finland. The impurities in the platinum were other PGMs, gold, silver, copper and base metals. The surface area of the working electrodes varied from 3 to 7 cm<sup>2</sup>.

A glass vessel with 200 cm<sup>3</sup> volume was used as test cell and the distance between working and counter electrodes was kept constant at  $2.5 \pm 0.1$  cm. Based on the actual waste water solution analysis (Table 1) the synthetic waste water composition was set as : 4 g/l of Fe and 0.1 g/l of Cu, while the solution pH was set to 2 by sulfuric acid additions. 0.5 M sodium sulfate was used as the background electrolyte to provide conductivity. The solution conductivity was approximately 70 mS/cm.

The synthetic solutions were prepared from analytical grade copper sulfate pentahydrate (CuSO<sub>4</sub> \* 5H<sub>2</sub>O), iron sulfate heptahydrate (FeSO<sub>4</sub> \* 7H<sub>2</sub>O), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98 %), so-

dium sulfate ( $\text{Na}_2\text{SO}_4$ ) and DI- water. The testing was done without stirring for 2 hours in potentiostatic conditions with applied voltage of  $-0.3\text{V}$  and  $-0.5\text{V}$  vs. SCE. During electro-winning also the cell voltage was observed with a multimeter attached to the counter electrode and working electrode.

Before each experiment was begun the working electrode was cleaned in 1 M HCl solution for 5 minutes and ultrasonicated in ethanol before drying in oven at  $70\text{ }^\circ\text{C}$  for 5 minutes to ensure the surface was clean and absorbed water was fully evaporated. After electro-winning the glassy carbon was rinsed in ethanol and dried in oven at  $70\text{ }^\circ\text{C}$  for 5 minutes. The weight of the glassy carbon working electrode was weighed before and after electro-winning with  $10\mu\text{g}$  accuracy to obtain the mass of the recovered copper. The copper deposited samples were first rinsed with distilled water and ethanol before SEM-EDS analysis (Scanning Electron Microscope, LEO 1450 VP- Energy Dispersive X-ray Spectroscopy, INCA software). The pure carbon nanotube film was imaged by SEM (Nova Nanosem, FEI). Grain size analysis was conducted with ImageJ software.

### Results and discussion

The waste water composition of multiple samples from various industrial locations in Sweden, Finland and Australia were investigated and are presented in Table 1. High concentrations of iron, at most approximately  $12.5\text{ g/l}$ , and lower concentrations of aluminium, zinc, arsenic, copper and cadmium were found.

**Table 1** Composition of waste water from multiple locations around mining sites.

Sample	As (mg/l)	Cd (mg/l)	Zn (mg/l)	Cu (mg/l)	Fe (mg/l)	Al (mg/l)
1	< 2	< 0.2	169	< 0.5	1862	623
2	< 2	< 0.2	13.6	< 0.5	11.4	60
3	< 2	< 0.2	7.4	< 0.5	3.7	12
4	< 2	< 0.2	41.8	0.6	12.7	46
5	< 2	2.3	1970	2.1	11525	577
6	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	N/A
7	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	N/A
8	< 0.2	< 0.2	< 0.2	13.1	13.5	N/A
9	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	N/A
10	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	N/A
11	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	N/A
12	< 0.2	< 0.2	< 0.2	< 0.2	27.2	N/A
13	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	N/A
14	52.1	N/A	99.6	428	12460	1350

In industrial electrowinning the typical operating conditions are at a cell voltage of 1.9- 2.5 V, copper ion concentration of ca 50 g/l, current density of 15-150 mA/cm<sup>2</sup>, temperature of 40-60 °C, a current efficiency 80-96 % and specific energy consumption of 1.9-2.5 kWh/kg of copper. Typically some form of solution movement (such as air sparging or forced circulation of electrolyte) is maintained to achieve faster and even mass transport. (Walsh 1990)

Typical time – current density graphs from electrowinning are shown in Figure 1. Here, synthetic waste water (100 ppm Cu, 4 g/l Fe, 0.5 M sodium sulfate at pH 2) and industrial waste water (sample 14) were used as the solution for copper electrowinning experiments with a carbon nanotube film and glassy carbon working electrode. The current was normalized with the apparent surface area of the samples. The glassy carbon surface is known to be smooth and homogenous, while the carbon nanotube film surface has a high surface area due to its porous nature (Figure 2a). Therefore, the actual current density is expected to be smaller than the value reported here.

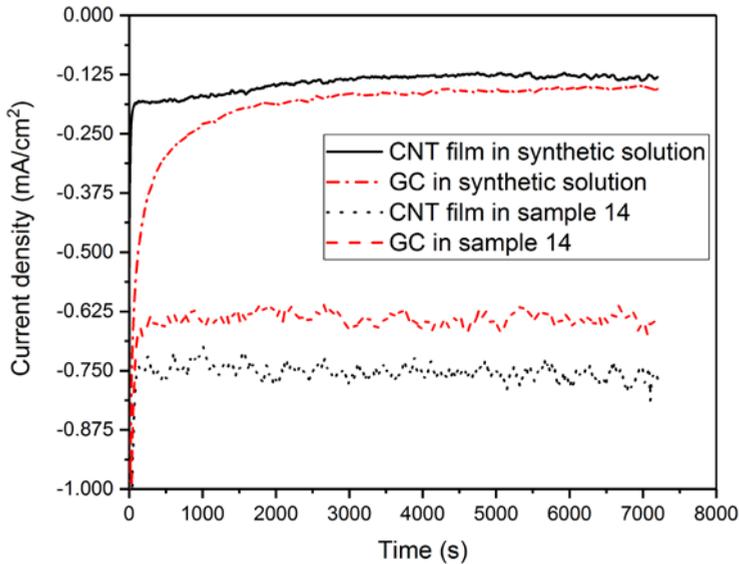
Overall, the stable current densities are small, two orders of magnitude smaller than in industrial electrowinning, reflecting the small concentration and lack of agitation in the solution. However, even at lower polarization in the industrial waste water sample 14, the reaction rate is higher than in the synthetic solution. This result is attributed to the higher concentration of copper ions in the authentic waste water sample (428 ppm Cu) compared to the synthetic solution (100 ppm Cu).

The simplest way to increase the reaction rate would be to increase the overpotential. However, this is expected to lead to unfavourable incorporation of less noble metals into the deposit and ruining the product purity. It can be reasonably assumed that the reaction rate could also be improved by improving the diffusion of copper ions i.e. mixing of the solution e.g. by a magnetic stirrer or by utilizing a more complex multi-cell structure. Another way to enhance the performance of this method is by increasing the electroactive area of the working electrode (Walsh 1990). In this respect, carbon nanotube films offer an exciting possibility through their highly porous surface area and tunable electrochemical activity through electro-oxidation (Hannula 2017).

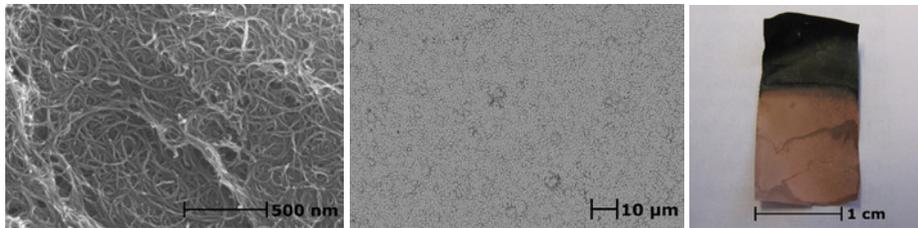
Previously, we have shown smooth copper deposits on carbon nanotube films by electrochemical deposition from industrial strength copper solutions, which contain no other metals (Hannula 2017). In the current work, the as produced CNT-Cu samples showed a similar smooth morphology of deposits (Figure 2b-c) for both samples deposited in synthetic and waste water solutions.

Deposition from the synthetic solution yielded a copper layer with 0.3 µm thickness (area 6.8 cm<sup>2</sup>) with no contamination by iron from EDS analysis. However, the deposits from industrial waste water solutions (sample 14) were also found to be pure copper and no co-deposition of other metals could be identified with SEM-EDS. The copper layer from industrial waste solution had thickness of 0.7 µm (area 3.1 cm<sup>2</sup>). The average grain size analy-

sis from SEM images showed a grain size of  $0.9 \mu\text{m}$  with s.d.  $0.2 \mu\text{m}$ . The CNT-Cu composite film showed good adherence of copper and could be bent to similar degree as the pristine CNT film without breaking. As such, impure industrial mining waters can be considered as a valuable and suitable metal source for the production of high-added value products such as CNT-Cu, producing a similar composite quality compared to pure industrial chemicals.



**Figure 1** Potentiostatic time – current density graph for samples deposited in synthetic solution ( $-0.5 \text{ V vs. SCE}$ ) and waste water solution ( $-0.3 \text{ V vs. SCE}$ ).



**Figure 2** Typical morphology of (a) carbon nanotube film surface, (b) copper deposit after electrowinning on top of CNT film and (c) CNT-Cu composite from authentic waste water.

The specific energy consumption [kWh/kg] for the recovery of copper from synthetic and industrial waste solutions on both carbon materials were calculated by (1):

$$\frac{zF E_{\text{cell}}}{\eta M \cdot 3600} \quad (1)$$

where  $z$  is the number of electrons ( $=2$ ),  $F$  is the Faraday constant ( $96485 \text{ C/mol}$ ),  $E_{\text{cell}}$  is the cell voltage observed during the experiment by a multimeter [V],  $\eta$  is the current efficiency

and  $M$  is the molar mass of copper (63.546 g/mol). The observed cell voltage for results shown in table 2 varied from 0.68 V to 0.85 V between experiments and were stable during electrowinning. It is well known that current density affects the power consumption in electrowinning and small operational current densities correlate with low power consumption (Panda 2001).

The compiled results of energy consumption are shown in Table 2. Here, it can be observed that the specific energy consumption for copper recovery is in all cases lower than in industrial electrowinning (Walsh 1990). When current efficiency is high more of the spent charge is used by the reduction of copper than other side-reactions, such as hydrogen evolution, and the specific energy consumption is improved. In the case of the synthetic solutions no co-deposition of iron was detected in the deposit and therefore the other side-reaction is expected to be hydrogen evolution. The same was shown to apply to electrowinning from industrial waste water (sample 14) as no other metals than Cu could be analysed on the surface by SEM-EDS. The current density and electrowinning time are directly related to the decrease in copper ion concentration in waste water solutions. In our work, the concentration of copper ions in the solution was decreased by approximately 10-30 % in 2 hours. With longer processing times the copper ion concentration could be further decreased but this was not a part of our investigation.

**Table 2** Specific energy consumption for copper recovery.

Electrode material	Solution	$V_{dep}$ (V vs. SCE)	Current efficiency, $\eta$	Specific energy consumption (kWh/kg)
Glassy carbon	Synthetic solution	-0.5	0.429	1.65
CNT film	Synthetic solution	-0.5	0.694	1.03
Glassy carbon	Waste water sample 14	-0.3	0.723	0.89
CNT film	Waste water sample 14	-0.3	0.361	1.59

## Conclusions

The recovery of copper from synthetic and industrial mine waste water samples was investigated. The specific energy consumption for recovering copper from waste waters was reported and two carbon electrode materials were compared: a standard glassy carbon plate and a novel carbon nanotube film. Both materials showed similar current efficiency and specific energy consumption in recovering copper from investigated solutions. The specific energy consumption was found to be lower than in industrial copper electrowinning operations.

Surface morphology of copper showed smooth and compact deposits from both synthetic and industrial mine waste water solutions. The copper was well adherent to both carbon electrodes. EDS analysis of the deposit surfaces showed that the recovered copper from actual industrial waste water sample (containing, Fe, Cu, As, Zn and Al) did not include any other

metals as impurities. The biggest caveat in using electrowinning to produce high quality metal deposits from low concentration waste waters is the low reaction rate of the process – about two orders of magnitude smaller than in industrial electrowinning conditions. It is expected, however, that the kinetics of the process can be markedly improved by adding agitation to the system and this will be covered in future research.

Carbon nanotube – copper composite structures produced from industrial mine waste water showed similar morphology as previously published composites produced from synthetic solutions and commercial chemicals. The results show promise for the energy efficient recovery of copper on carbon materials from copper containing (ca 100-400 ppm Cu) mine waste waters. In addition, the results show promise in the production of high quality and high added-value composite materials based on carbon nanotube films and valueless mine waste waters.

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