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Energy efficient copper electrowinning and direct deposition on carbon nanotube film from industrial wastewaters

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ABSTRACT

Heavy metal pollution is one of the most serious environmental issues of today. Removal of one common pollutant, copper, from synthetic wastewaters (containing copper, iron, sulfur and sodium) and complex authentic metallurgical plant wastewater (containing copper, iron, aluminum, zinc, nickel, arsenic, sulfur and lead among others) was studied by electrowinning. Due to the complexity and low concentration of these wastewater streams, energy efficient copper removal is challenging. The copper concentration in the investigated solutions varied from 100 to 428 ppm, while the iron concentration was an order of magnitude larger. Copper was recovered energy efficiently on glassy carbon from all investigated solutions that contained iron with a small specific energy consumption (1.5-2.5 kWh/kg Cu), depending on the solution composition and employed parameters. In the absence of iron, the specific energy consumption increased to ca. 3.5 kWh/kg Cu with the same parameters. The results indicate that the presence of iron in copper containing wastewater induces lower energy consumption during electrowinning, due to a decrease in cell voltage. Due to the low applied polarization the produced copper deposits from the authentic industrial wastewater were smooth and bright with no other metals as impurities, confirmed by energy-dispersive X-ray spectroscopy. Electrowinning was also applied on a carbon nanotube film as the working electrode to create carbon nanotube-copper composite structures of high purity directly from the industrial wastewater. These results highlight the energy efficient recovery of high purity copper from complex industrial wastewaters by electrowinning and furthermore, that the method may be used in producing high added value materials.

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1. Introduction

The ever increasing global demand of metals has led to quick expansion of mining and metallurgical industry operations, resulting in higher risk for environmental pollution by the acidic process and wastewaters of said industries (Simate and Ndlovu, 2014). The permissible limit for copper in water is ca. 0.1-4 ppm due to its harmful effects on humans, plants and aquatic life (Simate and Ndlovu, 2014; Kurniawan et al., 2006). Therefore, removal and re-use of such metals is crucial for the sustainable growth of metal industries. The recovery of metal ions from different industrial process and wastewaters is often difficult due to the chemical complexity of the solutions and the high costs of recovery as wastewaters typically contain only small concentrations of valuable metals (Fu and Wang, 2011). As such, there is an increasing demand for the purification of different wastewater streams and even further – to investigate these streams as secondary raw materials in circular economy (Hagelüken et al., 2016; Driussi and Jansz, 2006). The circular economy trend is further enhanced by increasingly stringent environmental regulations (Fu and Wang, 2011), creating a niche for the use of previously unemployed technologies for the removal and recovery of metals from different types of wastewater streams. This paper introduces an energy efficient method to recover pure copper and further, to create copper – carbon nanotube composites directly from industrial wastewater by electrowinning, offering a route to improved circular economy in the mining industry.

There exists a variety of different techniques for the removal of copper from wastewaters, but typically their associated cost-
efficiency is not favourable. Chemical precipitation is the most widely employed wastewater treatment technique due to its low cost and availability, but it requires the use of large amounts of chemicals, such as limestone, sodium hydroxide, calcium oxide and hydrogen sulfide, that react with metal ions to form insoluble precipitates, such as hydroxides and sulfides. Typically these precipitates are not utilized as raw material, but are discarded due to the required cost for processing. Limestone is used typically for precipitation of colloidal metal precipitates (Fu and Wang, 2011). Other copper ion removal techniques include ion exchange (Dabrowski et al., 2004; Cechinel et al., 2018), adsorption (Monser and Adhoum, 2002; de Freitas et al., 2018; Wan Ngah and Hanafiah, 2008) membrane filtration (Bessbousse et al., 2008), ion flotation (Yuan et al., 2008) and electrochemical methods (Moats and Free, 2007; Gorgievski et al., 2009). Typically, the inherent limitations in all of these methods are either in the use of complex chemicals, multiple process steps and/or high operation costs.

Electrowinning (EW) is a well-known method for the industrial production of high purity copper. About 20% of annual Cu production is conducted using EW (Moats and Free, 2007). However, the application of EW for dilute wastewater purification, specifically removal of Cu, is quite a difficult approach, since the recovery of metals from dilute wastewaters is known to involve high operating costs. This is a result of high energy consumption caused by high cell voltage and applied polarization, which are related to the dilute composition of wastewater and kinetics of metal recovery. However, unlike other methods for heavy metal removal, electrowinning is a “clean” single-step method that produces no secondary waste and which can be directly applied to produce high quality metal deposits from solutions without requiring additional chemicals. Thus, an effort to decrease the energy consumption of electrowinning from dilute wastewater would increase its viability as a sustainable recovery method for acidic metal containing wastewaters.

Mining waters from active or closed copper mines can contain up to ca. 1 g/L of copper, while the iron concentration is up to ca. 2 g/L due to e.g. bacterial leaching of sulfide copper and iron minerals (Gorgievski et al., 2009). On the other hand, metallurgical process wastewaters can contain a wide range of elements, such as Cu, Fe, Ni, Zn etc. depending on the utilized raw material and process. The synthetic and authentic wastewater solutions at pH 1–3 in this research consist mainly of iron and copper, in ranges typical for metallurgical process waters and mining waters.

The standard anodic reaction in copper electrowinning is oxygen evolution:

$$2H_2O = O_2 + 4H^+ + 4e^- \quad E_{eq} = ca. 1.1V \text{ at pH2} \quad (1)$$

Another possible anodic reaction in solutions containing iron (II) is:

$$Fe^{2+} = Fe^{3+} + e^- \quad E^0 = 0.77V \quad (2)$$

The main cathodic reaction is deposition of copper:

$$Cu^{2+} + 2e^- = Cu(s) \quad E^0 = 0.34V \quad (3)$$

Other possible cathodic reactions are:

$$2H^+ + 2e^- = H_2(g) \quad E_{eq} = ca. – 0.12 \text{ V at pH2} \quad (4)$$

$$Fe^{3+} + e^- = Fe^{2+} \quad E^0 = 0.77V \quad (5)$$

$$Fe^{2+} + 2e^- = Fe(s) \quad E^0 = -0.44V \quad (6)$$

In industrial electrowinning the typical operating conditions are cell voltage of ca. 2 V, copper ion concentration of ca. 50 g/L, current density of 20–45 mA/cm², temperature of 40–60 °C, current efficiency of 89–94% and specific energy consumption of 1.8–2.5 kWh/kg of copper. Typically, some form of solution movement is maintained to achieve fast and steady mass transport (Schlesinger et al., 2011). Higher copper concentrations reduce mass transfer limitations resulting in higher current efficiency (Das and Krishna, 1996). As high current density during electrowinning also increases the ohmic resistance losses in the solution, small operational current densities tend to correlate with low power consumption (Dew and Phillips, 1985; Monhemius and Costa, 1975). The theoretical minimum energy consumption of industrial copper electrowinning is 0.75 kWh/kg Cu when no efficiency losses occur (Schlesinger et al., 2011).

Depolarization of both the anodic (1) and cathodic reaction (3) have been studied extensively in industrial electrowinning due to their marked effect on the power consumption. For instance, the anodic reaction (1) constitutes ca. 70% of the total energy consumption for industrial copper electrowinning (Subbaiah et al., 2000). Previously explored anodic reactions in industrial copper electrowinning include oxidation of dissolved SO₂ and/or oxidation of iron (2), where a power consumption of less than 1 kWh/kg Cu has been achieved (Subbaiah et al., 2000; Cooper and Mishra, 1987).

Electrowinning dilute concentrations of copper from wastewaters has been explored previously, with a wide range of results arising from the various solution compositions and type of electrochemical cells used. Typically, when the concentration of copper is > 1 g/L the current efficiency is >50%. During recovery of copper by electrowinning, the concentration of copper is constantly decreasing, leading to a decrease in current efficiency and increase in specific energy consumption. Often a multiple cathode system is employed to increase the active surface area for copper recovery. Cooper and Mishra (1987) reported a prototype electrowinning system for 600 ppm Cu solutions with 85% recovery at specific energy consumption of 7.0 kWh/kg Cu and cell voltage of 4.7 V. Similarly, Gorgievski et al. (2009) reported a specific energy consumption of 7 kWh/kg Cu from acid mine drainage solutions containing 1.3 g/L Cu at ca. 77% copper recovery and ca. 5 V cell voltage. Electrowinning from very dilute solutions (150 ppm Cu) was investigated by Peng et al. (2011), who observed energy consumption of 11.1 kWh/kg Cu for a recovery of 90%. Typically, the focus in these reports is on the speed at which copper can be removed from the wastewater and not as much in obtaining high quality deposits and low energy consumption.

This study investigates the recovery process of copper from low concentration and complex wastewater solutions by electrowinning onto carbonaceous material. Contrary to previous research, a simple electrochemical cell was employed at small applied polarization and cell voltage in an effort to bring down the energy consumption for copper removal. To highlight the applicability of wastewater as a raw material source in circular economy, the production of a carbon nanotube–copper composite by electrowinning directly from industrial wastewater was also studied. Previously, similar composites have been produced by electrochemical deposition from concentrated high grade copper electrolytes onto carbon nanotube films (Subramaniam et al., 2013; Hannula et al., 2017) and fibers (Hannula et al., 2016), but to the best of the authors’ knowledge this is the first time real industrial wastewater solutions have been utilized. This class of composite
materials is being investigated due to its exceptional properties, which have shown improvements over pure copper in various electrical (Subramaniam et al., 2013), corrosion (Hannula et al., 2018) and mechanical (Tsai et al., 2017) applications.

2. Materials and methods

2.1. Materials

Table 1 shows the industrial and synthetic solution compositions, pH and conductivity used in this study. The synthetic wastewater solutions were prepared from analytical grade copper sulfate pentahydrate (CuSO₄·5 H₂O), iron sulfate heptahydrate (FeSO₄·7 H₂O), sulfuric acid (H₂SO₄, 98%), sodium sulfate (Na₂SO₄) and deionized water. Synthetic solutions I (Table 1) were adjusted with sulfuric acid to pH 1, 2 and 3 and synthetic solutions II had the same composition without the addition of iron. The industrial process wastewater originated from an autoclave-discharge solution of oxidated gold ore containing arsenic pyrites: after autoclave treatment, the solution was filtered and collected from pressure leaching process before solution neutralization. The solution composition was analyzed by ICP-OES (Inductively Coupled Plasma optical emission spectroscopy, Perkin Elmer Optima 7100 DV, USA). The authentic industrial wastewater had an original pH of 1.0. The same solution was also adjusted to pH 2 with sodium hydroxide (NaOH) with no signs of precipitation.

After electrowinning experiments the working electrode samples were rinsed with distilled water and ethanol before analyzing with a LEO 1450 VP scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) with Oxford Instruments INCA software. The pure carbon nanotube (CNT) film was imaged by SEM (Nova Nanosem, FEI). Grain size analysis was conducted from SEM images with ImageJ software. In order to quantify the amount of Cu deposited, the working electrode samples were placed in 50 cm³ of 10 wt% HNO₃ solution for 24 h to dissolve all of the deposit. The solution composition was then analyzed by atomic absorption spectroscopy (AAS) with a Varian AA240.

2.2. Electrowinning and polarization

Electrowinning was carried out in a typical three-electrode cell controlled by a potentiostat (IviumStat, Netherlands). The reference electrode was a standard calomel electrode (SCE, 0.244 V vs. SHE, SI Analytics, Germany) and the counter electrode was a platinum electrode was a standard calomel electrode (SCE, 0.244 V vs. SHE, SI Analytics, Germany) and the counter electrode was a platinum electrode. The working electrode was a standard calomel electrode (SCE, 0.244 V vs. SHE, SI Analytics, Germany) and the counter electrode was a platinum electrode. The reference electrode was a standard calomel electrode (SCE, 0.244 V vs. SHE, SI Analytics, Germany) and the counter electrode was a platinum electrode.

2.3. Equations

The cell voltage (V) consists of electrode potentials of anodic and cathodic reactions and from the IR drop, Eq. (1):

\[ E_{\text{CELL}} = (E_C + |\eta_C|) - (E_A + |\eta_A|) + V \]

where \( E_C \) is the electrode potential of cathodic reaction, \( \eta_C \) is the cathodic reaction overpotential, \( E_A \) is the electrode potential of anodic reaction, \( \eta_A \) is the anodic reaction overpotential, \( I \) is the current passing through the electrochemical cell and \( R_{\text{TOTAL}} \) is the total resistance of the electrochemical cell.

The specific energy consumption (kWh/kg) for the recovery of copper from synthetic and industrial waste solutions on both carbon materials were calculated by Eq. (2):

\[ \text{Specific energy consumption} = \frac{zFE_{\text{cell}}}{\eta M 3600} \]

where \( z \) is the number of electrons (≈2), \( F \) is the Faraday constant (96485 C/mol), \( E_{\text{cell}} \) is the cell voltage observed during the experiment (V), \( \eta \) is the current efficiency and \( M \) is the molar mass of copper (63.546 g/mol).

3. Results and discussion

3.1. Cathodic polarization

In order to determine the overpotential for copper electrowinning, cathodic polarization curves were measured in iron containing wastewater solutions, Fig. 1. The curves are characteristic of low concentration copper solutions i.e. even at high polarization the copper deposition rate is low compared to industrial electrowinning (Schlesinger et al., 2011). Due to the low copper concentration (100 ppm for synthetic solutions and 428 ppm in industrial solutions), the reaction rate becomes quickly controlled by the mass transport as polarization is increased. At potentials more negative than −0.7 V vs. SCE simultaneous hydrogen evolution and iron deposition start to take place (Grujicic and Pesic, 2005). The higher current density in the industrial wastewater is due to the higher concentrations of copper (428 ppm) present in the solution compared to synthetic wastewater 1 (100 ppm). The deposition potential for copper electrowinning was selected at −0.3 V vs. SCE.
quickly, on average in less than 15 min and the stable cell voltage was used in energy consumption calculations. The cell voltage during electrowinning in synthetic solution I and industrial wastewater solutions varied between 0.7 and 1.0 V. In synthetic solution II, where no iron was present, the cell voltage was noticeably higher at 1.7–1.9 V.

As expected, stirring of the solutions during electrowinning was shown to increase copper recovery from 32–40% to 36–61% due to enhanced mass transfer. However, stirring also decreased the current efficiency in synthetic solution I and industrial solution at pH 1 and 2. This is due to the well established side reaction of Fe(III) reduction to Fe(II), which decreases the current efficiency when solution agitation is applied (Monhemius and Costa, 1975; Cooper and Mishra, 1987). Conversely, in solutions without any iron (synthetic II), the current efficiency remained relatively stable while stirring was applied. Increasing the solution pH in any of the solutions (in the range of 1–3) did not have a marked effect on energy consumption or recovery when no stirring was applied. It is noteworthy, however, that – despite the generally negative effect of stirring on the energy consumption in iron containing solutions – energy consumption was still clearly lower when stirring was applied in the pH range of 2–3 (synthetic I: 1.3–2.2 kWh/kg) when compared with solutions without iron in the same pH range (synthetic II: 3.1–3.6 kWh/kg), i.e. the presence of industrial waste improved the energy consumption drastically. The considerably decreased current efficiency and recovery due to stirring at pH 1 in iron containing solutions could be related to enhanced corrosion of the deposited copper. The lower energy consumption during recovery from solutions containing iron is related to the clear decrease in the observed cell voltage as the anodic reaction is iron oxidation (2), instead of oxygen evolution (1).

In the industrial wastewater used in this study, a smaller current efficiency (12–25%) is observed when compared to synthetic solutions and this is believed to be due to two factors: a more complex solution composition and a higher iron concentration (12.5 g/L), which has been noted previously to decrease current efficiency at higher concentrations (Dew and Phillips, 1985). Similar to the synthetic wastewaters, the specific energy consumption increases with solution stirring. The observed specific energy consumption is ca. 2.5 kWh/kg Cu without stirring in both pH 1 and 2 and up to ca. 6.8 kWh/kg Cu with stirring in pH 2. The energy consumption in the industrial solution when no stirring is applied is low when compared with previous reports on electrowinning from dilute wastewaters (Gorgievski et al., 2009; Cooper and Mishra, 1987; Peng et al., 2011) and on par with actual industrial EW values (Schlesinger et al., 2011). This result confirms that the presence of a common impurity metal ion in wastewaters – Fe(II) – can be considered an advantage in energy efficient copper removal from wastewaters, due to the lower cell voltage obtained.

The morphology of the copper deposit on glassy carbon after electrowinning from industrial wastewater (pH 1) is shown in Fig. 3. The deposit was found to contain trace amounts of oxygen and sulfur by SEM-EDS but no other metals other than copper were detected despite the complexity of the solution. Table 3. This result is promising and confirms the importance of applying small polarization i.e. suitable deposition potential for the selective deposition of copper from complex solutions. Thus, not only low specific power consumption but also the formation of highly pure copper deposits can be achieved. Moreover, the deposited copper surfaces were smooth and bright with no indications of unfavorable dendritic growth. Previously, Pandà et al. (2004) reported no adverse effects on deposit quality from electrowinning in industrial conditions (Cu = 20 g/L) with a relatively small iron concentration (Fe(II) = 5 g/L). In this work, even with a copper concentration an order of magnitude smaller than the iron concentration, the deposit quality was not affected.
3.3. Carbon nanotube-copper composite

Electrowinning has the competitive advantage over other wastewater recovery methods in that it can be utilized to produce high quality solid metal directly on the surface of a desired conductive substrate material, even without the use of additional chemicals. Therefore, to highlight this feature a carbon nanotube (CNT) film was employed as the electrode material to produce carbon nanotube-copper composites, in Fig. 4, directly from the highly complex industrial wastewater solution (pH 1). As with the results on glassy carbon electrodes, SEM-EDS analysis was conducted and no metal contaminants were found in the CNT-Cu composite structure only pure copper. The surface of the composite material exhibits similar morphology (Fig. 4c) when comparing with a CNT-Cu composite prepared by traditional electrodeposition, i.e. from metal rich electrolyte (Fig. 4d) (Subramaniam et al., 2013; Hannula et al., 2017). Considering the highly complex and impure nature of the copper containing wastewater, this result is remarkable, since not only is the process producing pure copper metal, but it can also be utilized to manufacture CNT-Cu composites with morphology similar to those made from reagent grade solutions. The CNT-Cu composite film from industrial wastewater showed good adherence of copper (estimated Cu film thickness ca. 1 μm) and could be bent similarly as the pristine free-standing CNT film without breaking.

The energy consumption for Cu deposition on the CNT film without stirring was very close to the values shown for deposition on glassy carbon in Table 2: 1.5 kWh/kg Cu in pH 1 iron containing synthetic wastewater I and 2.7 kWh/kg Cu in pH 2 industrial wastewater. The energy consumption is slightly higher when depositing on the CNT film than on glassy carbon from industrial wastewater, but still very comparable with the energy consumption of industrial copper production (1.8–2.5 kWh/kg Cu (Schlesinger et al., 2011)). Overall, the presented results demonstrate that copper containing solutions often considered as toxic waste show great potential as metal sources for the production of high added value products, such as carbon nanotube–copper composites.

In summary, contrary to typical industrial Cu electrowinning solutions, authentic industrial wastewaters typically include many impurities such as Fe (12.5 g/L in this study) and have a low concentration of Cu (428 ppm in this study) and therefore, the prevailing cathodic and anodic reactions can differ from those typical in Cu electrowinning. As the studied wastewaters contain Fe(II), a lower cell voltage during electrowinning can be obtained with the anode reaction of Fe(II) oxidation into trivalent form according to reaction (2), which takes place at considerably lower voltage when compared to typical oxygen evolution reaction (1). The total cathodic current density during electrowinning is the sum of the partial current densities for all the cathodic reactions, such as Cu deposition, Fe(III) reduction and hydrogen evolution, when thermodynamically feasible. While a low cell voltage and specific

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**Table 2**

Compiled results from 24 h electrowinning experiments on glassy carbon.

<table>
<thead>
<tr>
<th>Solution</th>
<th>pH</th>
<th>Energy consumption (kWh/kg Cu)</th>
<th>Current efficiency (%)</th>
<th>Recovery (%)</th>
<th>Cell voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>No stirring</td>
<td>Stirring</td>
<td>No stirring</td>
<td>Stirring</td>
</tr>
<tr>
<td>Synthetic I</td>
<td>1</td>
<td>1.9</td>
<td>4.9</td>
<td>30.4</td>
<td>12.2</td>
</tr>
<tr>
<td>Synthetic II</td>
<td>1</td>
<td>3.4</td>
<td>3.6</td>
<td>47.0</td>
<td>45.8</td>
</tr>
<tr>
<td>Industrial I</td>
<td>2</td>
<td>2.5</td>
<td>3.3</td>
<td>24.9</td>
<td>19.9</td>
</tr>
<tr>
<td>Synthetic II</td>
<td>2</td>
<td>1.5</td>
<td>2.2</td>
<td>37.8</td>
<td>28.4</td>
</tr>
<tr>
<td>Industrial I</td>
<td>3</td>
<td>2.6</td>
<td>6.8</td>
<td>44.0</td>
<td>51.5</td>
</tr>
<tr>
<td>Synthetic I</td>
<td>3</td>
<td>1.6</td>
<td>1.3</td>
<td>23.7</td>
<td>12.2</td>
</tr>
<tr>
<td>Synthetic II</td>
<td>3</td>
<td>3.5</td>
<td>3.5</td>
<td>33.4</td>
<td>44.1</td>
</tr>
</tbody>
</table>

**Table 3**

SEM-EDS of recovered copper from industrial wastewater at pH 1 on glassy carbon.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>C</th>
<th>O</th>
<th>S</th>
<th>Cu</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>3.53</td>
<td>2.17</td>
<td>0.48</td>
<td>93.82</td>
<td>100</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>3.75</td>
<td>1.65</td>
<td>0.38</td>
<td>94.22</td>
<td>100</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>3.75</td>
<td>1.51</td>
<td>0.4</td>
<td>94.34</td>
<td>100</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>4.99</td>
<td></td>
<td></td>
<td>95.01</td>
<td>100</td>
</tr>
</tbody>
</table>

**Fig. 3.** SEM-EDS of copper surface morphology on glassy carbon electrode from industrial wastewater (pH 1 without stirring).

**Fig. 4.** (a) CNT–Cu film photograph, SEM images of (b) CNT film surface before deposition, (c) Cu deposit after electrowinning on CNT film from industrial wastewater (pH 1) and (d) CNT–Cu composite surface from traditional copper sulfate electrolyte (Cu = ~50 g/L) for comparison.
energy consumption can be obtained by oxidation of Fe(II) as the anodic reaction, the current efficiency for copper deposition might be simultaneously decreased due to reduction of Fe(III) at the cathode. Due to the low cell voltage during electrowinning in the authentic industrial wastewater the energy consumption of copper recovery (ca. 2.5 kWh/kg Cu) was similar to the values reported in industrial electrowinning (1.8–2.5 kWh/kg Cu), which are conducted in highly concentrated copper solutions (ca. 50 g/L) without a high concentration of iron. The selective recovery of pure copper from wastewater was possible as the difference in reduction potentials between copper and other less noble metals, such as Fe, Zn, Ni, is high. Thus, copper will be the only metal depositing on the electrode when the applied polarization is performed only in the Cu deposition range and nucleation of other metals cannot be initiated. The disadvantages of the utilized electrowinning method presented here for the recovery of pure copper deposits from dilute and complex wastewater solutions can be summarized as: a relatively long time period (24 h) is required to remove significant quantities of copper (30–60%) and iron must be a component in high concentration (in the range of g/L) in the wastewater for energy efficient copper recovery to be possible. Furthermore, the results presented here were achieved in laboratory conditions and should be verified with larger scale experiments.

4. Conclusions

The recovery of copper on glassy carbon from dilute synthetic (100 ppm Cu) and authentic industrial (428 ppm Cu) wastewater solutions was investigated. It was found that a typical impurity metal ion, Fe(II), common in mining wastewater provides an advantage over iron-free wastewaters. The specific energy consumption for recovering copper from wastewaters containing Fe(II) was substantially lower compared to solutions without any iron. This effect is ascribed to the strong decrease in cell voltage from ca. 1.9 V up to 0.7 V, with Fe(II) offering a favourable anodic reaction of iron oxidation instead of oxygen evolution (which occurs in the absence of iron). Elemental analysis of the deposited copper film from the industrial process wastewater (containing a high concentration of impurities such as Fe, Cu, As, Zn and Al) did not include any metal impurities. This result is caused by the small applied polarization, which did not reduce any non-noble elements from the solution. Therefore, the recovery of pure copper metal directly from iron containing wastewaters was achieved at low energy consumption (synthetic solution: 1.5 kWh/kg Cu and authentic wastewater: 2.5 kWh/kg Cu at pH 1). The two biggest disadvantages in using electrowinning to produce high quality copper deposits energy efficiently from complex and dilute wastewaters are (1) in the low reaction rate of the process – about two orders of magnitude smaller than in primary copper electrowinning plants and (2) the need for iron as a component of the wastewater. Energy efficient copper recovery by this electrowinning method is therefore most suited for situations where fast kinetics are not required or when only partial recovery of copper is necessary.

The novel possibility of producing a carbon nanotube–copper composite structure directly from the industrial process wastewater was also investigated. The composite structures manufactured from industrial wastewater showed similar morphology as previously reported results from high grade commercial chemicals. The resulting CNT–Cu composite showed pure copper deposits with good adherence to the carbon nanotube film and importantly, with similar energy consumption as electrowinning onto glassy carbon electrodes. Therefore, these results show great promise for the energy efficient recovery and direct utilization of copper from dilute and complex wastewaters.

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