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PhD thesis abstract

Electrochemical methods for recovery of copper from waste waters and solid wastes

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Nomenclature

A	electrode surface
a, b, c	constant
C	concentration
D	diffusion coeficient
E_B	cell voltage
$\mathcal{F}$	Faraday's constant
I	current
i	current density
k	reaction rate constant
k_m	mass transport constant
N_V	volumic flow rate
Q_R	recirculation flow rate
R	electrical resistance
$r_{\mathcal{F}}$	faradaic efficiency
t	time
v	scanning speed
W_S	specific energy consumption
X	conversion
z	number of transferred electrons

ε	potential
η	electrode overpotential
η_{TM}	mass transfer overpotential
ν	viscosity
τ	residence time
θ	roughness
ϕ	diameter
ω	rotational speed

Abbreviations

AAS	Atomic absorption spectroscopy
AEM	Anion exchange membrane
ANP	Apparently normal potential
BER	Batch electrochemical reactor
DSA	Dimension stabile anodes
CD	Cathodic deposition
CE	Counter electrode
CEM	Cation exchange membrane
CR	Chemical reactor
CSTER	Continuous stirred-tank electrochemical reactor
CuR	Copper recovery
CuE	Copper electroextraction
CV	Cyclic voltammetry
EC	Electronic components
ECP	Electrodeposition at controlled potential
EF	Ecological factor
EI	Ecological index
EIS	Electrochemical impedance spectroscopy
ER	Electrochemical reactor
ERPPE	Electrochemical reactor with parallel plate electrodes
ERRCE	Electrochemical reactor with rotating cylindrical electrode
G-Stat	Galvanostatic operation
GEI	General effect index
Hdr	Hydrogen discharge reaction
HMI	Heavy metal ions
HV	Hydrodynamic voltammetry
IC	Impact category
ICI	Impact category index
ICP-MS	Inductively coupled plasma mass spectroscopy
IEM	Ion exchange membrane

IG	Impact group
IGI	Impact group index
IMT	Intensification of mass transport
LSV	Linear scanning voltammetry
MAC	Maximum allowable concentration
MEA	Membrane-electrode assembly
MI	Mass indez
ND	Non-detectable
Orr	Oxygen reduction reaction
P-Stat	Potentiostatic operation
PAR	Potentially active reaction
PCB	Printed circuit boards
PFER	Plug flow electrochemical reactor
PPE	Pulsating potential electroextraction
RCE	Rotating cylindrical electrode
RDE	Rotating disk electrode
RE	Reference electrode
RVC	Reticulated vitreous carbon
SEM	Scanning electron microscope
SMD	Surface mounting devices
SNP	Standard normal potential
UDL	Under detection limit
VC	Vitreous carbon
WE	Working electrode
WEEE	Waste electrical and electronic equipment
XRD	X-ray diffraction

Introduction

In the last years there is a special concern for the recovery / removal of copper from different types of waste (waste water with low or high concentration of copper, waste printed circuit boards WPCBs from dismantling electrical and electronic equipment, used batteries, ash from the incineration of waste).

Recovery / removal of copper from waste water is achieved by non-electrochemical methods (precipitation, evaporation, absorption by ion-exchange resins, solvent extraction) or electrochemical methods (electrodialysis, cathodic electrodeposition, etc.) or combined chemical-electrochemical processes (chemical dissolutioncathodic electrodeposition).

Recovery of copper from waste water by cathodic electrodeposition is different depending on the concentration of copper ions from the effluent. In literature are analyzed separately the following cases:

- When Cu^{2+} ion concentration is in the g/L domain, is generally used, two-dimensional cathodes. In this case the concentration can be reduced by an order of magnitude. Subsequently, the resulting effluent can be recirculated in the process or can be purified through chemical or electrochemical method;
- When Cu^{2+} ion concentration is hundreds of ppm or less, using 3D electrodes. After recovery of the metals on these electrodes, resulting effluents can be recirculated in the process or discharged to emissaries.

Recovery of copper from solid waste is presented in the literature on different types of waste (WPCBs, used batteries with Li, ash from the incineration of household waste, treated wood with chromate arsenate).

To recovery of the valuable metals from WPCBs various methods have been developed: open uncontrolled incineration of waste, pyrometallurgical pyrolysis, physical and mechanical methods, biometallurgy, hydrometallurgy.

After recovering metals from WPCBs, materials resulting are formed from epoxi resins and fiberglass. These materials are recovered in the form of building materials (walls insulation panels, various types of tiles). In this way the WPCBs is completely recycled.

Metals recycling technologies from WPCBs include sorting, dismantling and separation of components steps followed by the transformation into useful products.

Due to the diversity of electrical and electronic waste, original methods are needed to separate metals from alloys, chemical combinations, complex materials.

The PhD thesis aimed to bring a series of original contributions in a very complex field of copper recovery from wastes.

The purpose of the thesis is the recovery / removal of metallic copper from different types of wastes (waste water with low or high content of copper, WPCBs) by electrochemical processes or chemical-electrochemical methods.

Part I. Bibliographic study

Chapter 1

General aspects about the importance of copper

1.1. Importance of copper for the life of plants, animals and humans

Copper is a metal that can be found in the nature in his native form. In rocks (in fig. 1.1) the copper crystals are asociated with calcites. Copper is, on the same time, an important element for the life of plans, animals [1–5].

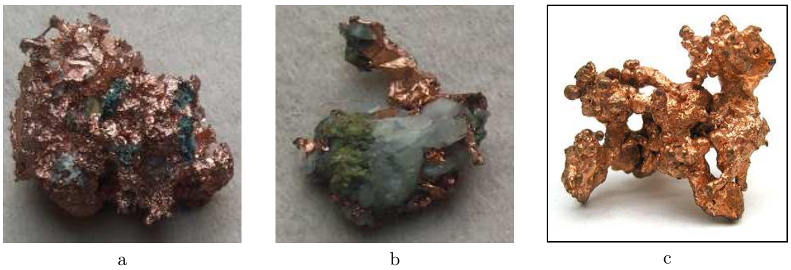

a
b
c

Figure 1.1. Copper crystals.

a, b - copper asiciated with calcites [3, 6]
c - native copper [3].

1.2. The economic importance of copper

Metallic copper is produced in many countries, in Fig. 1.2 is represented the distribution on continents of the primary copper production. About 88 % of copper production comes from the processing of the minerals of this metal. The remaining of 12 % is provided by recycling of copper from wastes.

The increasing demand of copper has made the production to increse quite a lot in the last years.

Substantial savings can be obtained by reusing copper recovered from scrap.

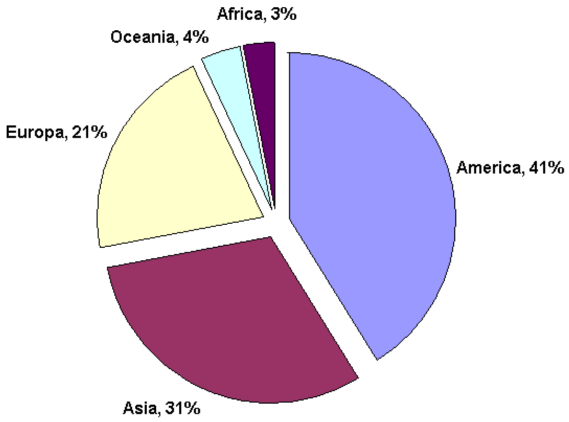


Figure 1.2. The distribution on continents of the copper production [7].

1.2.1. Uses of copper

Due to its properties (malleable, ductile, good conductor of heat and when is very pure it is a very good electricity conductor, corrosion resistant and durable), copper is widely used in many fields.

Copper has contributed to the validation of many technological breakthroughs. Among these we can include telegraphic communications and electricity. It is also widely used in form of pipes (for heating, air conditioning, water distribution networs), roof, brass fixtures, for many electrical products (TV, radio, lighting, computers, mobile phones), all requiring cables, adapters, transformers and motors.

1.3. Modern applications of copper

1.3.1. Solar cells for obtaining "green" power

Copper and its alloys are part, for many years, of production systems for so-called "green" energy (solar energy, eolian energy). Less known is the role that copper plays in the production of electricity from solar energy (photovoltaic systems).

These systems produce electricity through the action of sunlight on certain semiconductors, including silicon mono-, polycrystalline and amorphous materials and so famous thin film materials, such as Cd–Te, Ga–As, and the most promising new material, copper-indium-gallium-diseleniu, $Cu(InGa)Se_2$ or (CIGS).

1.3.2. Copper-based nanocomposite materials [8, 9]

A new material based on copper makes possible the recovery of cesium, creating a highly selective sorbent called "super-sponge" that can quickly extract most of the cesium from aqueous solutions. Sorbent is an organic-inorganic nature nanocomposites, a class of self assembled materials, fixed on a porous support. The support is based on ceramics with high porosity silica (mesoporous support).

1.3.3. Integrated circuits and printed circuit boards based on copper

Copper has the highest electrical conductivity of all base metals found on earth. This quality, along with strength and resistance to corrosion makes it unique in its use as electrical conductor. Recent studies have shown expansion of copper use in the manufacture of components for computers [10].

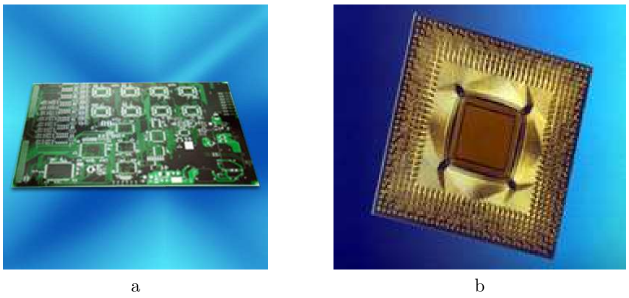


Figure 1.3. Electronic components.

a - printed circuit boards [11]
b - integrated circuit [10].

In Fig. 1.3 is shown a printed circuit board and an integrated circuit.

With the diversification of copper applications in various fields, have multiplied the pollution problems with copper and other heavy metals. For these reasons below are summarized some specific issues related to heavy metal pollution.

CHAPTER 2

Heavy metal pollution

2.1. Sources of pollution with heavy metal ions

Waste waters containing heavy metal ions from various industrial sectors, of which the most important are:

Hydrometallurgy:

- primary extraction of ore;
- waters resulting from solvent extraction;
- electrochemical extraction and electrorefining;
- waters resulting from mining processes and washing water.

Surface engineering - metal finishing:

- solutions from engraving industry;
- cleaners and other pretreatment;
- passivation treatments;
- depleted solutions from electroplating baths and chemical coatings (chemical bath);
- water resulting from washing baths.

Sectors involving:

- reprocessing and refining of scrap;
- "catalytic fluids" (from the catalysts production processes);
- redox reagents for chemical processing;
- solutions resulting from photographic processing;
- production of printed circuit boards and batteries;
- used batteries;
- effluents from chemical manufacturing processes.

Therefore in the case of heavy metal ions recovery, electrochemical pollution control solutions are conditioned by the diversity of industrial sectors, as contaminants state(solid, liquid, gas, colloids), and the complexity of the electrolyte (waste water loaded with metal ions and several species unloaded) [1, 2, 12].

Processing of industrial waste containing substantial amounts of toxic and/or valuable components for separation or recovery becomes an absolute necessity.

There are two important aspects of the problem:

- economic one is to maximize the raw materials,

- second, environmental protection, to avoid dispersion of toxic compounds, especially heavy metals.

Therefore, many studies try to develop new processes and technologies to separate metals from industrial waste especially [1].

2.2. Effects of pollution with heavy metals ions

Water is the source of life, the fundamental requirement for health and essential need for industrialization. This is the most valuable thing for the humankind. Water availability is decreasing and therefore it is necessary to maintain the water quality.

Removal of metal ions (MI) from water is a major concern as these contaminants can accumulate in humans and their presence manifest long-term effects and various diseases.

Among the metal ions that have major impacts on human health, can be mentioned: cadmium, mercury, lead, copper.

2.2.1. Pollution with copper

All copper compounds are potentially toxic. Thus, man may be exposed to copper by breathing air, drinking water, food we eat through skin contact with copper or its compounds [3–5].

For example, 30 g of copper sulfate can cause the death of a human. Copper concentration in drinking water vary depending on the source, but mandatory limits are established between 1.5 to 2 mg/L according to the EU. Upper limit of copper for adult diet, from all sources is 10 mg/day [3]. Copper poisoning is similar to arsenic poisoning. The final manifestations in fatal cases were: seizures, paralysis and numbness.

A part of copper toxicity is due to the formation of monovalent ions. It catalyzes the production of highly reactive free radicals. Copper can induce diseases affecting the brain, liver, kidneys and nervous system. A concentration of copper in sea water above permissible limits could damage marine life. This affects fish and other marine species. Copper alters, for example, the ability to guide the fish by smell [3].

Copper may reach the environment from mines, farms, industrial plants by wastewater discharged into rivers and lakes. Copper can be reached also in the atmosphere from natural sources such as volcanoes, decaying vegetation, forest fires.

Drinking water may contain high levels of copper if the pipes through which is pumped are made of copper. Lakes and rivers have been treated with copper compounds to control algae growth, or water leaking from power plants can have a high copper content.

Soils may contain also higher concentrations of copper [3–5].

Chapter 3

Modern methods of recovering heavy metals from waste

Procedures for recovery / separation of heavy metal ions from various waste can be grouped as follows [13]:

- Chemical methods (precipitation, separation with selective solvents, complexing, ion exchange, etc.);
- Biological methods;
- Physical methods (grinding, separation in electric field, magnetic field separation);
- Electrochemical methods;
- Combined methods (ion exchange - electrochemical deposition).

3.1. Electrochemical methods

Electrochemical methods in general are becoming more frequently used in the prevention of environmental pollution but also for clean (electro)synthesis, process efficiency and pollutant monitoring, removal of contaminants, recirculation of technological flows, water sterilization, clean energy conversion, storage and efficient use of electric energy [14, 15].

Therefore, Chapter 4 is dedicated to the presentation of the literature on procedures for recovery / removal of copper by cathodic deposition.

Waste from electronic and galvanic industry have high concentrations in metals such as: Cu, Ni, Mn, Pb, Sn, W.

Chemical dissolution process coupled with the electrochemical extraction is used to recover valuable metals selectively, such as Cu and Ni.

During the chemical dissolution process waste is dissolved in sulfuric acid with control on various factors: acid concentration, temperature, treatement duration.

The resulting solution from this process is treated successively by electrochemical extraction to recover Cu and Ni. The Cu and Ni deposition were tested under acidic and alkaline conditions.

Energy consumption was 2.13 kWh/kg for Cu and 4.43 kWh/kg for Ni. At the end of the process, 94−99 % of initial content of Cu and Ni was recovered at the cathode, which demonstrates the technical feasibility of the processes [16].

The main electrochemical processes for the recovery of metals from waste water are presented in Table 3.1 and specific issues related to them will be presented in Chapter 4 of this thesis.

Table 3.1. Electrochemical methods for recovery of metals from waste water.

The method	Description of the method	Ref.
Cathodic electrodeposition	Recovery of metals by using this method can be performed depending on the concentration of metal ions in the effluent: the g/cm^3, when were used, generally, two-dimensional cathodes and the hundreds of ppm, or less, when volumic cathodes were used.	[1, 2, 13]
Electrodialysis	The process by which electrically charged membranes are used to separate ions, the driving force of the process is a potential difference.	[1, 2, 12, 13, 17]
Reactiv electrodialysis	The process uses the reaction $Fe^{2+} \longrightarrow Fe^{3+} + e^-$ as anodic reaction. In the case of copper recovery, copper electrodeposition reaction is the cathodic reaction and the anodic reaction is the oxidation Fe^{2+} to Fe^{3+}.	[18–21]
Electrochemical ion exchange	It is an advanced method in which ion exchangers are present in the interelectrodic space and the intensity of ion exchange is controlled by the polarization of the electrodes.	[17, 22–24]
Electrocoagulation	Consists in electrochemical generation of ions needed in coagulation of impurities present in wastewater (Zn^{2+} ions can be removed in the form of zinc hydroxide wich coprecipitate or adsorb on the surface of electrochemically generated iron or aluminum hydroxide).	[25]
Electroflotation	The process of floating on the surface of a solution of its volume through small bubbles of hydrogen and oxygen (generated by electrolysis of water) which is fixed to the pollutant particles.	[25–27]

Chapter 4

Procedures for removal / recovery of copper based on cathodic deposition

Advantages of electrochemical processes are: (i) use as reactant electron transfer at the electrode interface, (ii) avoiding the use of redox reagents (which by their reaction byproducts complicate the technology and increase the cost of operations by subsequent separation and purification) and (iii) possibility of using complex automation solutions [1, 2].

Basic equipment used in electrochemical processes is the electrochemical reactor.

General aspects of cathodic deposition in electrochemical reactors

4.1. General aspects of cathodic deposition in electrochemical reactors

Electrochemical reactor (RE) is the technological version of the electrochemical cell, is a reactor in that takes place a process that involves a charge transfer at the electrode interface.

Most important factors in electrochemical reactor design are:

- productivity;
- the energy needed and cell voltage;
- temperature control;
- hydrodynamics and mass transport;
- reactor operating factors;
- electrodes, membranes and other materials.

The performances of an electrochemical reactor are appreciated, especially by its production capacity and by its energy consumption:[13].

Electrochemical reactors can be classified according to several criteria. These classifications follow a systematization of information related to RE, a easier design and/or choosing the best type of RE for a targeted application.

Ideal electrochemical reactors can be classified as [28]:

- batch electrochemical reactor (BER)
- plug flow electrochemical reactor (PFER)
- continuous stirred-tank electrochemical reactor (CSTER) [13, 27, 28].

In Table 4.1 are described these types of electrochemical reactors.

Table 4.1. Types of ideal electrochemical reactors.

Type of ER	Description of ER	Examples of operation of ER
BER	• It is loaded with electrolyte, then mixed during processing; • The electrolyte is removed from the ER and the byproducts are recovered by their isolation from the electrolyte solution; • Reactant and reaction product concentrations, are modified by the kinetics of the electrode reaction, by the electrode geometry, stirring conditions and the volume of electrolyte; • Electrolyte composition is uniform throughout its volume; • Residence time of electrolyte in the reactor equals the reaction time.	Use: • During the research process, when studying the kinetics in various operating conditions; • When using other reactors is not recommended due to toxicity or electrolyte, reactants or products cost; • When electrosynthesis need to be stopped from time to time.
PFER	• Electrolyte solution flow is continuous, with a constant speed and is considered there is no mixing of the electrolyte in the direction of flow between the inlet and outlet of PFER; • Product and reactants concentration is a function of distance from the entry into BER and residence time in PFER.	• ER with static cylindrical electrodes; • ER with parallel plate type electrodes - filter-press type and • ER with porous electrode or three-dimensional type (3D).
CSTER	• There is a continuous and vigorous mixing of the electrolyte • The reactant is continuously added and product is continuously extracted; • Thanks to a perfect mixing, inlet and outel have both the same concentration.	• ER with rotating cylindrical electrodes or models whith very vigorous shaking; • Also a very simmilar behaviour to the CSTER can be observed in the case of with ER with fluidized bed electrodes

4.2. Specific issues on recovery / removal of copper from waste by cathodic deposition

In the literature from recent years there is a special concern for the recovery / removal of copper from different types of waste (waste water with low or high concentration of Cu, waste printed circuit boards (PCI) from dismantling electrical and electronic equipment, used batteries, ash from the incineration of waste, etc.).

Addressing the recovery of copper from waste waters by cathodic electrodeposition is different depending on the concentration of copper ions in the effluent. In literature are analyzed separately the following cases:

- when the concentration of Cu^{2+} ion is in the domain g/L, are generally used two-dimensional cathodes, and the concentration can be reduced by an order of magnitude. Subsequently, the resulted effluent can be recirculated in the process or can be subject to new chemical or electrochemical purification steps;
- when the concentration of Cu^{2+} ions is hundreds of ppm or less, there are used volumic electrodes. After recovery of the metal on these electrodes, resulting effluent can be recirculated or discharged to emissaries [2].

Common feature of these processes is competition exerted on the desired cathode reaction by hydrogen discharge reaction (Hdr). The latter will take place with a greater speed as the concentration of both species to be reduced is lower – specific situation in the case of depollution processes.

Usually due to low levels of species to be reduced, the ER are operated at low current densities, causing fast enough treatment of the effluent. In this case is recommend to use electrodes with high specific surface (eg volumic electrodes), to increase the mass transport (through convective transport) or to concentrate the species to be reduced, for example by ion exchange [21, 29].

Copper is present in waste water in the form of simple and complex ions (organic or inorganic). Their removal by cathodic deposition can be represented by the general reaction [22, 30, 31]:

$$\mathrm{Cu^{2+} + 2e^- \longrightarrow Cu} \tag{4.1}$$

that in case of complex ions [21, 30–32]:

$$\mathrm{Cu(CN)_3^{2-} + e^- \longrightarrow Cu + 3CN^-} \tag{4.2}$$

$$\mathrm{CuCl_3^{2-} + e^- \longrightarrow Cu + 3Cl^-} \tag{4.3}$$

These reactions can be competed by some unwanted side reactions such Hdr [3, 12, 13, 32]:

$$\mathrm{pH<7} \qquad \mathrm{2H^+ + 2e^- \longrightarrow H_2} \tag{4.4}$$

$$\mathrm{pH>7} \qquad \mathrm{2H_2O + 2e^- \longrightarrow H_2 + 2HO^-} \tag{4.5}$$

or oxygen reduction reaction (Orr):

$$\mathrm{pH<7} \qquad \mathrm{O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O} \tag{4.6}$$

$$\mathrm{pH>7} \qquad \mathrm{O_2 + 2H_2O + 4e^- \longrightarrow 4HO^-} \tag{4.7}$$

especially when the concentration of metal ions is very small. Reactions (4.5, 4.6, 4.7) lead to an increase in pH, particularly near the cathode, which could favor the codeposition of metal hydroxides [33]:

$$\mathrm{Cu^{2+} + 2HO^- \longrightarrow Cu(HO)_2} \tag{4.8}$$

Such reactions can lead to less pure cathode deposits and also to the danger of blocking cathode surface.

Another category of unwanted side reactions are the reduction of other species present in solution as ferric ions in acid solutions [32]:

$$\mathrm{Fe^{3+} + e^- \longrightarrow Fe^{2+}} \tag{4.9}$$

In acid solutions containing arsenic (or antimony) can occur, also the following reaction [32]:

$$\mathrm{As^{3+} + 3H^+ + 6e^- \longrightarrow AsH_3} \tag{4.10}$$

To ensure the success of the electrochemical process of removing copper from waste waters by cathodic deposition are required the following conditions:

- an uniform distribution of potential at the cathode surface to achieve high power efficiency and high selectivity, especially when treating a solution that contains copper ions together with several metal ions that can be deposited on the electrode;
- a cell voltage low enough to minimize energy consumption;
- large electrode area per volume unit of electrochemical reactor to provide a intensive use of current in relation to space occupied by the ER;
- an enhanced mass transport;
- a more uniform current distribution in and on the electrode in order to achieve maximum exploitation of the electrode active area and get a product with more uniform properties;
- appropriate choice of the cathode substrate (copper or other material) and of the physical form of presentation of cathode deposit (adherent and uniform deposits or deposition of metalic powder) [2].

4.3. Summary of literature data on recovery / removal of copper from waste by cathodic deposition

In a table with 68 lines are presented, synthetically, literature data concerning the recovery of copper from dilute solutions (like waste water) and real or synthetic concentrates obtained after solubilisation of solid waste in various media of dissolution. The information in this table refers to the electrochemical reactors used in research, detailing aspects of electrode materials, electrolyte solution composition, its pH, electrochemical parameters (current density, electrode potential, etc.) and experimental techniques used within each analyzed study. Are presented, also, purposes of the researches and obtained results.

Part II. Experimental results

Chapter 5

Electroextraction of copper from synthetic solutions

5.1. Electroextraction of copper from diluted synthetic solutions with a similar composition to wastewaters [34]

Wastewaters from various industrial processes contain different heavy metal ions (HMI). Due to economical and environmental reasons, these ions must be removed from the wastewaters before these waters are released into rivers. The maximum admitted concentration of HMI in wastewaters before discharging them into rivers is strictly regulated by EU standards, which enforce a rigorous control and the treatment of these wastewaters. The concentration limits for HMI are between 0.05−1.0 mg/L (ppm) [35].

The purpose of this study was to optimize the parameters of copper electroextraction (CuE) from diluted synthetic solutions (10 mg/L Cu^{2+}) with a similar composition to wastewaters but with a low chloride and sulphate content (NaCl and Na_2SO_4<15 mM) and the reduction of Cu^{2+} concentration below a value of 0.1 ppm.

The CuE tests from diluted synthetic solutions were made in an electrochemical reactor (ER, homemade, Figure 5.1) in a continuous flow mode. The performance of the system were evaluated using the residual final concentration of Cu ($C_{f,\mathrm{Cu}}$) and energy consumption (W_S).

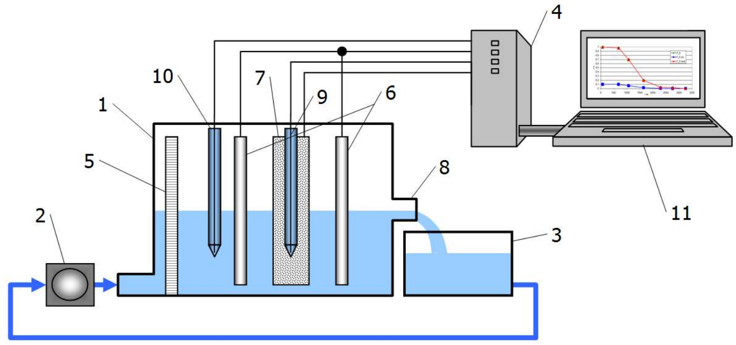


Figure 5.1. Electrolysis ER: 1 - single compartment ER; 2 – peristaltic pump; 3 – buffer vessel; 4 - potentiostate; 5 - diaphragm; 6 - anode; 7 – cathode; 8 - overflow; 9 – RE for WE; 10 – RE for CE; 11 - PC.

5.1.1. The study of CuE parameters from chloride based synthetic solutions

The effects of chloride concentration, cathodic potential and electrolyte flow rate upon CuE were evaluated.

5.1.1.1. Chloride ions concentration

Tests of CuE

In order to evaluate the influence of chloride concentration on the electroextraction parameters, CuE tests were performed using different concentrations of NaCl, applying a cathodic potential of –200 mV/RE and an electrolyte flow rate (Q_R) of 50 mL/min.

The global parameters of the process are presented in Table 5.1.

Table 5.1. Global parameters values for CuE; $\varepsilon_C = -200$ mV; $Q_R = 50$ mL/min.

C_{NaCl} [mM]	E_B [V]	W_S [kW/m^3 treated electrolyte]	$r_{\mathcal{F}}$ [%]	$C_{f,\mathrm{Cu}}$ [ppm]
5	2.55	0.73	4.2	0.05
10	1.79	0.18	9.2	0.06
15	1.53	0.12	11.4	0.14

Increasing the NaCl concentration in electrolyte leads to an increase of faradaic efficiency of the process ($r_{\mathcal{F}}$) and a decrease of W_S. Unfortunately, the residual Cu concentration doesnt decrease below the expected values in the presence of high concentrations of chloride. Moreover, the formation of Cu complexes, such as $[\mathrm{CuCl_x}]^{-(\mathrm{x}-1)}$ and CuCl (with a low solubility in aqueous solutions with a low $\mathrm{Cl^-}$ content), inhibits CuE [19, 31, 36, 37]. The presence of chloride ions has a complex influence on CuE and a moderate concentration of $\mathrm{Cl^-}$ (∼10 mM NaCl) proved to be a good compromise which ensures a reasonable conductivity of the solution as well.

5.1.1.2. Cathodic potential

The experiments were performed using a 10 mM NaCl as electrolyte with a 50 mL/min flow rate. The results of the tests performed in order to evaluate the cathodic potential influence on the CuE parameters are presented below, in Table 5.2.

Table 5.2. Global CuE parameters at different ε_C values C_{NaCl}=10 mM; Q_R=50 mL/min.

ε_C [V/ER]	E_B [V]	W_S [kW/m^3 treated electrolyte]	$r_{\mathcal{F}}$ [%]	$C_{f,\mathrm{Cu}}$ [ppm]
–0.100	2.17	0.81	2.6	0.63
–0.200	1.79	0.18	9.2	0.06
–0.300	2.16	0.52	3.8	0.06

For a potential value of –100 mV/RE, the system is unstable and performs poorly (low $r_{\mathcal{F}}$

and high W_S). Moreover, the oxygen generated on the anode is being reduced by the cathode, generating a supplementary consistent current even in the absence of CuE.

The change of the cathodic potential to –200 mV/RE results in an increase of $r_{\mathcal{F}}$ and a decrease of W_S. On top of that, the formation of a compact Cu deposit hinders the oxygen reduction reaction (Orr) and decreases the Cu^{2+} concentration below 0.1 ppm.

A value of –300 mV/RE proves to be inappropriate for CuE, leading to a porous cathodic deposit and an increase of W_S. The oxygen generated at the anode gets reduced at the cathode, influencing the quality of the Cu deposit and diminishing the faradic efficiency of the process.

Taking into consideration the observations made above, all further experiments were performed at a –200 mV/RE cathodic polarisation value.

Regarding the residual final concentration of Cu, after 90 minutes of electrolysis time at –100 mV/RE, it was calculated that 94 % of the initial Cu content was reduced, without decreasing the final concentration below 0.1 ppm. When applying –200 and –300 mV/RE, 99.4 % of the initial Cu content was reduced, the final concentration going below 0.1 ppm.

5.1.1.3. Electrolyte flow rate / mass transfer coefficient

In order to evaluate the effect of increasing the mass transfer upon CuE, several tests were performed at different Q_R values, 25, 50, 75 and 100 mL/min. The results are presented in Table 5.3. The Cu concentration evolution in time at different Q_R values is depicted in Figure 5.2.

Table 5.3. Global CuE parameters at different Q_R values; C_{NaCl}=10 mM; ε_C=–200 mV/ER.

Q_R [mL/min]	E_B [V]	W_S [kW/m^3 treated electrolyte]	$r_{\mathcal{F}}$ [%]	$C_{f,\mathrm{Cu}}$ [ppm]
25	1.97	0.35	5.6	0.68
50	1.79	0.18	9.2	0.06
75	1.90	0.30	6.1	0.07
100	1.97	0.49	4.4	0.05

From Table 5.3 and Figure 5.2 it can be seen that the intensification of mass transfer (IMT) has a positive effect upon CuE, as expected to be in the case of diluted solutions. On top of that, the IMT improves the cathodic oxygen reduction. This complex interaction makes the effect of flow rate change from 50 to 75 mL/min insignificant. At higher flow rates (100 mL/min) the oxygen concentration present in the solution cannot be increased further, the solution being saturated in oxygen. Therefore, although the current generated initially at this high flow rate, it rapidly decreases at values similar to those at low flow rates.

One has to consider that an efficient CuE which generates homogeneous Cu deposits is ultimately strictly dependent on a moderate and constant current density. Based on these facts, a flow rate value of 50 mL/min proves to be sufficient for our purposes.

For Q_R values > 25 mL/min less than 90 minutes are necessary to reduce the Cu concentration below 0.1 ppm (see Figure 5.2).

Based on the ER construction, operation and results, the electrochemical reactor used for the tests described above was assimilated with an continuous stirred-tank electrochemical reactor (CSTER). This classification was made based upon its characteristics and mass transfer based functioning.

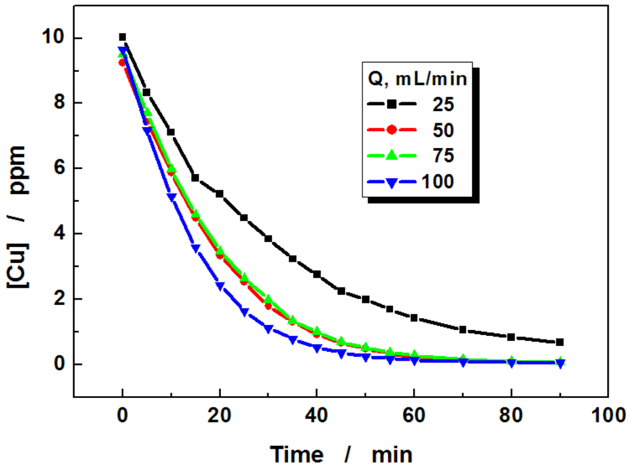


Figure 5.2. The decrease of Cu concentration in time at different Q_R values; ε_C=–200 mV/RE; C_{NaCl}=10 mM.

For an CSTER with recirculation the fractional conversion X is [13, 28]:

$$X = 1 - \exp\left[-\frac{t}{\tau}\left(1 - \frac{1}{1 + \dfrac{k_m A}{Q_R}}\right)\right] \tag{5.1}$$

where t is the time (min.) and $\tau = V_S/Q_R$ is the stationary time in ER, V_R=250 mL.

After rearranging the terms, we get:

$$1 - X = \exp\left[-\frac{t}{\tau}\left(1 - \frac{1}{1 + \dfrac{k_m A}{Q_R}}\right)\right] \tag{5.2}$$

If we extract the logarithm the following results::

$$\ln(1 - X) = -\frac{t}{\tau}\left(1 - \frac{Q_R}{Q_R + k_m A}\right) \tag{5.3}$$

similar to a linear equation:

$$y = a + bx, \quad \text{where}$$

$$y = \ln(1 - X), \quad x = t, \quad a = 0$$

and

$$b = -\frac{1}{\tau}\left(1 - \frac{Q_R}{Q_R + k_m A}\right) \tag{5.4}$$

A graphical representation of $\ln(1 - X) = f(t)$, at different electrolyte flow rates is beiong depicted in Figure 5.3. The obtained lines, $y = -bx$, have the following equations:

- y=–0.0326x, for Q_R=25 mL/min. The slope, b = –0.0326
- y=–0.0584x, for Q_R=50 mL/min. The slope, b = –0.0584
- y=–0.0718x, for Q_R=100 mL/min. The slope, b = –0.0718.

If we group the terms of (5.4) we get:

$$b\tau = -1 + \frac{Q_R}{Q_R + k_m A} \quad \text{or}$$

$$1 + b\tau = \frac{Q_R}{Q_R + k_m A} \tag{5.5}$$

For Q_R=25 mL/min, b=–0.0326; t=10 and equation (5.5) becomes:

$$1 - 0.0326 \cdot 10 = \frac{25}{25 + k_{m_{25}} A} \tag{5.6}$$

Solving (5.6) we get $k_{m_{25}}A = 12.09$ cm^{3}min^{-1} or $k_{m_{25}}A = 0.20$ cm^{3}s^{-1}.
For Q_R=50 mL/min, b=–0.0584; t=5 and equation (5.5) becomes:

$$1 - 0.0584 \cdot 5 = \frac{50}{50 + k_{m_{50}} A} \tag{5.7}$$

Solving (5.7) we get $k_{m_{50}}A = 20.62$ cm^{3}min^{-1} or $k_{m_{50}}A = 0.34$ cm^{3}s^{-1}.
For Q_R=100 mL/min, b=–0.0718; t=2.5 and equation (5.5) becomes:

$$1 - 0.0718 \cdot 25 = \frac{100}{100 + k_{m_{100}} A} \tag{5.8}$$

When doubling the recirculation flow rate from 25 to 50 mL/min the product kmA increases from 0.2 to 0.34 cm^{3}s^{-1}. A further increase to 100 mL/min increases $k_m A$ only slightly to 0.36, leading to the decision of operating at 50 mL/min.

5.1.2. The study of CuE parameters from sulphate based synthetic solutions

The effects of sulphate concentration, cathodic potential and electrolyte flow rate upon CuE were evaluated, similar to the chloride case.

5.1.2.1. Sulphate ions concentration

When working with small concentrations of Na_2SO_4 (1.0 mM), the conductivity of the solution is very low and therefore W_S is large. An improvemebnt of the $r_{\mathcal{F}}$ is obtained when increasing the Na_2SO_4 concentration.

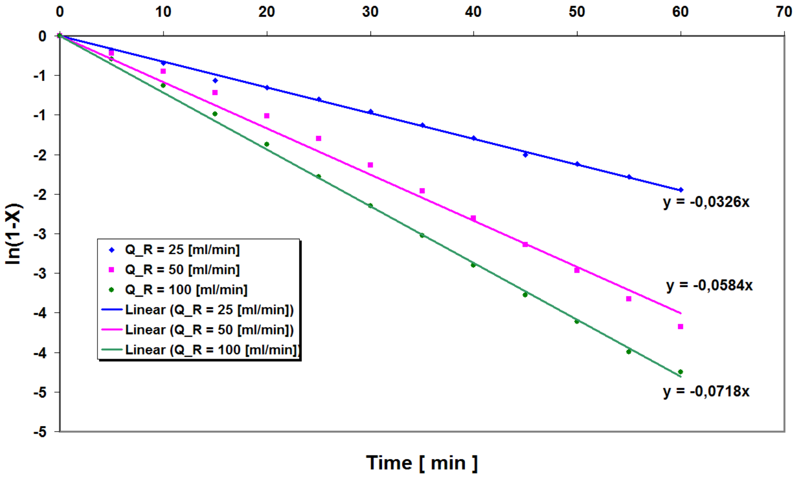


Figure 5.3. The fractional conversion *vs* time at different Q_R values.

Tests of CuE

In order to evaluate the influence of sulphate concentration on the electroextraction parameters, CuE tests were performed using different concentrations of Na_2SO_4, applying a cathodic potential of –200 mV/RE and an electrolyte flow rate (Q_R) of 50 mL/min. The global parameters of the process are presented in Table 5.4.

Table 5.4. Global parameters values for CuE at different $C_{\mathrm{Na_2SO_4}}$; ε_C=–200 mV/ER; Q_R=50 mL/min.

$C_{\mathrm{Na_2SO_4}}$ [mM]	E_B [V]	W_S [kWh/m^3 treated electrolyte]	$r_{\mathcal{F}}$ [%]	$C_{f,\mathrm{Cu}}$ [ppm]
2.5	1.88	0.19	8.4	0.16
5.0	1.74	0.35	5.2	0.35
7.5	1.69	0.18	7.9	0.09
10.0	1.69	0.21	6.7	0.13

At small Na_2SO_4 concentrations the conductivity of the solution is very low generating an oscillating system; the anode generated oxygen is reduced at the cathode to hydrogen peroxide increasing the current and the energy consumption. When using 2.5 mM Na_2SO_4 the solution becomes conductive enough for the Cu to get deposited and to inhibit Orr. At 7.5 mM and 10 mM, the electrolysis proceses are comparable from the point of view of ebergy consumption. Therefore, we decided to continue the experiments at 7.5 mM Na_2SO_4.

5.1.2.2. Cathodic potential

The experiments were performed using a 7.5 mM Na_2SO_4 as electrolyte with a 50 mL/min flow rate. The cathodic polarisation potentials were studied between values of –100 and –350 mV/RE.

The results of the tests performed in order to evaluate the cathodic potential influence on the CuE parameters are presented below, in Table 5.5.

Table 5.5. Global CuE parameters at different ε_C values; Q_R=50 mL/min; $C_{\mathrm{Na_2SO_4}}$=7.5 mM).

ε_C [V/ER]	E_B [V]	W_S [kWh/m^3 treated electrolyte]	$r_{\mathcal{F}}$ [%]	$C_{f,\mathrm{Cu}}$ [ppm]
–0.100	1.51	0.15	8.8	0.86
–0.200	1.69	0.18	7.9	0.09
–0.300	2.05	0.33	5.4	0.08
–0.350	2.76	1.33	1.9	0.09

In sulphate based solutions the increase of cathodic polarisation results in an current increase and a rF decrease. For potential values of –100 mV, –200 mV and –300 mV/RE, the Cu deposit hinders the oxygen reduction reaction. At –350 mV, the electrochemical system becomes unstable and the large quantity of oxygen generated at the anode gets reduced at the cathode generating an extra current and the decrease of $r_{\mathcal{F}}$.

Taking into consideration the observations made above, all further experiments were performed at a –200 mV/RE cathodic polarisation value. At this potential value the residual final concentration of Cu decreases below 0.1 ppm.

5.1.2.3. Electrolyte flow rate / mass transfer coefficient

In order to evaluate the effect of increasing the mass transfer upon CuE, several tests were performed at different Q_R values, 25, 50, 75 and 100 mL/min. The results are presented in Table 5.6.

Table 5.6. Global CuE parameters at different Q_R values; (ε_C=–200 mV/ER; $C_{\mathrm{Na_2SO_4}}$=7.5 mM).

Q_R [mL/min]	E_B [V]	W_S [kWh/m^3 treated electrolyte]	$r_{\mathcal{F}}$ [%]	$C_{f,\mathrm{Cu}}$ [ppm]
25	1.42	0.11	11.8	0.73
50	1.69	0.18	7.9	0.09
75	1.72	0.19	7.8	0.26
100	1.87	0.29	5.8	0.06

When the recirculation flow rate is low, Orr is competing with CuE and the Cu deposit is insufficient to inhibit Orr.

When Q_R is increasing, the mass transfer amplification ensures enough Cu^{2+} at the interface and a rapid accumulation of a Cu deposit, which inhibits Orr. If the flow rate increases further, the oxygen generated at the anode reaches the cathode, gets reduced and generates an extracurrent with negative effects upon energy consumption. The time dependency of the Cu concentration at different flow rate values is illustrated in Figure 5.4.

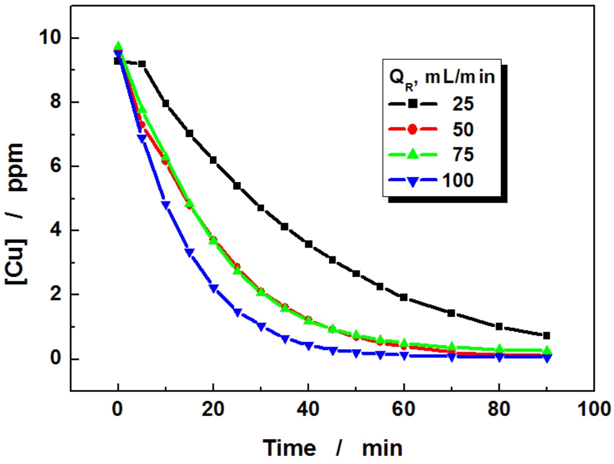


Figure 5.4. The decrease of Cu concentration in time at different Q_R values; ε_C=−200 mV/RE; 7.5 mM Na_2SO_4.

In the case of the sulphate based electrolyte, an identical approach as for chloride was used in order to evaluate the fractional conversion of the reactor (equations 5.1 to 5.4).

A graphical representation of $\ln(1-X) = f(t)$, at different electrolyte flow rates is beiong depicted in Figure 5.5. The obtained lines, $y = -bx$, have the following equations:

$y = -0.0246\,x$, for $Q_R = 25$ mL/min

The slope, b = –0.0246.

$y = -0.0519\,x$, for $Q_R = 50$ mL/min

The slope, b = –0.0519.

$y = -0.0746\,x$, for $Q_R = 100$ mL/min

The slope, b = –0.0746.

Solving the equations we get:

- for 25 mL/min $k_{m_{25}}A$=8.16 cm^3min^{-1} or $k_{m_{25}}A$=0.14 cm^3s^{-1}
- for 50 mL/min $k_{m_{50}}A$=17.52 cm^3min^{-1} or $k_{m_{50}}A$=0.29 cm^3s^{-1}
- for 100 mL/min $k_{m_{100}}A$=22.92 cm^3min^{-1} or $k_{m_{100}}A$=0.38 cm^3s^{-1}

When doubling the recirculation flow rate from 25 to 50 mL/min the product k_mA increases from 0.14 to 0.29 cm^3s^{-1}. A further increase to 100 mL/min increases k_mA to 0.38.

When comparing the two electrolytes (chloride and sulphate), one can see that the k_mA

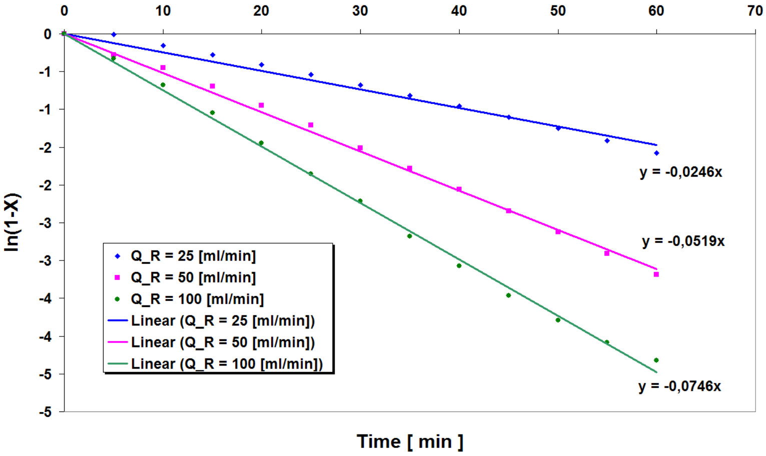


Figure 5.5. The fractional conversion *vs* time at different Q_R values.

product has a similar behaviour in both electrolytes up to 50 mL/min flow rate. A comparison between the two electrolytes is given in Table 5.7 and it can be seen that no significant differences arise.

Table 5.7. Comparison of CuE parameters in chloride *vs* sulphate based electrolytes at (ε_C=–200 mV/RE).

Nr. crt.	Q_R [mL/min]	Chloride [10 mM]		Sulphate [7.5 mM]	
		$X_{60\text{ min}}$ [%]	k_mA [cm^{3}s^{-1}]	$X_{60\text{ min}}$ [%]	k_mA [cm^{3}s^{-1}]
1	25	85	0.20	79	0.14
2	50	97	0.34	96	0.29
3	100	98	0.36	98	0.38

In conclusion we can see that Cu can be removed from diluted aqueous solutions with the same efficiency irrespective of chloride or sulphate based electrolytes. Based on this conclusion, the further galvanostatic tests were performed only in sulphate based solutions.

5.1.3. Conclusions

The results generated from the experimental tests lead to the following conclusions:

- The optimum polarisation potential for a potentiostatic CuE was –200 mV, at a flow rate of 50 mL/min, using 10 mM NaCl or 7.5 mM Na_2SO_4;
- When working under optimal conditions, the concentration of Cu^{2+} could be reduced below 0.1 ppm, which is within the accepted limits for HMI concentrations in waters;
- Based on the ER construction, operation and results, the electrochemical reactor used for

the tests described above was assimilated with an electrochemical completely mixed reactor (ECMR) [13, 28];

- Based on the calculated conversion efficiency and the $k_m A$ product we consider that Cu can be removed from diluted aqueous solutions with the same efficiency irrespective of chloride or sulphate based electrolytes;
- The $k_m A$ found by us are bigger compared with the literature where kmA for chloride was found to be 0.28 $cm^3 s^{-1}$ and for sulphate 0.26 $cm^3 s^{-1}$ on 100 ppi reticulated vitreous carbon [30, 31];
- The final conversion in both cases is above 98 %;
- For all our experiments the maximum energy consuption was 2.04 kWh/m^3 electrolyte; the costs of energy can be translated to 0.714 RON/m^3 electrolyte ((1 kWh = 0.35 RON for industrial consumers) or 0.25 USD/m^3 electrolyte (1 USD = 2.9223 lei at 28.03.2011). This cost is much smaller than a previous literature report of 1.97 USD/m^3 of electrolyte [38].

5.2. Electroextraction of Cu from mixed synthetic solutions with a similar composition to real solution resulted from a sulphuric acid solubilisation of PC electronic components from printed circuit boards [39]

The solution resulted after solubilising the metallic parts of electronic components (ECs) from printed circuit boards (PCBs) contains Cu, Al, Fe, Zn, Pb and Sn, Cu being the largest amount (5 g/L) [40].

The purpose of this study was to optimize the parameters of copper electroextraction (CuE) from mixed and concentrated synthetic solutions with a similar composition to real solution resulted from a sulphuric acid (2 M) solubilisation of Computer ECs from PCBs [39].

Experimental studies were made in a 250 cm^3 glass ER (Fig. 5.6).

5.2.1. Hydrodynamic voltammetry tests (HV)

To evaluate the possibility of copper electrowinning from concentrated mixed solutions, HV tests were performed in mono-element solution (5 g/L Cu^{2+} in 2 M H_2SO_4) and mixed solution. Synthetic mixed solution with composition similar the solution resulting from dissolution of metals from electronic components (EC) on the WPCBs in 2 M H_2SO_4 have the composition shown in Tab. 5.8.

The measurements were performed with a scanning speed of 10 mV/s, at different values of RDE rotation speed (100 to 1600 rpm), on a range of potential from 0.6 to –0.8 V/RE. Corresponding polarization curves are shown in Fig. 5.7.

Table 5.8. The composition of mixed solution.

Element	Cu	Al	Fe	Ni	Zn	Pb	Sn
Concentration [g/L]	5.0	0.056	0.045	0.041	0.050	0.061	1.91

In mono-element solution (Fig. 5.7.a) on the anodic potential scan reveals one peak around 0.3 V/RE characteristic of copper oxidation. For mixed solution (Fig. 5.7.b), one can see two different oxidation peaks, corresponding of Sn and Cu. Moreover, the corresponding cathodic currents increase due to of simultaneously electrodeposition of Cu and Sn.

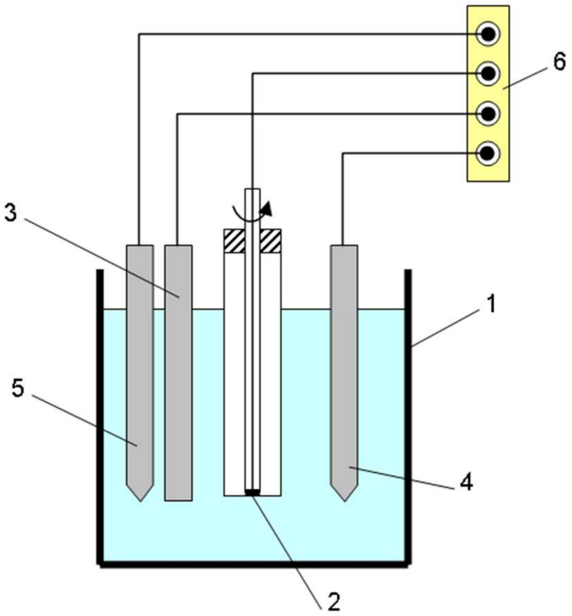


Figure 5.6. Glass un-compartmented ER; 1 – ER body;
2 – graphite RDE cathode; 3 – graphite anode bar;
4 and 5 – reference electrodes Ag/AgCl/KCl$_{\text{sat.}}$;
6 – potentiostat driven by computer.

5.2.2. The cathodic potential influence on copper electrowinning process

The measurements were made at different values of cathodic polarization potential and at different values of RDE rotation speed.

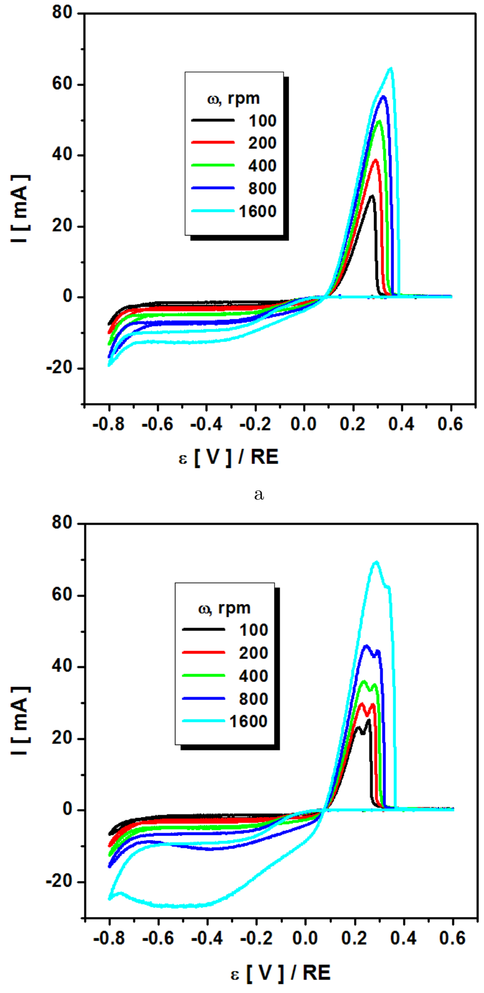
For the electrode potential of –100 and –150 mV/RE, forming a compact deposit of copper maintains a relatively constant surface on the electrode. Under these condition the current does not increase significantly.

The increasing of the cathodic polarisation at –200 to –300 mV/RE, the available electroactive surface increases, due to growth of dendrites on the surface of the deposit. This allows the current increase while the time required for the same amount of copper deposit and current cantities, decrease (200 C).

After each experiment, the obtained deposits were dissolved in aqua regia and the metallic impurities was measured by ICP-MS spectroscopy.

The influence of the cathodic potential polarisation on the purity of copper deposits is shown in Tab. 5.9.

ICP-MS analysis shows that the content of Fe, Ni and Pb in copper deposits are under detection limit (UDL <0.0001 %) and Al and Zn is found in very low concentrations. In terms of Sn, increasing cathodic polarization potential to negative values leads to a significant increase in



a

b

Figure 5.7. Hydrodynamic voltammetry (HV) on Pt for different RDE rotation speeds; a – single-element solution; b – mixed solution; scan rate: v=10 mV/s.

its content. However, the purity of copper deposits in all experiments was over 99 % and current efficiency around 100 %.

Table 5.9. The cathodic potential influence on the purity of copper deposits (ω=200 rpm).

Metallic impurities	ε_C [mV/ER]				
	–100	–150	–200	–250	–300
Al, %	0.0018	-	0.0066	0.0001	0.0035
Zn, %	0.0015	0.0007	0.0027	0.0039	0.0039
Sn, %	0.0018	0.0022	0.0040	0.1516	0.6795
Total, %	0.0051	0.0029	0.0133	0.1556	0.6869

In these conditions, a polarization potential of –200 mV/RE was considered the best compromise between electrodeposition speed and purity of copper deposits.

5.2.3. The influence of RDE rotation speed on copper electrowinning

The influence of RDE rotation speed on copper electrowinning was assessed in mixed solution at a potential working electrode polarization of –200 mV/RE.

The cathodic current evolution for different values of RDE rotation speed is shown in Fig. 5.8.

The investigation to minimum RDE rotation speed (ω=100 rpm), mass transport is insufficient to ensure a constant concentration of electrolyte on the electrode surface.

For higher values of RDE rotation speed ($\omega > 200$ rpm), mass transport is sufficient to ensure a relatively constant concentration of copper on the electrode surface, which increases the current, decreasing the time required for copper electrodeposition for the same amount of current (200 C).

For low RDE rotation speed (ω=100 rpm), the concentration of copper on the surface electrode is insufficient favoring co-deposit of Sn and for large values of RDE rotation speed ($\omega > 100$ rpm), the concentration of copper on the working electrode surface is sufficient to ensure the purity deposit of copper, as can be seen from Tab. 5.10 and from XRD pattern in Fig. 5.9.

At the polarization potential of –200 mV/RE, for all values of RDE rotation speed, the content of Fe, Ni and Pb deposits of copper is UDL (<0.0001 %) and Al and Zn are found in very low concentrations.

Table 5.10. The influence of RDE rotation speed on the purity deposits of copper (ε_C=–200 mV/ER).

Metallic impurities	ω [rpm]			
	100	200	400	800
Al, %	0.0017	0.0066	0.0050	-
Zn, %	0.0032	0.0027	0.0044	0.0022
Sn, %	0.0120	0.0040	0.0045	0.0040
Total, %	0.0169	0.0133	0.0139	0.0062

In Fig. 5.9 the XRD patterns of obtained copper deposits, at different values of RDE rotation speed, are presented.

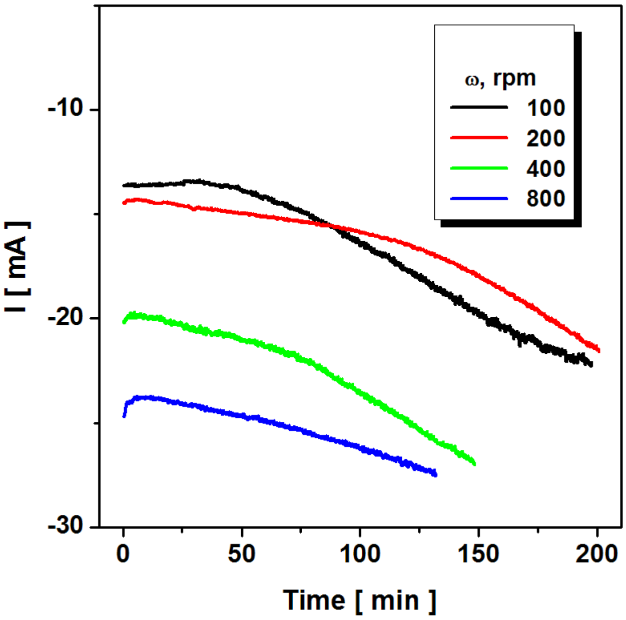


Figure 5.8. The cathodic current evolution at different values of RDE rotation speed; (ε_C=–200 mV/ER).

The analysis of XRD spectra of the deposit (obtained at a speed of 100 rpm) its seen specific copper peaks at diffraction angle values of 43.2; 50.5 and 74.1 degrees. The main metallic impurity present in the copper deposit (at this speed of rotation) is Sn appearing at 35.2 degrees. At the RDE rotation speed $\omega > 200$ rpm, XRD spectra show only specific peaks of copper.

5.2.4. Conclusions

The findings on the copper electrowinning from complex solution, with composition similar those resulting from solubilisation in 2 M H_2SO_4 of metal part of electronic components from WPCBs, leads to the following conclusions:

- It confirms the possibility of recovering copper from these solutions;
- Preliminary tests of hydrodynamic voltametry show that at potentials more negative than –200 mV/RE, copper electrowinning is controlled by mass transport. Also, in mixed solution hydrodynamic voltametry tests confirm that, on the studied potential range, we obtain a co-deposit of Cu–Sn;
- The potentiostatic experiments of copper electrowinning, at a constant rotation speed of 200 rpm, shows that the polarization potential of –200 mV/RE, is the best compromise between process speed and the purity of copper deposits;

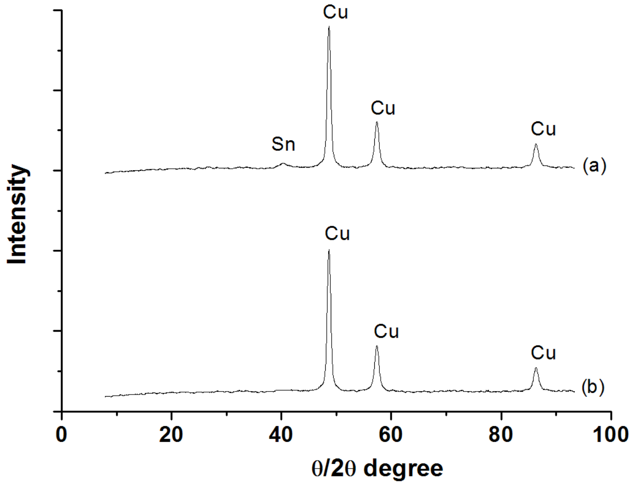


Figure 5.9. XRD patterns for copper deposits at various rotation speed of RDE: (a) - ω=100 rpm; (b) - $\omega \geqslant$200 rpm; (ε_C=–200 mV/ER).

- The measurements at different speeds of RDE rotation and constant polarization potential determined to be –200 mV/RE, shows that an increase in RDE rotation speed leads to an improvement in purity copper deposits at the same time increasing the speed of electrodeposition;
- ICP-MS and XRD analysis of copper deposits obtained show that, for all experiments, content of iron, nickel and lead is insignificant and aluminum and zinc are found in very low concentration. Also, the purity of copper deposits is more than 99 % in all experiments;

The obtained results will be further used in the future for the elaboration of a Cu recovery method from solid wastes.

CHAPTER 6

Recovery of copper from solid wastes

6.1. Copper recovery from printed circuit boards waste (WPCBs), without electronic components, by anodic dissolution and cathodic electrodeposition

The aim of this study was to recover Cu by anodic dissolution in sulphuric acid medium, without chemical dissolution [41].

Experiments were carried out on two waste types: Type 1 - network interface card and Type 2 - data acquisition board.

Tests have been performed in an electrochemical reactor (Fig. 6.1).

Figure 6.1. ER for Cu recovery from WPCBs by anodic dissolution and cathodic electrodeposition.

The process performances were evaluated based on current efficiency and specific energy consumption (W_S).

6.1.1. WPCBs surface treatment without electronic components

To access the Cu layers from plates, for anodic dissolution, the protective lacquer was removed with concentrate sulphuric acid.

6.1.2. Copper extraction degree by anodic dissolution

The waste without protective lacquer was placed in RE for anodic dissolution and simultaneous copper cathodic deposition, using as electrolyte an aqueous solution of sulfuric acid (2 M H_2SO_4).

The metals extraction degree was determined after anodic dissolution and copper cathodic deposition by AAS measurements of cathode deposits (dissolved in aqua regia) and electrolyte when dissolved metals completion of WPCBs. Results are shown in Table 6.1. Time evolution of the amount of electrodeposited copper, total current efficiency: $r_{\mathcal{F}}$, time variation of total current efficiency $r_{\mathcal{F},t}$ and anodic potential (ε_{ea}) are presented in Fig. 6.2.

Table 6.1. Distribution of metals in waste after anodic dissolution / electrodeposition.

Metal	Cu	Zn	Ni	Sn	Fe	Ag	Au	Pb
Deposit, [%]	77	3	2	15	1	73	1	23
Electrolyte, [%]	23	97	98	85	99	27	99	77

Extraction degree of Cu and other metals is 100 %. When the anodic dissolution was completed, 77 % from Cu dissolved amount was deposited on cathode and 23 % remained in electrolyte solution.

From the time evolution of the current efficiency can be observed that the process is slow at first, in the sense that after 5 hours current efficiency is only 50 % and then grows and maintains appox. 80 %. Although the total yield decreases after 20 hours, perhaps a parallel process is stimulated (download oxygen) electroextraction yield of copper ($r_{\mathcal{F}}$) remains high even after 25 hours due to the presence of copper in solution.

Anodic potential increases as the waste is exhausted and the current efficiency decreases when metal dissolution is finished.

Metal content of copper deposit is shown in Tab. 6.2. Tin is the most important impurities present in the copper cathode deposit while other metallic impurities are found in small quantities. Purity of copper cathode deposit is slightly over 98 %. The deposit obtained can be inserted into the flow of anode copper development for electrowinning when the concentration of copper should be in the 97.5−99.8 % [42, 43].

Table 6.2. Metallic composition of Cu deposit.

Metal	Cu	Zn	Ni	Sn	Fe	Ag	Au	Pb
[%]	98.03	0.01	0.03	1.78	0.12	0.01	0.0002	0.02

Metal content of the electrolyte solution, at the time of anodic dissolution termination (time when the anode potential increases due to unloading of oxygen), is presented in Tab. 6.3. Electrolyte solution can be recycled 10 times, when the concentration of metallic impurities reach the maximum acceptable value (Ni: max.12.0 g/L, Fe: max.3.0 g/L) [42].

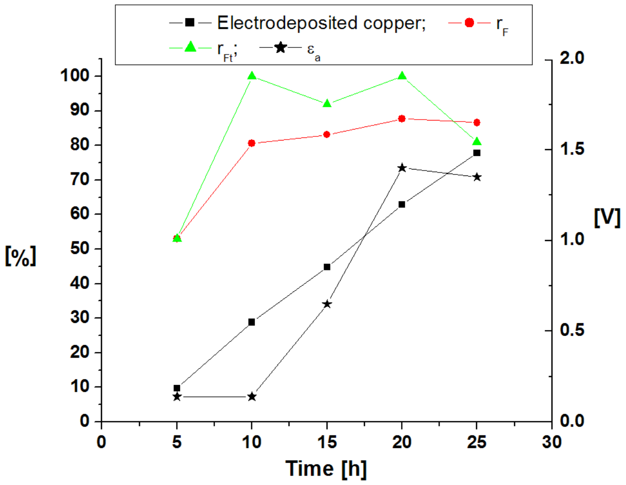


Figure 6.2. Time evolution of the amount of electrodeposited copper, total current efficiency $r_{\mathcal{F}}$ (%), time variation of total current efficiency $r_{\mathcal{F},t}$ (%) and anodic potential ε_{ea} (V/ER), electrolyze time: 25 hours.

This solution treatment can be applied to solutions similar to results from industrial refining of copper [42].

Table 6.3. Metallic composition of the electrolyte solution at the end of the anodic dissolution.

Electrolyte composition, [g/L]							
Cu	Zn	Ni	Sn	Fe	Ag	Au	Pb
1.20	0.02	0.06	0.43	0.40	0.0001	0.0016	0.002

6.1.3. Conclusions

Following experiments on the recovery of copper from waste PCI by anodic dissolution, we can conclude that:

- It was developed an original method to remove the laque from the surface of PCI without EC in order to have access to copper from the epoxy boards followed by anodic dissolution;
- Based on the results, a flow recovery technology of Cu from PCI without EC was proposed, by anodic dissolution and cathodic electrodeposition;
- The efficiency of Cu extraction from waste is 100 % and specific energy consumption W_S

= 1.06 kWh/kg Cu is lower than the Cu recovery achieved with Cu from the copper matte of 1.5 kWh/kg Cu [44];
- The deposit obtained has a purity of ~98 %;
- The costs for raw materials and utilities are calculated for 1 kg of pure Cu 26.514 lei.

6.2. Copper recovery from WPCBs by leaching with $FeCl_3$ and cathodic electrodeposition

The aim of the present study was to develop an original and ecological technology for copper recovery from WPCBs by chemical dissolution with Fe^{3+}, in HCl medium, combined with simultaneous copper electrowinning and oxidant regeneration.

All measurements were made using the experimental setup from Fig. 6.3. The dissolution of metals was achieved in a chemical reactor with a perforated rotating drum which contained the WPCBs while the electrochemical process was performed in a three chamber electrochemical reactor with plan parallel electrodes (Fig. 6.4).

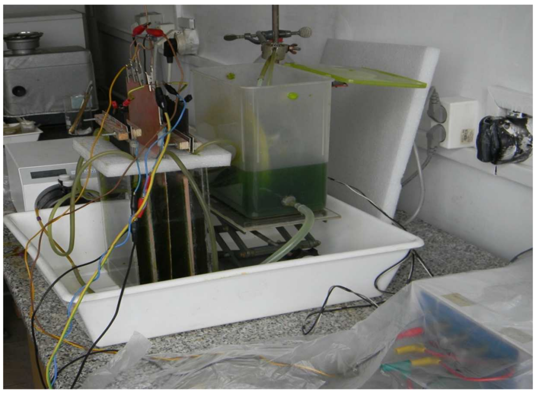


Figure 6.3. Schematic illustration of the lab-scale copper recovery equipment.

The dependents of the leaching process and copper electrodeposition of electrolyte flow rate was investigated. The reactor performance was evaluated based on the current efficiency, energy consumption, global conversion and cathodic deposit composition.

6.2.1. Metals leaching from WPCBs

The metals from the WPCB samples were dissolved in a chemical reactor, which was equipped with a perforated rotating drum, by using a 2000 mL 0.3 M $FeCl_3$ and 0.6 M HCl solution. The redox equilibrium constants were calculated based on the dissolution reactions of the metals in the leaching process.

For a general redox reaction the equilibrium constant can be defined as:

$$m\ Ox_1 + p\ Red_2 \rightleftarrows m\ Red_1 + p\ Ox_2 \tag{6.1}$$

Figure 6.4. The plan parallel electrodes of the electrochemical reactor.

where: m, p number of transferred electrons in the reaction and ε_i - standard normal potentials.

From eq. (6.1) it is evident that redox equilibrium constant value is greater as (equilibrium shifted to the right) the number of transferred electrons and the difference between the standard normal potentials is greater. If the redox equilibrium constant is greater than 10^4 the redox reaction becomes quantitative. The values of the redox equilibrium constants for the dissolution reactions are presented in Table 6.4 [45]. Based on these values, Table 6.4, we can conclude that the redox reactions are strongly shifted towards dissolution of metals through the formation of chloro-complexes. Since the redox equilibrium constant and the rate constant of the dissolution reactions are interdependent we can estimate the rate of these reactions. Therefore, the dissolution of metals will take place in the following order: Zn, Sn, Fe, Ni, Pb, Cu and Ag.

To evaluate the influence of mass transport on the leaching process of metals, experimental measurements were made at the following flow rates: 100, 200, 300, 400, 500, 700 mL/min.

The total amount of metals dissolved from the WPCBs and the ratio between the dissolved copper and the total amount of dissolved metals is presented in Fig. 6.5. As we can see from Fig. 6.5 the highest amount of metals was dissolved at the lowest flow rate, 100 mL/min, because the residence time in the chemical reactor at this flow rate is the largest (20 min). Therefore, the reaction time between the metals and Fe^{3+} is enough long to achieve a high dissolution degree. The ratio among the dissolved copper and total dissolved metals attains a maximum at 400 mL/min. For this reason the best flow rate for the chemical dissolution of metals was considered to be 400 mL/min. Based on these results we can conclude that the selectivity of the dissolution process can be modified by changing the electrolyte flow rate.

6.2.2. The copper electrowinning and the oxidant regeneration

After the dissolution of metals from the WPCBs in the chemical reactor, the electrolyte with the composition presented in Table 6.5, enters into the cathodic chamber of the electrochemical reactor by freefall.

At the cathode the main electrochemical process is the electrodeposition of copper according

Table 6.4. Redox equilibrium constants values for the dissolution reactions.

Redox reaction	Redox equilibrium constants
$3FeCl_4^- + Au + 4Cl^- \rightleftarrows AuCl_4^- + 3FeCl_4^{2-}$	$5.35 \cdot 10^{-17}$
$FeCl_4^- + Au + 2Cl^- \rightleftarrows AuCl_2^- + FeCl_4^{2-}$	$4.76 \cdot 10^{-10}$
$FeCl_4^- + Ag + 2Cl^- \rightleftarrows AgCl_2^- + FeCl_4^{2-}$	$5.35 \cdot 10^{3}$
$FeCl_4^- + Cu + 2Cl^- \rightleftarrows CuCl_2^- + FeCl_4^{2-}$	$2.01 \cdot 10^{8}$
$FeCl_4^- + CuCl_2^- \rightleftarrows CuCl_{2_{aq.}} + FeCl_4^{2-}$	$3.91 \cdot 10^{5}$
$2FeCl_4^- + Cu + 2Cl^- \rightleftarrows CuCl_{2_{aq.}} + 2FeCl_4^{2-}$	$5.79 \cdot 10^{13}$
$2FeCl_4^- + Sn + 4Cl^- \rightleftarrows SnCl_4^{2-} + 2FeCl_4^{2-}$	$1.47 \cdot 10^{30}$
$2FeCl_4^- + SnCl_4^{2-} + 2Cl^- \rightleftarrows SnCl_6^{2-} + 2FeCl_4^{2-}$	$9.61 \cdot 10^{18}$
$4FeCl_4^- + Sn + 6Cl^- \rightleftarrows SnCl_6^{2-} + 4FeCl_4^{2-}$	$1.42 \cdot 10^{49}$
$2FeCl_4^- + Pb + 4Cl^- \rightleftarrows PbCl_4^{2-} + 2FeCl_4^{2-}$	$3.1 \cdot 10^{29}$
$2FeCl_4^- + PbCl_4^{2-} \rightleftarrows PbCl_6^{2-} + 2FeCl_4^{2-}$	$2.09 \cdot 10^{-33}$
$4FeCl_4^- + Pb + 6Cl^- \rightleftarrows PbCl_6^{2-} + 4FeCl_4^{2-}$	$6.5 \cdot 10^{-4}$
$2FeCl_4^- + Ni + 4Cl^- \rightleftarrows NiCl_4^{2-} + 2FeCl_4^{2-}$	$1.66 \cdot 10^{33}$
$2FeCl_4^- + Fe + 4Cl^- \rightleftarrows 3FeCl_4^{2-}$	$2.2 \cdot 10^{37}$
$2FeCl_4^- + Zn + 4Cl^- \rightleftarrows ZnCl_4^{2-} + 2FeCl_4^{2-}$	$3.1 \cdot 10^{49}$

Table 6.5. The initial electrolyte composition at the entrance of electrochemical reactor.

Flow rate [mL/min]	The initial metallic composition of the inlet solution, [g/L]							
	Ag	Au	Cu	Fe	Ni	Pb	Sn	Zn
100	0.002	0.008	12.2	33.2	0.16	0.82	3.62	3.91
200	0.002	0.006	5.6	25.6	0.10	0.50	2.16	1.70
300	0.000	0.004	4.1	20.8	0.09	0.31	2.07	1.30
400	0.002	0.004	4.5	21.8	0.10	0.34	2.30	1.44
500	0.002	0.006	4.3	20.6	0.08	0.35	2.24	1.45
700	0.000	0.006	6.7	25.6	0.12	0.54	2.30	2.41

to the following reactions:

$$CuCl_{2_{aq.}} + 2e^- \rightarrow Cu + 2Cl^- \tag{6.2}$$

$$CuCl_{2_{aq.}} + e^- \rightarrow CuCl_2^- \tag{6.3}$$

$$CuCl_2^- + e^- \rightarrow Cu + 2Cl^- \tag{6.4}$$

The secondary cathodic reactions are the followings:

$$SnCl_6^{2-} + 2e^- \rightarrow SnCl_4^{2-} + 2Cl^- \tag{6.5}$$

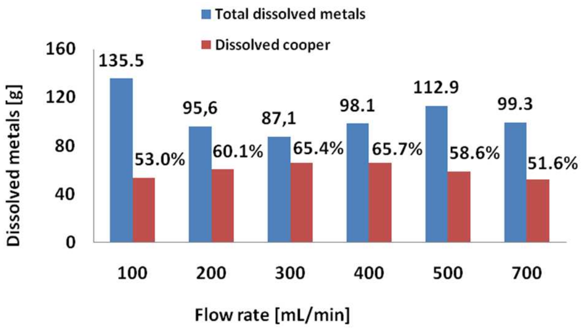


Figure 6.5. The total amount of dissolved metals / the ratio between dissolved copper and the total amount of dissolved metals.

$$\mathrm{FeCl_4^{2-} + e^- \rightarrow FeCl_4^{2-}} \tag{6.6}$$

The electrolyte, with high Fe^{2+} content, is passed from the cathodic chamber to the anodic chambers where the main electrochemical process is the oxidation of Fe^{2+} to Fe^{3+}:

$$\mathrm{FeCl_4^{2-} - e^- \rightarrow FeCl_4^-} \qquad \varepsilon = 0.77\ \mathrm{V/ENH}$$

while the secondary anodic reactions are the followings:

$$\mathrm{SnCl_4^{2-} + 2Cl^- - 2e^- \rightarrow SnCl_6^{2-}} \qquad \varepsilon = 0.14\ \mathrm{V/ENH}$$

$$\mathrm{2H_2O - 4e^- \rightarrow 4H^+ + O_2} \qquad \varepsilon = 1.24\ \mathrm{V/ENH}$$

$$\mathrm{2Cl^- - 2e^- \rightarrow Cl_2} \qquad \varepsilon = 1.36\ \mathrm{V/ENH}$$

6.2.2.1. The influence of electrolyte flow rate on electrochemical process performances

The evolution of electrode potentials and cell voltage with electrolyte flow rate was investigated and results are presented in Table 6.6. Also, it was evaluated the dependents of current efficiency, energy consumption, global conversion and cathodic deposit composition on the hydrodynamic conditions.

The results, Table 6.6, show that the increase of flow rate has a positive effect on the thermodynamic parameters of the process. This can be explained by the interdependence between the electrolyte conductivity, electrode potentials and electroactive species concentration. Also, the electrode potentials are influenced by the mass transport over-potentials which decrease with the increase of flow rate.

The variation of catholyte flow rate affects different the global conversion of copper compared with the electrode potential. While the electrode potential decreases continuously with the increase of flow rate the global conversion of copper reaches a maximum between 200÷400 mL/min after which decreases sharply, Fig. 6.6–6.7. By comparing the pairs of values, cathodic current efficiency and copper conversion, it was found that for both the best results are obtained at 400 mL/min. The same results were obtained for the specific energy consumption, see Fig. 6.8.

Table 6.6. Electrode potentials and cell voltage at different flow rates.

Flow rate, [mL/min]	ε_c, [V]	ε_a, [V]	E_B, [V]
100	−0.166	1.79	2.20
200	−0.151	1.17	1.65
300	−0.145	0.94	1.51
400	−0.136	0.91	1.37
500	−0.110	0.90	1.26
700	−0.073	0.93	1.26

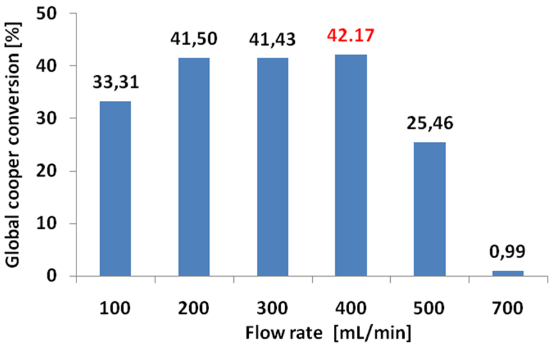


Figure 6.6. The global conversion of copper in ER.

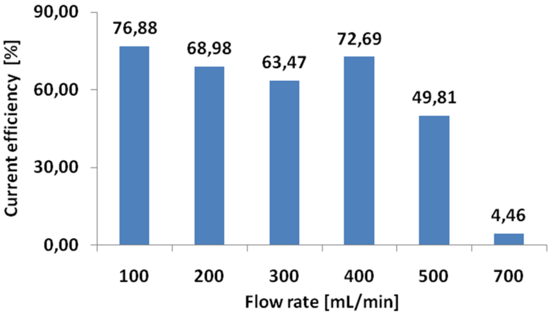


Figure 6.7. Cathodic current efficiency function of flow rate at constant current $I = 2$ A.

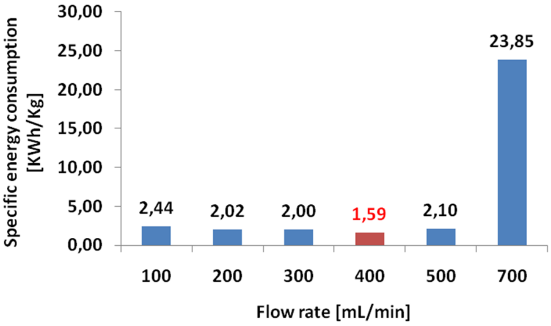
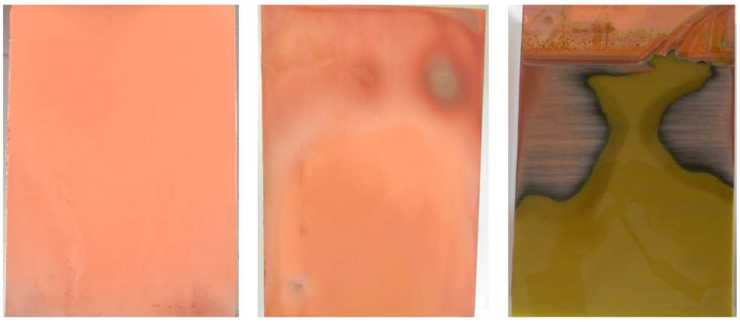


Figure 6.8. Specific energy consumption function of flow rate at constant current.



100-400 mL/min 500 mL/min 700 mL/min

Figure 6.9. Cu deposits at different recirculation flow rates.

The chemical composition is another important factor in the characterisation of the cathodic deposit. Therefore, the chemical composition of the deposits was determined for all flow rates at the end of the experiments, Table 6.7. The results show that the cathodic deposits are uniformly distributed and adherent until 400 mL/min. After that, at 500 mL/min, the cathode surface areas are partially dissolved and at 700 mL/min these areas are extended blocking the process, Fig. 6.9.

6.2.3. Conclusions

Based on the experimental results of copper recovery from WPCBs we can conclude the following:

- An original technological process was developed for copper recovery from WPCBs by combining the chemical dissolution of metals by $FeCl_3$ with the electrowinning of copper;
- The results show that $FeCl_3$ is a regenerative and efficient oxidant in the dissolution of

Table 6.7. The final metallic composition of the electrolyte function of recirculation flow rate.

Flow rate [mL/min]	Final metallic composition of the electrolyte, [g/L]							
	Ag	Au	Cu	Fe	Ni	Pb	Sn	Zn
100	0.002	0.009	5.34	33.8	0.21	0.94	5.74	5.83
200	0.002	0.006	3.58	21.0	0.12	0.86	2.81	3.79
300	0.002	0.004	4.17	18.2	0.08	0.28	1.67	3.99
400	0.002	0.004	4.63	19.0	0.09	0.32	1.86	4.44
500	0.002	0.006	7.44	22.7	0.16	0.89	3.40	4.72
700	0.002	0.006	9.75	24.8	0.14	0.93	2.38	3.63

metals;

- By studying the influence of flow rate on the performances of the process it can be concluded that the optimal hydrodynamic conditions are provided at 400 mL/min;
- The extraction degree of copper from the waste is 100 % at a specific energy consumption of 1.59 kWh/Kg Cu which is similar to those mentioned in the literature;
- For all the experiments the content of copper in the obtained cathodic deposits was over 99.9 %.

Chapter 7

Environmental assessment process for copper recovery from waste

7.1. Environmental impact assessment method

The method has a simple structure and is based on data that can be accessed easily.

In the first stage are collected all available data relevant to the process. Mass balance is drawn up with all the inputs and outputs of the process. These data are supplemented with data from literature.

The environmental impact factors of the components are obtained from the inputs and outputs of the technological process in the second stage of implementation of the method. Finally, the quantities of raw materials and products, with ecological factors, are combined in a set of indices. These indices lead to the global environmental impact.

7.2. Conclusions

The results of environmental impact assessment lead to the following conclusions:

- For the first method, the global $\mathbf{EI}_{\text{Mediu}}$ of the inputs is 0.0782 points / kg of product and overall $\mathbf{EI}_{\text{Mult}}$ inputs is 2.94 points / kg of product. The global $\mathbf{EI}_{\text{Mediu}}$ of the outputs is 0.0695 points / kg of product and overall $\mathbf{EI}_{\text{Mult}}$ outputs is 2.78 points / kg of product.
- For the second method, the global $\mathbf{EI}_{\text{Mediu}}$ of the inputs is 0.0382 points / kg of product and overall $\mathbf{EI}_{\text{Mult}}$ inputs is 1.44 points / kg of product. The global $\mathbf{EI}_{\text{Mediu}}$ of the outputs is 0.0337 points / kg of product and overall $\mathbf{EI}_{\text{Mult}}$ outputs is 1.49 points / kg of product.
- For both methods the average indices of inputs and outputs have very low values, appropriated to the minimum possible, the interval for the $\mathbf{EI}_{\text{Mediu}}$ is $0 \div 1$ respectively $1 \div 256$ for the $\mathbf{EI}_{\text{Mult}}$, indicating a generally low environmental impact of materials used in the proposed procedures.

Chapter 8

General conclusions

The PhD thesis aimed to bring a series of original contributions in very diverse and complex field of copper recovery from wastes. The purpose of the thesis was the recovery / removal of metallic copper in different types of waste (waste water with low or high copper content, the waste of PCBs) by electrochemical processes or chemical-electrochemical methods.

In the first part of the thesis a systematic investigation was made about the rich bibliographic material with general and specific issues regarding: the importance of copper and its methods of recovery from different types of waste, environmental pollution with copper and other heavy metals, general procedures for the removal / recovery of heavy metals from waste and electrochemical processes for removal / recovery of heavy metals from waste. The study of the literature concentrated on the electrochemical methods which were widely presented in the original contribution part of the thesis. Therefore, a study was made about the electrodeposition of heavy metals and the parameters which describe the electrochemical process (current density, electrode material, electrolyte composition).

In Chapter 5, based on literature models for cooper recovery from waste, was established an optimal procedure for cooper electrowinning from diluted and concentrated synthetic solutions with the following details:

- By using a 3D electrodes and by increasing mass transport, the concentration of cooper was reduced from 10 ppm to 0.1 ppm which is the MAC for drinking water;
- Maximum specific energy consumption was 2.04 kWh/m^3 treated electrolyte;
- The selective recovery of copper from mixed solutions with obtaining deposits over 99 % purity.

In Chapter 6, the recovery of copper from solid waste was conducted by two original methods:

- An original method of anodic dissolution / cathodic electrodeposition of Cu from WPCBs, without electronic components, in sulphuric acid medium, without a previous chemical dissolution;
- An original method of copper recovery from WPCBs by combining a chemical dissolution process, with $FeCl_3$ in HCl medium, with a cathodic electrodeposition process and regeneration of the oxidant at the anod.

Chapter 7 includes environmental assessment of input and output materials of the processes. For both original proposed methods the average indices of inputs and outputs have very low values, appropriated to the minimum possible; the interval for the $\mathbf{EI}_{\mathrm{Mediu}}$ is $0 \div 1$ respectively $1 \div 256$ for the $\mathbf{EI}_{\mathrm{Mult}}$, indicating a generally low environmental impact of materials used in the proposed procedures.

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