STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIII, 1, 2008

In memoriam prof. dr. Liviu Oniciu

ELECTRODEPOSITION OF SOME HEAVY METALS ON RETICULATED VITREOUS CARBON ELECTRODE

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ABSTRACT. Nowadays, the damage of the environment quality has reached alarming levels requiring severe measures for stopping this process. In order to harmonise with the maximum admitted concentrations (MAC) of heavy metal ions (HMIs) in the discharged effluents, the electrochemical procedures represent a clean, flexible and efficient alternative of decontamination. In this context, the present paper describes the results of our researches concerning the electroextraction of heavy metals from synthetic diluted solutions. Starting from simple or complex solutions with initial HMI contents of 10 ppm (parts per million), the MAC can be reached after 90 min. of electrolysis in a continuous flow electrochemical reactor equipped with a three-dimensional (3D) electrode made of reticulated vitreous carbon.

Keywords: *electrodeposition, heavy metal ions, reticulated vitreous carbon electrode, waste waters*

INTRODUCTION

Many manufacturing sectors like galvanotechnical, metallurgical, electronic or chemical industries produce huge quantities of high pollutant residual waste waters containing HMIs. At the end of the past century, the production of hazardous wastes was estimated, as described in Table 1, at about 7000 millions tons/year, from millions tons/year are generated only in the European Community [1].

Table 1.

Estimated global production of industrial wastes [1]

Manufacturing sectors	Contained metals	Quantity (tons/year)
Electronic	As, Cr, Hg, Se, Ni, Cu	1200000
Mineral oil and coal	As, Pb, V, Cd, Ni, Zn	1200000
Mining and metallurgy	Hg, Cr, Cu, As, Zn, Pb	390000
Agriculture	Mg, As, Cu	1400000
Metals’ Processing	Cr, Co, Ni, Fe	240000
Others		720000

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The recycling of heavy metals represents an economical and ecological solution for the treatment of these huge quantities of wastes. The liquid effluents containing HMIs, resulted from the metals processing industry, can be electrochemically treated in order to extract the metals by means of the cathodic deposition: $M^{z+} + ze^{-} \rightarrow M$. The recovery of pure metals represents the main advantage of the electrodeposition.

Depending on the HMIs' concentrations, the heavy metals recovery from waste waters by electrodeposition can be done in different manners. For high concentrations (over few grams per litter), two-dimensional cathodes can be used and the content of HMIs can be reduced with one order of magnitude. The resulting effluent can be reused in the process or it can be introduced in a new stage of chemical or electrochemical decontamination. For low HMIs' concentrations, under hundreds milligrams per litter, 3D electrodes can be used and the content of HMIs can be reduced to levels that allow the discharge of the effluents in environment.

The 3D electrodes are generally made from carbonaceous materials, among witch the reticulated vitreous carbon (RVC), having the best performances, is the mainly used material. The RVC is made exclusively from vitreous carbon and has an open honeycomb-shaped structure, conferring to the material a small electric resistance, a high porosity and a high specifically surface area. It is produced at different degrees of porosity between 10 and 100 pores per inch (ppi), having a pores' fraction between 90 and 97% [2]. At pH = 7, the RVC electrochemical stability domain is ranged between -1.2 and +1.0 V *vs.* SCE. In the absence of Cl^{-} ions and depending on the pH value, the anodic limit corresponds to the water decomposition to oxygen; the useful cathodic potential domain is limited by the reduction reaction of the hydrogen (rrH) and can be extended to more negative values by deposition of a Hg thin layer on the RVC surface [3].

Concerning the use of RVC for the heavy metals recovery from waste waters, the literature presents many studies [4-12], but, in the majority of them, the composition of the aqueous solutions was modified by adding of concentrated supporting electrolytes in order to increase the electrolyte conductivity.

In this paper, we present our results concerning the electroextraction of heavy metals from synthetic diluted solutions by using RVC. Simple or complex solutions with initial HMIs contents of 10 ppm were prepared using diluted HNO_3. The specific electrodeposition potentials were evaluated by cyclic voltametry (CV) and the prepared solutions were electrolysed potentiostatically in a continuous flow electrochemical reactor (ER), equipped with a 3D RVC electrode. The residual concentrations of HMIs were measured by atomic adsorption spectroscopy (AAS).

RESULTS AND DISCUSSION

CV studies

Arming to evaluate the possibilities of the HMIs' electroextraction from extremely diluted electrolytes, preliminary studies were completed by CV in mono-elemental solutions. The measurements were performed at a scan rate of 50 mV/s, all the solutions being deaerated by nitrogen bubbling in order to eliminate the interferences due to the oxygen electroreduction. For each studied HMI, the working electrode compartment was firstly filled with 5 mL of 10 mM HNO_3 and the voltamogram of the supporting electrolyte was recorded. After this, 1, 1, and respectively 3 mL of 10 mg/L dissolved metal solutions in 10 mM HNO_3 were added successively (resulting HMI's concentrations of 1.66, 2.85 and 5 ppm, respectively) and the corresponding voltamograms were recorded. Two examples of the acquired curves in 1.66 and 5 ppm HMIs' solutions during the cathodic scan are presented in Figure 1.

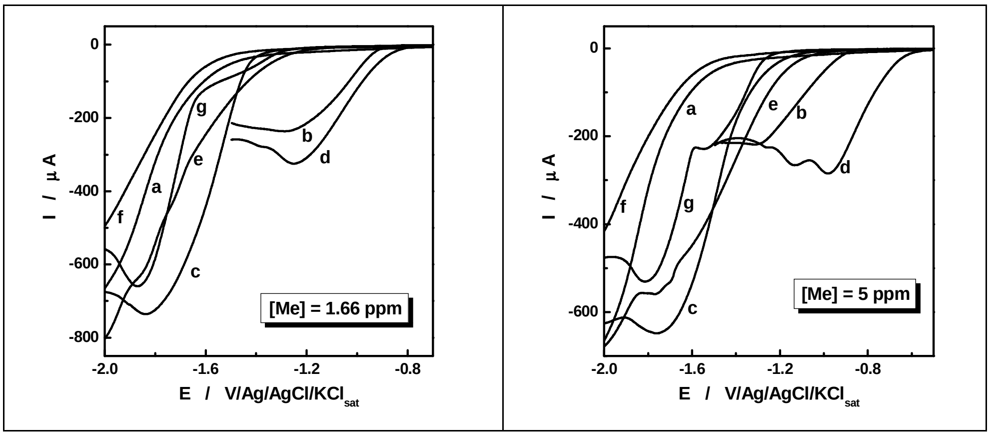

Figure 1. Recorded curves by CV in 1.66 and 5 ppm of corresponding HMIs solutions during the cathodic scan: a – supporting electrolyte only; b – Cd; c – Co; d – Cu; e – Ni; f – Pb; g – Zn. (anodic polarization curves are not presented)

As it can be seen from Figure 1, excepting the Pb case, where the electrodeposited metal blokes the rrH, the HMIs' additions induce increases of the cathodic currents even at the 1.66 ppm concentration level. Moreover, the increase of the HMIs' concentrations shifts the start of the net cathodic current to more positive potential values, suggesting that the heavy metal electrodeposition process starts before the rrH. Unfortunately, an optimal electrodeposition potential cannot be evaluated by CV studies due the fact that the rrH occurs simultaneously with the heavy metal electrodeposition process.

Electrodeposition studies

The studies concerning the heavy metal electrodeposition from mono-elemental or complex solutions were performed using electrolyte volumes of 250 or 350 mL, respectively. At 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 70 and 90 minutes after the experiments' begin, aliquots of 3 or 10 mL respectively, were sampled from the overflow outlet and were analysed by AAS. During the experiments, the working electrode current ($I_{W.E.}$), the counter-electrode potential ($E_{C.E.}$) and the cell voltage (E_C) were also recorded, allowing us to estimate the current efficiency (η_C) and the specific electricity consumption (W_S).

Single metal electrodeposition results

Figure 2 presents two examples of recorded signals during the electroextraction of Cu and Ni from the corresponding mono-elemental solutions at working electrode potentials ($E_{W.E.}$) of – 200 mV and -1200 mV respectively, in rapport with the previously mentioned reference electrode. Based on the recorded data and the AAS results, the final parameters (as presented in Table 2) were evaluated after 90 min. of electrolysis

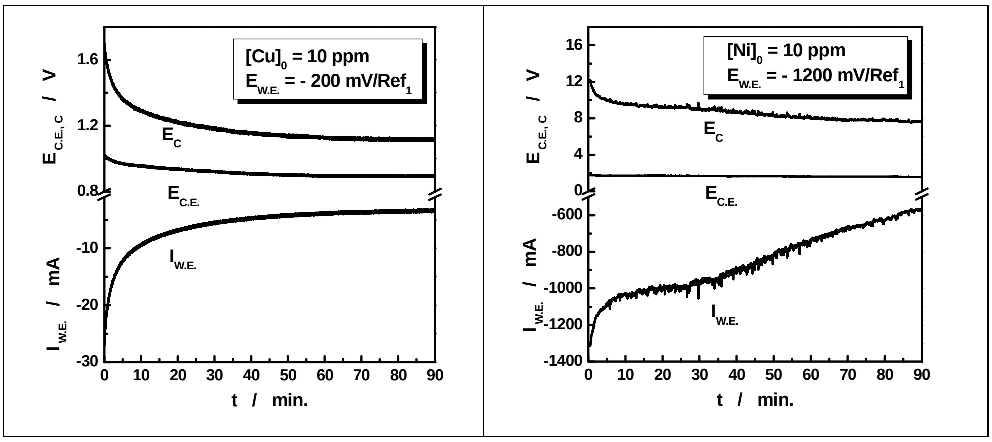

Figure 2. Recorded signals during the electroextraction of Cu and Ni from the corresponding mono-elemental solutions.

Table 2.

Estimated final parameters after 90 min. of electrolysis

Metal	Residual concentration	η_C	W_S
Cu	0.09 ppm	24.2 %	0.043 kWh m^{-3}
Ni	0.29 ppm	0.16 %	44.2 kWh m^{-3}

As it can be seen from Figure 2 and Table 2, the recorded signals and also the η_C and the W_S present acceptable values in the case of Cu, but degrade significantly for the Ni electrodepositions due to the parallel rrH process. The evolution of HMIs' concentrations during their electroextraction from the corresponding mono-elemental solutions is presented in Figure 3.

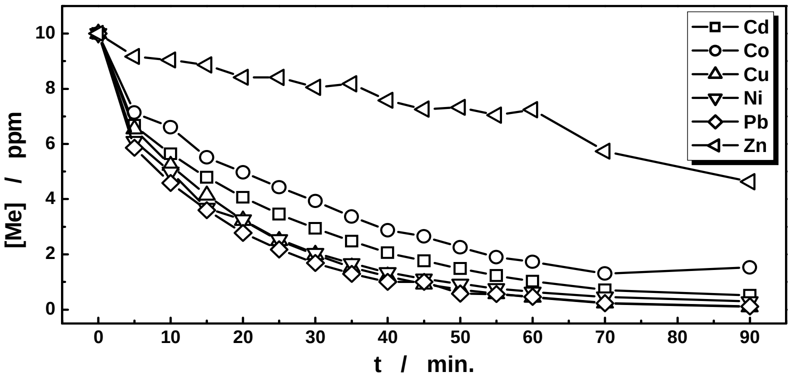

Figure 3. The evolution of studied HMIs' concentrations during their electroextraction from the corresponding mono-elemental solutions

As it can be see from Figure 3, excepting the Zn case, all the concentrations of the studied HMIs quickly decrease during the first hour of their electroextraction from the corresponding mono-elemental solutions. The residual concentrations values ($[Me]_{Res.\ Mono}$, presented in Table 3, together with the values of the applied working electrode potentials, $E_{W.E.\ Mono}$) are similar with the MAC levels [13].

Simultaneous metals electrodeposition results

The evolution of studied HMIs' concentrations during their electroextraction from the complex multi-elemental solution is presented in Figure 4 and the residual HMIs' concentration values ($[Me]_{Res.\ Multi}$) are presented in Table 3.

Table 3.

Comparison of the HMIs' electrodeposition parameters from mono and multi-elemental solutions

Metal	Cd	Co	Cu	Ni	Pb	Zn
$E_{W.E.\ Mono}$ / V	- 0.8	- 1.1	- 0.2	- 1.2	-0.6	-1.2
$[Me]_{Res.\ Mono}$ / ppm	0.51	1.52	0.09	0.29	0.12	4.63
$[Me]_{Res.\ Multi}$ / ppm	0.60	1.01	0.006	1.06	0.40	1.76
MAC / ppm	0.30	-	0.20	1.00	0.50	1.00

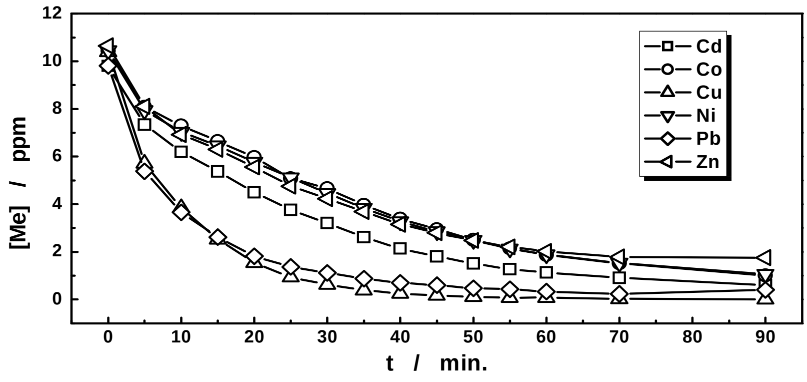

Figure 4. The concentrations evolution of studied HMIs during their electro-extraction from the complex multi-elemental solution on RVC electrode polarised at -1100 mV *vs.* Ag/AgCl/KCl$_{sat}$ reference electrodes

As it can be observed from Figure 4 and Table 3, the $[Me]_{Res.\ Multi}$ evaluated after the HMIs electrodeposition from multi-elemental solutions decrease for Co, Cu and Zn and increase for Cd, Ni and Pb. Moreover, it is worth to note that the $[Me]_{Res.\ Multi}$ values for Cu, Ni and Pb are very similar with the MAC levels.

CONCLUSIONS

The results of our researches concerning the electroextraction of some heavy metals (Cu, Co, Cd, Ni, Pb and Zn) from diluted solutions allow us to formulate the following conclusions:

- the electroextraction of Cu, Ni and Pb from extremely diluted solutions allows to achieve directly the MAC levels;
- for Cd and Zn, the obtained residual concentrations are in close proximity to the MAC levels;
- the mixture of studied HMIs doesn't obstruct the components electrodeposition, the individual residual concentrations being similar with the obtained ones in mono-elemental solutions;
- surprisingly, for Zn, the residual concentration after the electro-deposition from multi-elemental solution is smaller that the obtained one after the electrodeposition from mono-elemental solution;
- this preliminary results prove the feasibility of the electrochemical decontamination of the heavy metal polluted waste waters, but, in the same time, they require further researches in order to optimise the experimental parameters and also to validate the results using real waste waters.

EXPERIMENTAL SECTION

Reagents

The all solutions were prepared starting from mono-elemental AAS standard solutions (Merck) of Cd, Co, Cu, Ni, Pb and Zn, each one containing 1 g/L of dissolved metal and 0.5 M HNO_3. All prepared mono-elemental solutions contained 10 mg/L of the corresponding dissolved metal and 10 mM HNO_3. The tested complex solution contained 10 mg/L of each mentioned metal and 30 mM HNO_3. In order to achieve the desired compositions, 63 % HNO_3 solution (Merck, p.a.) and double-distilled water were also used.

Experimental setups

For CV measurements, a three-compartment glass electrochemical cell was used. A vitreous carbon disc (Φ = 3 mm), an Ag/AgCl/KCl_{sat} system and a Pt wire (Φ = 0.8 mm, L = 15 mm) were utilized as working, reference and counter electrode, respectively. The LabView 6.1 software and a PCI 6024 E data acquisition board (National Instruments, USA) were also used for driving a computer controlled home-made potentiostat.

The electrodeposition measurements were completed using the experimental setup described in Figure 5.

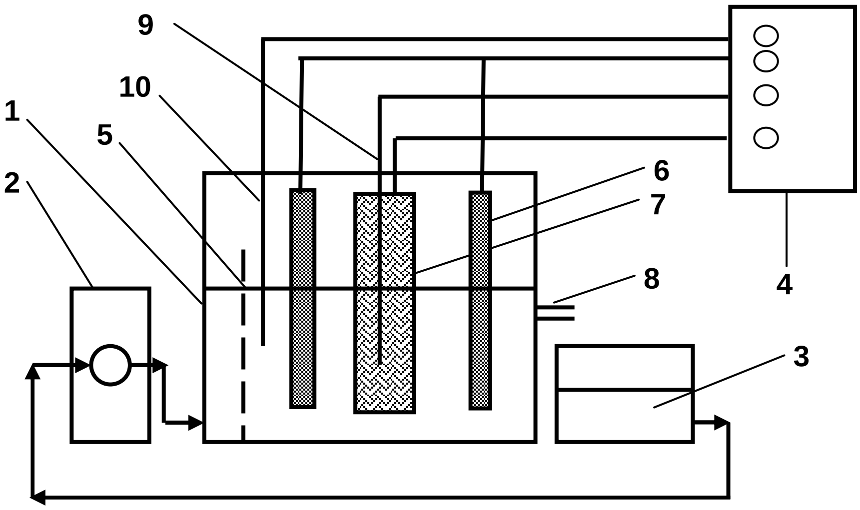

Figure 5. Experimental setup for the heavy metals electrodeposition: 1 – uncompartmented ER; 2 - peristaltic pump; 3 – electrolyte tank; 4 – computer controlled potentiostat; 5 – drilled diaphragm for flow uniforming; 6 – graphite bar anodes; 7 – RVC cathode; 8 – overflow outlet; 9 – cathode reference electrode; 10 – anode reference electrode.

The second experimental setup includes a home-made plexiglas uncompartmented ER, a Reglo-Digital peristaltic pump (Ismatec, Switzerland) and a HP72 potentiostat (Wenking, Germany). A 100 ppi RVC parallelepiped (L x W x H = 48 mm x 24 mm x 30 mm) was used as cathode and four graphite cylindrical bars (Φ = 12 mm, L = 30 mm) were utilised as counter-electrodes. Two $Ag/AgCl/KCl_{sat}$ reference electrodes were used to record the cathode's and anode's potentials during the electrodeposition. In order to assure a laminar and uniform electrolyte flow, a drilled PVC diaphragm was fixed between the inlet port and the electrodes compartment. The overflow outlet maintains a constant electrolyte level inside of the ER, allowing also periodical electrolyte sampling for the HMIs' content analysis.

The AAS measurements were completed with an Avanta PM spectrometer (GBC, Australia). The LabView 6.1 software and a PCI 6024 E board (National Instruments, USA) were used to drive the HP72 potentiostat and for data acquisition. During the heavy metals electrodeposition experiments, the peristaltic pump assures a constant electrolyte flow rate of 46 mL/min.

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