Combined Electrocoagulation/Electrowinning Process for Recovery of Metallic Copper from Electroplating Effluents

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Abstract

In the present work a combined process is proposed for recovery of metallic copper from industrial electroplating wastewaters comprising electrocoagulation, acidic digestion and electrowinning. The wastewater with the initial Cu2+ ion concentration of 92 mg/L was first subjected to electrocoagulation where it successfully decreased under the upper allowed limit of 2 mg/L. Then, the obtained electrocoagulation sludge was treated with sulfuric acid for digestion and with caustic soda to reach pH 4.8 for precipitation and separation of insoluble aluminum hydroxide, whereas Cu2+ ions remain in solution. Finally, pure metallic copper was produced by electrowinning from the obtained concentrated Cu2+ ions solution. The work proposes the possibility of effectively treating toxic industrial electroplating wastewater accompanied by recovery of significant amounts of valuable pure metals, such as copper.

Keywords: copper, electroplating effluents, electrocoagulation, electrowinning

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1. Introduction

Copper is a bio-accumulative, not easily metabolized essential trace element which can be harmful to human health when exceeding the tolerance limit. Copper contamination of water and soil originates from many industrial applications, such as mining, metal finishing, electronic, textile glass coloring and electroplating activities.

Copper removal from industrial effluents has been conducted by the classical heavy metal abatement processes: adsorption [1], ion exchange [2], chemical coagulation/ precipitation [3].

Furthermore, many studies for extraction of heavy metals from wastewater treatment sludge have used inorganic acids, such as HNO_3, H_2SO_4 and HCl [4-8].

Chelating agents, such as ethylene diamine tetraacetate (EDTA) and diethylene triamin pentaacetate (DTPA) have also been used for effective extraction of copper from waste sludge. However, both extractants, EDTA and DTPA have the disadvantage of being quite persistent due to their low biodegradability [9]. To avoid secondary pollution environmentally friendly and biodegradable extractants have been applied that do not produce persistent or toxic byproducts, such as molasses hydroxylate and organic acids [10-12].

Electrochemical methods, such as electrocoagulation [13], electrodialysis [14,15], electrodeionization [16,17] and electrowinning [18] can effectively remove heavy metals from synthetic and actual industrial wastewater, enabling also the recovery of EDTA for reuse [19,20].

As we are aware, no other paper except for our previous work [21] appeared up to now in literature for simultaneous removal and recovery of copper or other heavy metals from industrial electroplating effluents comprising the three processes, electrocoagulation, acid digestion and electrowinning. Veglio et al, 2003 [22] studied the recovery of Cu, Ni, Mn, Sn and W from solid galvanic industrial wastes using the sulfuric acid leaching and the electrodeposition of Cu and Ni through electrowinning on carbon cathodes. Hannula et al, 2019 [23] suggested copper electrowinning and direct deposition on carbon nanotube film cathode from synthetic and real metallurgical plant wastewater containing Cu, Fe, Al, Zn, Ni, As, S and Pb. Huang et al, 2010 [24] worked on electrowinning of copper from sulfate bath with polyaniline and Pb-Ag anodes in the presence of cobalt ions achieving a significant reduction of the anode potential and the overall electrical energy consumption: 93 kWh/t with 0.789 g/L Co^{2+} ion concentration for polyaniline anode and 57 kWh/t with 1.315 g/L Co^{2+} for Pb-Ag anode.

Many industrial units produce significant amounts of industrial effluents laden with heavy metals, such as copper, nickel chromium which result in landfill without recovery of these valuable metals [22].

In this work an integrated process is suggested for recovery of pure metallic copper from industrial copper electroplating wastewaters. The process consists of following three subsequent stages:

i. Electrocoagulation of the copper containing electroplating wastewater with sacrificial Al electrodes for production of a mixture sludge mainly composed of copper hydroxide and aluminum hydroxide.

ii) Acidic digestion-solubilization of the sludge by addition of H_2SO_4 at the slightly elevated temperature of 50 ^{0}C followed by addition of NaOH until pH 4.8 for unilateral precipitation of only aluminum hydroxide. The precipitated solid aluminum hydroxide flocks can then be separated by filtration leaving a concentrated copper solution.

iii.) Recovery of pure electrolytic copper through electrowinning from the concentrated copper solution.

2. Materials and Methods

H_2SO_4, NaOH and KCl were of analytical grade (Merck). pH was adjusted by 0.1 M solutions of H_2SO_4 and NaOH as required. The actual copper bearing industrial effluent was received from an electroplating unit of northern Greece with following main characteristics according to Tab. 1:

Table 1. Analysis of the electroplating effluent sample

Parameter:	Value:
pH	5.5
Conductivity (μS/cm)	1486
COD (mg/L)	316
Cu^{2+} (mg/L)	92
Cl- (mg/L)	28
SO_4^{2-} (mg/L)	145

Current and voltage were measured by an agilent DC power supply apparatus, conductivity by a WTW conductometer and pH by a Hanna pH-meter. The electrochemical reactor for the electrocoagulation as well as the electrowinning experiments was a 500 ml glass vessel. Two outer sacrificial aluminum plate anodes and a middle aluminum plate cathode were used as electrodes for electrocoagulation, whereas two outer copper plate cathodes and a middle Ti/Pt plate anode for electrowinning. All electrodes were symmetrical and of same surface with dimensions 10 x 5 x 0.2 cm, immersed to 6 cm in the treated solution and had a total effective area of 30 cm^2 each.

The study was monitored by concentration measurements of copper and chemical oxygen demand (COD). Perkin Elmer 5100 Atomic adsorption spectroscopy (AAS) served for determination of the residual copper concentration, Hitachi 2000 UV-Vis spectrophotometry for measurement of Cl- and SO_4^{2-} ion concentrations and Thermoreaktor TR 420 (MERCK) coupled with spectrophotometer Spectroquant Pharo 100 (MERCK) for investigation of COD.

3. Results and Discussion

3.1 Electrocoagulation treatment
During the electrocoagulation treatment aluminum hydroxide flocks are produced inside the treated solution, due to electrodissolution of the sacrificial aluminum anodes and OH- ions together with hydrogen gas bubbles at the cathode. The anodically produced Al^{3+} ions react with the cathodically produced OH- ions to form the gelatinous insoluble $Al(OH)_3$ which is a well-known coagulant and adsorbent for heavy metals, such as copper, and many organic compounds:

Furthermore, Cu^{2+} ions combine with the generated OH- ions at the cathode and precipitate as insoluble $Cu(OH)_2$.

In addition, also the electro-generated H_2 bubbles at the cathode contribute to removal of particulates from the solution by electroflotation. All phenomena act synergistically resulting in a rapid removal of copper and organic pollutants from treated wastewater [21,25].

Wastewater samples with initial Cu^{2+} ion concentration of 92 mg/L were treated by electrocoagulation at the constant applied current density 20 mA/cm^2, electroprocessing time 30 minutes and various initial pH values 2, 4, 6, 8, 10. The distance between the central and the two outer Al electrodes was held at 0.5 cm. To increase the conductivity 1 g/L KCl was added to the treated solution. The removal percentage of copper is negligible at pH <2. It is very high (>90 %) in the pH range 4-8 and slightly reduced at pH 10 (Figure 1).

This behavior of low efficiency of electrocoagulation at low and high pH values was confirmed by other researchers' findings [26,27]. It was ascribed to an amphoteric behavior of $Al(OH)_3$ which leads to soluble cations Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ at acidic pH and to monomeric anions $Al(OH)_4^-$, $Al(OH)_6^{3-}$ at alkaline pH. It is well known that these species are not useful for coagulation treatment. For these reasons the electrocoagulation process was conducted in the pH range 2-10.
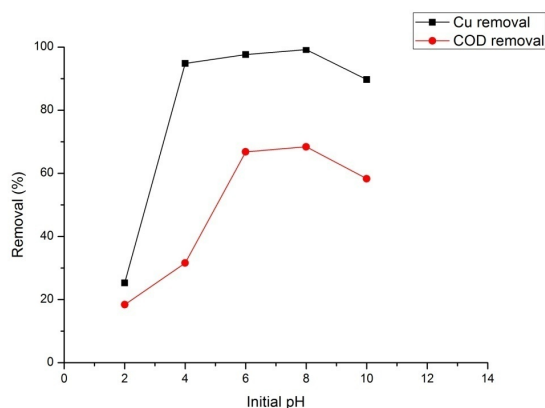

Fig. 1. Removal percent of copper and COD versus various initial wastewater pHs

Apart from heavy metals, real electroplating baths contain various organic compounds, such as brighteners, complex formers, buffering and wetting agents. These organic additives attribute the relatively increased COD of 316 mg/L in the electroplating effluent. The organics are also adsorbed by the $Al(OH)_3$ coagulant. As can be obtained from Figure 1, simultaneously to copper removal also the wastewater COD was reduced by 67.8 and 68.4 % at the corresponding optimal pH values 6 and 8.

Thus, the utilization of electrocoagulation aims at a double useful objective, namely effective removal of heavy metals and simultaneously significant reduction of COD from wastewater.

3.2. Acid leaching of the electrocoagulation sludge
The precipitated electrocoagulation sludge is a mixture mainly of copper- and aluminum hydroxides, and of some absorbed organic additives present in actual electroplating effluent. The sludge was left to settle down, then was filtered, dried at 102 ºC for 24 hours, cooled and weighed. Its quantity follows the Faraday's law of electrolysis and is expressed as mass in g of Total Suspended Solids per g of copper removed from treated

solution (6.17 g TSS / gCu). Compared to the conventional chemical coagulation process the electrochemical coagulation leaves a reduced amount of sludge [26,27].

The acidic leaching procedure occurred with 500 ml H_2SO_4 of different concentrations 0.05, 0.1 and 0.2 M which were added each time to 5 g of dried sludge under stirring at 250 rpm and constant temperature of 50 ^{0}C. The extractions of copper and aluminum was almost quantitative, namely 97 and 92 % respectively and lasted only a few minutes of leaching time. The copper concentration and pH of the obtained leachate were measured by means of AAS and pH-meter respectively. According to Tab. 2, the observed increase of pH after the digestion indicates the consumption of H_2SO_4. The acid consumption was estimated to range between 0.65 and 0.92 g of H_2SO_4 per g of dried sludge.

Veglio et al, 2003 [22] experimented acidic leaching of galvanic wastes with 0.05-0.15 M concentrations of H_2SO_4, at temperatures 30-90 ^{0}C and reported similar results of 99 % copper extraction with initial and final leachate pH values of 1.16 and 0.78 respectively.

Table 2. Initial and final pH values during acidic leaching of electrocoagulation sludge with various H_2SO_4 concentrations

Temperature (°C)	[H₂SO₄] (M)	pH initial	pH final
	0.05	1.14	2.18
50	0.1	0.91	1.53
	0.2	0.58	1.01

3.4 pH controlled separation of Cu from Al

Our interest was focused on developing a process to separate Cu^{2+} from Al^{3+} ions from the obtained acidic leachate based on the pH dependence and the different solubility products of their hydroxides: $Ksp_{Al(OH)3} = 1.99x10^{-33}$ and $Ksp_{Cu(OH)2} = 10^{-20}$. According to Jander and Blasius [28], the precipitation of Al^{3+} ions from aqueous solution as $Al(OH)_3$ starts at pH 3.8 and is completed at pH 4.8, while the precipitation of Cu^{2+} ions as $Cu(OH)_2$ starts at the higher pH 5.1 and is completed at pH 6.6. Consequently, Cu^{2+} ions can be separated from Al^{3+} ions by adjusting the solution pH. Thus, after the acid addition for dissolution of the generated mixed $Al(OH)_3/Cu(OH)_2$ electrocoagulation sludge, the solution pH values of 1.01, 1.53 and 2.18 (Tab. 2) were adjusted to pH 4.8 by addition of appropriate amount of 0.1 M NaOH solution. At pH 4.8 Cu^{2+} ions still remain quantitatively in solution, whereas Al^{3+} ions are quantitatively precipitated as insoluble $Al(OH)_3$. The solid $Al(OH)_3$ flocks are separated by filtration. In this way, concentrated solutions of 1.2 to 8 g/L copper can be obtained which are now appropriate for recovery of pure metallic copper by the final step of electrowinning.

3.5 Electrowinning of metallic copper

Metallic copper is cathodically electrodeposited mainly from acidic solutions [9] with optimum pH between 2 and 2.2. The electrowinning procedure was carried out under stirring at 250 rpm in galvanostatic operations. The temperature was held constant at the slightly elevated temperature of 45 °C by means of a thermostatic water jacket connected with thermostatic bath. The distance between the central Ti/Pt anode and the two outer Cu cathodes was held at 0.5 cm. With the applied constant current densities of 5, 10 and 20 mA/cm², pure electrodeposited metallic copper was almost quantitatively obtained on the copper cathodes in 80, 50 and 40 minutes of electroprocessing time respectively, leaving a copper ion

concentration in the residual solution under 5 mg/L, as seen in Figure 2. The recovery of metallic copper was evaluated by weight measures of the cathode before and after the electrodeposition process, while the residual concentration of Cu^{2+} ions was analyzed by AAS. The final yield of obtained pure metallic copper was 0.15 g from 1 g of dried electrocoagulation sludge.
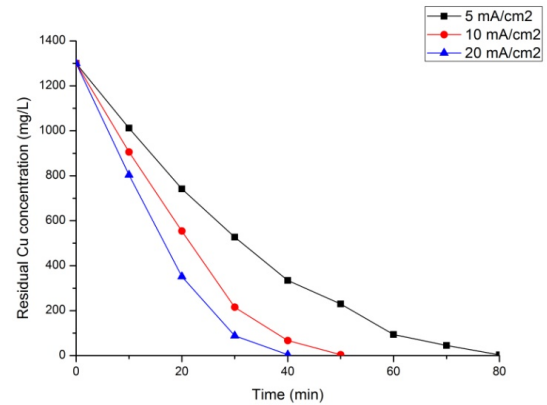

Fig. 2. Residual concentration of copper versus electrolysis time during electrowinning with various constant current densities

The electrocoagulation treatment at the applied current density of 20 mA/cm² consumed an electrical energy amount of 12.27 kWh per kg of copper removed from treated solution, while the electrowinning treatment needed 2.92 kWh per kg of metallic copper electrodeposited on the cathodes. Our results concerning the yield of obtained metallic copper and the electrical energy consumption are in good correlation with the findings of Veglio et al. [22]: 0.1-0.2 g from 1 g of dried electrocoagulation sludge and 2.13 kWh per kg of electrodeposited metallic copper.

4. Conclusions

The electrocoagulation processing of copper bearing galvanic effluents, in the optimal pH range 4-10 achieved a removal percent of copper >90 %. Simultaneously, dissolved organic additives contained in wastewater were also effectively removed by 66.7 and 68.4 % at the optimum pH values of 6 and 8 respectively.

The acidic sludge digestion with sulfuric acid and pH adjustment to 4.8 with caustic soda enabled the preparation of a concentrated copper ion solution and its separation from insoluble $Al(OH)_3$ precipitate. Finally, pure metallic copper could be recovered from the concentrated copper solution by electrowinning.

The combined process yields 1.5 g of high value metallic copper from 10 g of dried electrocoagulation sludge. The residual solid waste is almost copper free and the residual water contains less than 5 mg/L copper. The whole technology offers relevant industrial units the possibility of a not negligible cost benefit via copper recovery and prevention of disposal of toxic industrial waste in landfill.

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References

1. S. Verbych, M. Bryk, G. Chornokur, Sep. Sci. Technol. **40** 1749-1759 (2005).
2. S. Veli, B. Pekey, Fres. Environm. Bull. **13** 244-250 (2004).
3. C.D. Kang, S.J. Sim, Y.S. Cho, W.S. Kim, Korean J. Chem. Eng. **20** 482-486 (2003).
4. J. Deng and Q.X.F. Xinhong, Chem.Eng. J. **152** 177-182 (2009).
5. Y.C. Kuan, I.H. Lee, J.M. Chen, J. Hazard. Mater. **177** 881-886 (2010).
6. S.H. Gaber, M.S. Rizk, M.M. Yehia, Biokemistri **23** 41-48 **215** (2011).
7. D. Wozniak and J. Huang, J. Pollut. Control Fed. **54** 1574-1580 (1982).
8. C.H. Wu, C.Y. Kuo, S.L. Lo, J. Environ. Sci. Health A **A39** 2205-2219 (2004).
9. F.C. Chang, S.L. Lo, C.H. Ko, Sep. Purif. Technol. **53** 49-56 (2007).
10. B. Sun, F.J. Zhao, E. Lombi, S.P. McGrath, Environ. Pollut. **113** 111-120 (2001).
11. E.E. Özbas, C.E. Gökce, S. Güneysu, H.K. Özcan,N.Sezgin, S. Aydin, N. Balkaya, J. Chem. Technol. Biotechnol. **88** 2046-2053 (2013).
12. Z. Lihua, Z. Zhiliang, Z. Rongua, Z. Chengsong, Z.H. Yanling, Z. Jianfu, J. Environ. Sci. **20** 970-974 (2008).
13. C. Escobar, C. Soto-Salazar, M.I. Toral, J. Environm. Manage. **81** 384-391 (2006).
14. S. Caprarescu, D.I. Vaireanu, A. Cojocaru, I. Maior, V. Purcar, Optoelectr. & Adv. Mater.-Rapid Comm. **5** 1346-1351 (2011).
15. F.S. Eberhard, I. Mamawand, Intern. J. Environm. Res. **11** 1-13 (2017).
16. S. Guan and S. Wang, Sep. Sci. Technol. **42** 949-961 (2007).
17. K. Dermentzis, A. Davidis, D. Papadopoulou, A. Christoforidis, K. Ouzounis, J. Engin. Sci. Technol. Rev. **4** 33-42 (2009).
18. B. Panda and S.C. Das, Hydrometallurgy **59** 55-67 (2001).
19. D. Voglar and D. Lestan, J. Hazard. Mater. **180** 152-157 (2010).
20. R.S. Juang and S.W. Wang, Water Res. **34** 3179-3185 (2000).
21. K.I. Dermentzis, D.I. Marmanis, A.K. Christoforidis, N.C. Kokkinos, D.K. Stergiopoulos, Proc. 4th Int. Conf. Sustainable Solid Waste Management, Limasol, Cyprus, pp. 1-8 (2016).
22. Veglio F., Quaresima R., Fornari P., Ubaldini S., Waste Management **23** 245-252 (2003).
23. P-M. Hannula, M.K. Khalid, D. Janas, K. Yliniemi, M. Lundström, J. Clean. Production **207** 1033-1039 (2019).
24. H. Huang, J.Y. Zhou, Z.C. Guo, Trans. Nonferrous Met. Soc. China **20** 55-59 (2010).
25. M. Kobya, O.T. Can, M. Bayramoglu, J. Hazard. Mater. **B100** 163 (2003).
26. N. Adhoum, L. Monser, N. Bellakhal, J-E. Belgaied, J, Hazard. Mater. **B112** 207-213 (2004).
27. S. Vasudevan, J. Lakshmi, G. Sozhan, Clean: Soil, Air, Water 3745-51 (2009).
28. Jander-Blasius, S. HIRZEL VERLAG STUTTGART, 1973, ISBN 3 7776 0246 9