STUDIES ON COPPER RECOVERY BY CHEMICAL REDUCTION METHOD FROM RESIDUAL SOLUTIONS OF GALVANIC WORK

Gavriş Georgeta[*], **Stoia Marcela**[**], **Hodişan Sorin**[*], **Joiţa Dan–Marian**

[*]University of Oradea, Faculty of Sciences, 1 Univ. St., 410087, Oradea, Romania,
e-mail: georgeta_gavris@yahoo.com
[**]"Politehnica" University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 2 P-ţa Victoriei St., 300006, Timişoara, Romania

Abstract

The recovery of copper from residual solutions of galvanic work was studied using sodium hypophosphite. Optimum recovery conditions were determined for Cu, Cu_2O and a copper (II) oxychloride compound: atacamite and paratacamite. The influence of several parameters on copper recovery was investigated: the nature and quantities of acids used as extraction agents (HCl, H_2SO_4, H_3PO_4), the concentration of reducing agent – sodium hypophosphite –, pH and temperature. Recovered copper salt can be used as a pigment in art or architecture. The insoluble mixture of atacamite and paratacamite achieved 90 % efficiency and pure copper around 100 %.

Key words: Copper, Wastewater, Hydrochloric acid, Sodium hypophosphite, Recovery.

INTRODUCTION

Copper poisoning is increasingly common due to the widespread occurrence of copper in our food (Hashemi et al., 2008; Oliva et al., 2009; Piovár et al., 2011) and our hot water pipes. Electroplating companies are responsible for a part of copper emissions.

Total copper emissions in 2009 in mainland France amounted to 165 t, which is the minimum observed since 1990. The manufacturing industry was responsible for 8 % of total copper emissions in 2009.

Since galvanic deposition of copper is widely used, there is a large number of copper pollutants that threaten the environment. Methods for eliminating this threat are needed and most preferred are those that lead to the recovery of the metal. Copper from electrodes used in electroplating is in ionic form. Reducing methods need to be applied in order to recover it. Chemical reduction is proposed in this study.

Other methods for copper recovery/removal are electromigration (Klishchenko et al., 2010), adsorption (Gaikwad et al., 2011; Michael Angelo et al., 2010; Pradhan, Rai et al., 2001), flotation (Lazić et al., 2010), bioleaching (Sukla et al., 2009), bioreduction (Robson et al., 2010), biosorption (Fagundes-Klen et al., 2010; Mallick et al., 2002), electrodialysis (Mohammadia et al., 2005; Moreira et al., 2005; Rojo et al., 2010), membrane based (Li, Chen et al., 2005), chemical precipitation (Kang et al., 2002), nanomaterials based (Kurczewska et al., 2010).

The main aim of this paper is to investigate the influences of quantity and nature of acids used as extraction agents (HCl, H_2SO_4, H_3PO_4), concentration of reducing agent – sodium hypophosphite – , pH and temperature on the efficiency of copper recovery.

MATERIAL AND METHODS

All chemicals used were of at least p.a. purity: $CuSO_4 \times 5\ H_2O$ (Fluka), $NaH_2PO_2 \times H_2O$ (Fluka), HCl 2 M (Fluka) and H_2SO_4 0,5 M Titrisol (Merck), H_3PO_4 c. p. (Fluka), NH_4Cl (Fluka), $C_{19}H_{14}O_7S$, pyrocatechin violet, (Fluka) NH_3 and $C_{10}H_{14}N_2Na_2O_8$, Titriplex III, 0.1 M (Merck).

Desired temperatures were achieved by heating on an electric hob.

Different quantities of reducing agent were weighted using a analytical balance with four decimal accuracy.

FAAS analyses were conducted on a Thermoelectron M Serie M5 Dual spectrophotometer, with the following parameters: L–217.0 nm, air–acetylene flame, 15.7 mm flame height, 0.9 acetylene L min^{-1}. Each value is the mean value of three reads.

Phase analysis was achieved with D8 Advance–Bruker AXS diffractometer, using the Mo–K_α radiation ($\lambda_{Mo} = 0.7093$ Å).

Thermal analysis was performed on a 1500D MOM Budapest Derivatograph. The heating was achieved in static air, up to 500 °C, with a heating rate of 5 °C min^{-1}, on Pt plates using α–Al_2O_3 as the inert material.

The synthesized powders were characterized by FT–IR spectrometry with a Shimadzu Prestige FT–IR spectrometer, in KBr pellets, in the range 400 – 4000 cm^{-1}.

A synthetic sample of copper (II) sulfate, containing 500 mg copper, was heated. Reducing agent was added with constant stirring.

Resulting mixture was filtered and residual copper was measured by FAAS and complexonometric determination at pH = 10 (ammonia buffer) in the presence of pyrocatechin violet.

Recovery efficiency was measured as follows:

$$E_r\ (\%) = \frac{Cu_i - Cu_f}{Cu_i} \times 100$$

Each efficiency value is the arithmetic average of three identical samples.

According to Paralescu (Popa, Paralescu et al., 1977) the following takes place:

$$3\ NaH_2PO_2 + 4\ CuSO_4 + 6\ H_2O = 4\ CuH + 3\ NaH_2PO_4 + 4\ H_2SO_4 \qquad (1)$$

with the following electronic equations:

$P^{1+} - 4\ e^- \rightarrow P^{5+}$ |3
$Cu^{+2} + e^- \rightarrow Cu^{1+}$ |4
$H^{1+} + 2\ e^- \rightarrow H^{1-}$ |4

and in acid pH at high temperatures, metallic Cu is obtained. Considering sulfuric acid is formed in the neutral pH reaction, only heat would be needed for metallic Cu to deposit. Hence our proposed process reaction:

$$NaH_2PO_2 + 2\,CuSO_4 + 2\,H_2O = 2\,Cu + 2\,H_2SO_4 + NaH_2PO_4 \qquad (2)$$

with the following electronic equations:

$$\begin{array}{ll} P^{1+} - 4\,e^- \rightarrow P^{5+} & |1 \\ Cu^{+2} + 2\,e^- \rightarrow Cu^0 & |2 \end{array}$$

In the presence of chloride, the following could also take place:

$$2\,CuCl \rightarrow CuCl_2 + Cu \qquad (3)$$

Taking into account Lourie’s (Lourie et al., 1975) standard potentials:

$$\begin{array}{ll} H_2PO_2^- + e^- \rightarrow P\downarrow + 2\,OH^- & E^0,\ v = -\,2.05 \\ Cu^{2+} + 2\,e^- \rightarrow Cu\downarrow & E^0,\ v = +\,0.337 \end{array}$$

the potential difference is more than enough for reaction (3) to take place.

As acid pH tends to favor metallic Cu, different acids were tested to find the one that favors metallic Cu the most. Hydrochloric acid has shown to cause problems that can be explained by the close standard potentials of forming CuCl and dissociating CuCl:

$$\begin{array}{ll} Cu^{2+} + Cl^- + e^- \rightarrow CuCl\downarrow & E^0,\ v = +\,0.54 \\ CuCl\downarrow + e^- \rightarrow Cu\downarrow + Cl^- & E^0,\ v = +\,0.137 \end{array}$$

where it is obvious that CuCl is favored. X–ray analysis of a 70 °C process has shown that sulfuric acid gives Cu_2O and below are two competing reactions:

$$2\,NaH_2PO_2 + 2\,CuSO_4 + H_2SO_4 \rightarrow 2\,NaH_2PO_4 + Cu_2O + 3\,SO_2 + H_2O \qquad (4)$$

$$2\,NaH_2PO_2 + CuSO_4 + 2\,H_2SO_4 \rightarrow 2\,NaH_2PO_4 + Cu + 3\,SO_2 + 2\,H_2O \qquad (5)$$

with the following electronic equations:

$$\begin{array}{lllll} P^{1+} - 4\,e^- \rightarrow P^{5+} & |2 & & P^{1+} - 4\,e^- \rightarrow P^{5+} & |2 \\ Cu^{2+} + e^- \rightarrow Cu^+ & |2 & \text{and} & Cu^{2+} + 2\,e^- \rightarrow Cu^0 & |1 \\ S^{6+} + 2\,e^- \rightarrow S^{4+} & |3 & & S^{6+} + 2\,e^- \rightarrow S^{4+} & |3 \end{array}$$

where metallic Cu is still the major component. The same percentages of Cu_2O and metallic Cu have emerged from the X–ray analysis in the case of phosphoric acid, but the stoichiometry is different:

$$2\,NaH_2PO_2 + CuSO_4 + 2\,H_3PO_4 \rightarrow$$
$$\rightarrow 2\,NaH_2PO_4 + Cu + 3\,H_2O + SO_2 + P_2O_3 \qquad (6)$$

$$4\,NaH_2PO_2 + 4\,CuSO_4 + 2\,H_3PO_4 \rightarrow$$
$$\rightarrow 4\,NaH_2PO_4 + 2\,Cu_2O + 3\,H_2O + 4\,SO_2 + P_2O_3 \qquad (7)$$

with the following electronic equations:

$$\begin{array}{lllll} P^{1+} - 4\,e^- \rightarrow P^{5+} & |2 & & P^{1+} - 4\,e^- \rightarrow P^{5+} & |4 \\ P^{5+} + 2\,e^- \rightarrow P^{3+} & |2 & \text{and} & P^{5+} + 2\,e^- \rightarrow P^{3+} & |2 \\ Cu^{2+} + 2\,e^- \rightarrow Cu^0 & |1 & & Cu^{2+} + 2\,e^- \rightarrow Cu^0 & |4 \\ S^{6+} + 2\,e^- \rightarrow S^{4+} & |1 & & S^{6+} + 2\,e^- \rightarrow S^{4+} & |4 \end{array}$$

RESULTS AND DISCUSSIONS

FAAS and complexonometric analysis

Reagent excess influence was studied at 70 °C in neutral pH, Table 1.

Table 1

Results at 70 °C in neutral pH.

Sample no.	Reducing agent quantity		Titration volume (ml)	Efficiency (%)
	mole	% excess		
1	0.0039	0	27.0	14.20
2	0.0078	100	27.5	12.62
3	0.0097	150	26.3	16.59
4	0.0112	188	29.5	6.27
5	0.0137	250	28.0	11.04

Our reagent is oxidized in the presence of air (Negoiu et al., 1972) and gives dark shades to the precipitate. It is possible that higher quantities of reducing agent would give better results.

Due to inconclusive results the key factor, temperature, was raised to 90 °C, and the results can be seen in Table 2.

Table 2

Results at 90 °C in neutral pH.

Sample no.	Reducing agent quantity		Titration volume (ml)	Efficiency (%)
	mole	% excess		
6	0.0039	0	7.00	77.76
7	0.0056	44	7.20	77.12
8	0.0070	80	5.25	83.32
9	0.0075	92	2.00	93.65
10	0.0084	116	0.47	98.51
11	0.0094	140	0.09	99.71
12	0.0095	142	0.38	98.78
13	0.0097	149	0.30	99.05
14	0.0103	164	0.03	99.90
15	0.0108	176	0	100
16	0.0112	188	0.20	99.36
17	0.0117	200	0.24	99.25

Higher temperatures give efficiencies of 100 %, between 1.1 – 1.15 g.

The influence of pH was studied at 90 °C, at the optimum reducing agent excess, as shown in Table 3.

Table 3

Results at 90 °C in acid pH, at the optimum reducing agent excess.

Sample no.	Acid	Acid (ml)	Reducing agent quantity		Titration volume (ml)	Efficiency (%)
			mole	excess %		
18	hydrochloric acid, 1 N	1	1.0103	164	0.031(6)	99.9
19		2			0.1	99.68
20		3			1.58(3)	94.97
21		4			1.7	94.59(6)
22	sulfuric acid, 1 N	1			0.28	99.11
23		2			0.08(6)	99.72(3)
24		3			0.24(3)	99.22(6)
25		4			0.425	98.65
26	phosphoric acid, 1 N	1			0.198(3)	99.37
27		2			0.455	98.55(3)
28		3			0.775	97.53(6)
29		4			1.008(3)	96.79(6)

The differences between the two temperatures are compared in Fig. 1 and 2. In both cases, there was a drop of efficiency near 150 % of reducing agent excess. At 70 °C the efficiency drop lasted longer, until 188 % excess, while at 90 °C efficiency improved and afterwards droped again at 188 % excess. Fig. 2 shows an important efficiency gain at 85 %.

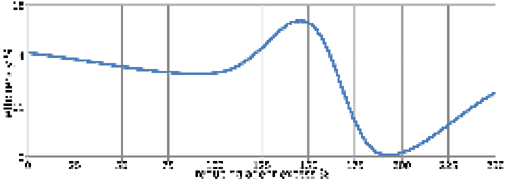

Fig. 1 Efficiency vs. reducing agent excess at 70 °C.

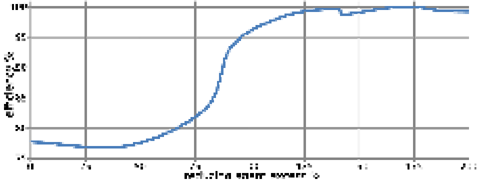

Fig. 2 Efficiency vs. reducing agent excess at 90 °C.

Paralescu's (Popa, Paralescu et al., 1977) acid conditions for the wanted reaction to take place are correct and can be noticed in Fig. 3, but adding more acid caused trouble, especially in the case of hydrochloric acid, where basic copper chlorides take form.

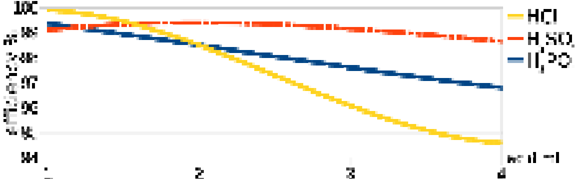

Fig. 3 Efficiency vs. volume of acid added at 90 °C and 164 % reducing agent excess.

X–Ray Diffraction analysis

For better understanding the process in acid pH, three 70 °C samples were analyzed through X–Ray diffraction, Fig. 4.

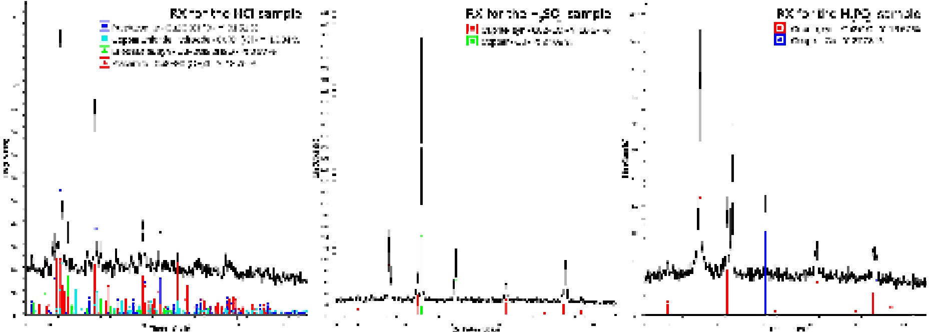

Fig. 4 X–Ray diffractograms for acid pH at 70 °C.

As pointed out by Paralescu and Lourie (Popa, Paralescu et al., 1977; Lourie et al., 1975), chloride interfered with our process. The above diffractogram, for the HCl sample, points to atacamite and paratacamite. Basic copper chlorides appear just as pointed out for fig. 4, but in higher quantities, over 70 %. The percentages of cuprite vs. metallic copper in oxidative acids (sulfuric acid and phosphoric acid) are the same. There is consistence with our proposed reactions (4), (5), (6) and (7).

Thermogravimetric analysis

Thermogravimetric analyses were performed on three phosphoric acid samples, Fig. 5. A pure Cu sample would have a weight gain of 24.4 % and Cu_2O, 10.8 %. The weight gain was of 20 % for 1 g reagent and 20.7 % for 3 g. This is consistent with Fig. 3 and reaction (2). Raising the reagent quantity to 3 g gives similar results as the 70 °C sample in Fig. 4. These are consistent with reactions (6) and (7). Considering the initial weight loss, the total weight gain was of 9 %. This is very close to Cu_2O which indicates something else is responsible for the initial weight loss.

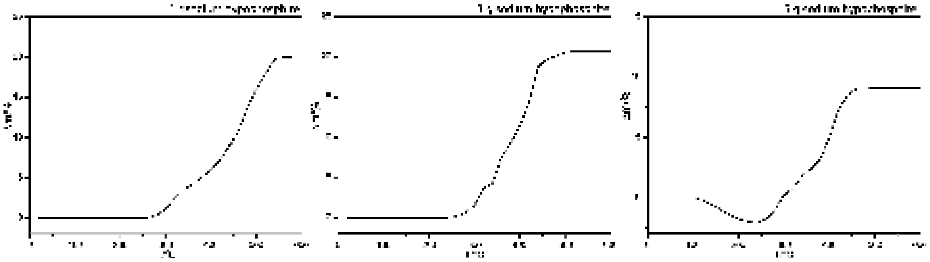

Fig. 5 TG analyses for 1, 3 and 5 g of reagent at 90 °C.

Fourier transform infra–red spectroscopy

In phosphoric acid samples, CuO bands are obvious, Fig. 6. This suggests that there was a low quantity of CuO in the reaction at 90 °C, alongside the metallic major component.

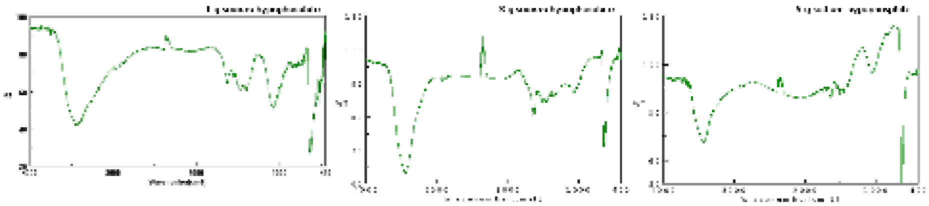

Fig. 6 IR analyses for 1, 3 and 5 g of reagent at 90 °C.

CONCLUSIONS

The proposed copper recuperation method takes place at pH values of 5.5–6.

In this method bivalent copper, from galvanic work and other wastewaters, is chemically reduced to metallic copper.

The necessary time of reaction is short.

Since sodium hypophosphite is inexpensive, it presents economic interest.

The obtained results at 90 °C, pH 5,5 – 6, from a residual solution of 0.1574 copper content, using a 176 % excess of reagent is in concert with current legislation concerning wastewater. These waters can be legally discharged, concerning copper, in natural rceptors.

Reducing agent in excess of 176 % slowly dissolves copper.

In high quantities of acid or using an excess of reagent less than 164 %, metallic copper output lowers in favor of CuO, Cu_2O, atacamite or paratacamite. Under these conditions, resulting water is still under the legal limits, and resulting compounds can be capitalized on.

REFERENCES

[1] Fagundes-Klen M. R., M. T. Veit, C. E. Borba, R. Bergamasco, L. G. de Lima Vaz, E. A. da Silva, 2010, Copper biosorption by biomass of marine alga: study of equilibrium and kinetics in batch system and adsorption/desorption cycles in fixed bed column, Water Air Soil Pollut, Vol 213, pp. 15–26

[2] Gaikwad R. W., 2011, Mass transfer studies on the removal of copper fromwastewater using activated carbon derived from coconut shell, Jnl of the University of Chem Tech and Metallurgy, Vol 46, 1, pp. 53–56

[3] Hashemi S., R. Blust, G. De Boeck, 2008, Combined effects of different food rations and sublethal copper exposure on growth and energy metabolism in common carp, Arch Environ Contam Toxicol, Vol 54, pp. 318–324

[4] Kang C. D., S. J. Sim, Y. S. Cho, W. S. Kim, 2002, Process development for the removal of copper from wastewater using ferric/limestone treatment, Korean J. Chem. Eng., Vol 20, 3, pp. 482–486

[5] Klishchenko R. E., R. D. Chebotareva, V. V. Goncharuk, 2010, Electromigration purification of galvanic sludge of copper ions, Jnl of Water Chem and Tech, Vol 32, 4, pp. 206–211

[6] Kurczewska J., G. Schroeder, U. Narkiewicz, 2010, Copper removal by carbon nanomaterials bearing cyclam-functionalized silica, Cent eur J Chem, Vol 8, 2, pp. 341–346

[7] Lazić P., D. Vučinić, J. Stanojev, B. Micović, 2010, Direct selective lead, copper and zinc minerals flotation from polymetallic ore "Podvirovi", Jnl of Mining Sci, Vol 46, 6, pp. 690–694

[8] Li D., R. Chen, 2005, Selective separation of copper by membrane-electro-winning and its application in etchant recychng, J Cent South Univ Technol, Vol 12, 1, pp. 94–97

[9] Lourie Y., 1975, Aide-mémoire de chimie analytyque, Ed. Mir, Moscow, pp. 10–550

[9] Mallick N., 2002, Biotechnological potential of immobilized algae for wastewater N, P and metal removal: A review, BioMetals, Vol 15, pp. 377–390

[10] Michael Angelo M., P. Dhandapani, M. H. Kalavathy, L. R. Miranda, 2010, Chemically activated Ipomoea carnea as an adsorbent for the copper sorption from synthetic solutions, Adsorption, Vol 16, pp. 75–84

[11] Mohammadia T., A. Mohebb, M. Sadrzadehb, A. Razmi, 2005, Modeling of metal ion removal from wastewater by electrodialysis, Separation and Purification Technology, Vol 41, 1, pp. 73–82

[12] Moreira E. E., A. B. Ribeiro, E. P. Mateus, J. T. Mexia, L. M. Ottosen, 2005, Regressional modeling of electrodialytic removal of Cu, Cr and As from CCA treated timber waste: application to sawdust, Wood Sci Technol, Vol 39, pp. 291–309

[13] Negoiu D., 1972, Tratat de chimie anorganică, Ed Tehnică Bucureşti, vol II, pp. 10–1100

[14] Oliva S. R., M. D. Mingorance, B. Valdés, E. O. Leidi, 2009, Uptake, localisation and physiological changes in response to copper excess in Erica andevalensis, Plant Soil, Vol 328, pp. 411–420

[15] Piovár J., E. Stavrou, J. Kaduková, T. Kimáková, M. Bačkor, 2011, Influence of long-term exposure to copper on the lichen photobiont Trebouxia erici and the free-living algae Scenedesmus quadricauda, Plant Growth Regul, Vol 63, pp. 81–88

[16] Popa Gr., I. A. Paralescu, 1977, Chimie analitică, Ed. Didactică şi pedagogică, Bucureşti, pp. 10–400

[17] Pradhan S., L.C. Rai, 2001, Copper removal by immobilized Microcystis aeruginosa in continuous flow columns at different bed heights: study of the adsorption/desorption cycle, World Journal of Microbiology & Biotechnology, Vol 17, pp. 829–832

[18] Robson A., B. C. Okeke, S. Pieniz, A. Brandelli, M. R. Lambais, F. A. O. Camargo, 2010, Bioreduction of Cu(II) by cell-free copper reductase from a copper resistant pseudomonas sp. NA, Biol Trace Elem Res, Vol 143, pp. 1182–1192

[19] Rojo A., H. K. Hansen, J. del Campo, 2010, Electrodialytic remediation of copper mine tailings with sinusoidal electric field, J Appl Electrochem, Vol 40, pp. 1095–1100

[20] Sukla L. B., K. C. Nathsarma, J. R. Mahanta, S. Singh, S. Behera, K. S. Rao, T. Subbaiah, B. K. Mishra, 2009, Recovery of copper values from bio–heap leaching of low grade Malanjkhand chalcopyrite ore, Korean Jnl Chem Eng, Vol 26, 6, pp. 1668–1674.