



Studies and Research on the Recovery of Copper from Industrial Waste Solutions by the Cementation Method

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Abstract

The paper brings original contributions in the particularly complex field of copper recovery from industrial wastewater. The purpose of this experimental research is to recover copper metal powder from wastewater with low copper ion content, by the method of cementation using a scrap iron electrode and to calculate the yield of copper cementation, influenced by the following parameters: initial concentrations of copper ions, pH values and contact time. Recipes were experimentally studied by the cementation method for the recovery of copper from industrially used solutions using iron waste, without consumption of other reagents or energy. Work recipes were designed and one chose three different concentrations: for each solution of prepared concentration: 0.5% CuSO₄, 1% CuSO₄ and 3% CuSO₄, and one performed laboratory experiments at two types of pH (natural pH obtained by dissolving CuSO₄ * 5H₂O in water, pH = 2 (adjustment with 0.1 M sulfuric acid solution). The optimal conditions for each recipe have been identified, based on the experimental data obtained from the monitoring of each experiment, to the WTW Multi 350i multiparameter and AAS ZEE nit 700 Analytik Jena spectrometer. The calculation of the yield of obtaining copper powder for each day of the experiment and for each recipe together, the other experimental data led us to the conclusion that the optimal variant for our study is: concentration of 0.5%, at an initial pH of 3.6 after 3 days of experiment and yield of 95.23%.

Keywords: *the recovery of copper, wastewater treatment, copper cementation method*

1. Introduction

Copper is one of the most valuable and widely used metals in the industry. It is an essential metal for organisms, but in excessive concentrations it can be very toxic for both humans and animals (Peña M.M., Lee J., Thiele D.J., 1999). Copper is a heavy metal found in large quantities in wastewater due to its various applications in industrial sectors, such as the manufacture of printed circuit boards, the metal finishing industry, galvanizing, electrolysis, painting, wood preservation, printing operations, etc. Copper can reach the environment from mines, farms, industrial installations through wastewater discharged into rivers, lakes, but also from natural sources, such as: volcanoes, degraded vegetation, forest fires (Mubarak A., 2006). Copper was the first metal used in undetermined amounts by man. The oldest craftsmen who worked with copper soon found that it is easy to form into sheets with a hammer and sheets in turn worked into other shapes that became more and more complex as their skill increased.

Through the project (<https://umfcd.ro/cercetare...SARS-COV-2>) PN-III-P2-2.1-SOL-2020-2-0208 Development of innovative solutions for the protection of personnel (exposed professionally) and the population against contamination with the virus SARS-CoV-2, studies of impregnation of cotton or medical equipment made of cotton fabric. Various impregnation recipes were used that allowed to obtain "in situ" the nanoparticles of copper and zinc oxides for the impregnation of cotton fabrics, in different concentrations and ratios. The stability of the impregnation of the nanoparticles was confirmed by chemical analysis and analysis by scanning tissues

of the tissues after 1, 3 or 5 washes. It has proved to be a good enough stability and it is expected that even after 10 washes an amount of about 40–50% of the initially impregnated amount will still be fixed on the fabric. The washes involve a pH-neutral detergent for 30–50 minutes at a temperature of 30–40°C (<https://umfcd.ro/cercetare...SARS-COV-2>) PN-III-P2-2.1-SOL-2020-2-0208).

Copper is present in normal human serum (the liquid part of the blood) at concentrations of 120–140 µg/l. Signs of toxicity will be observed if the copper concentration increases significantly above this level. All copper compounds are potentially toxic. Thus, man can be exposed to copper by breathing air, drinking water, food he consumes, by skin contact with copper or its compounds (Solomon F., 2009).

The use of copper to kill algae, fungi and mollusks proves to be very toxic to aquatic organisms. In fact, copper is one of the most toxic metals to aquatic organisms and ecosystems. Copper recovery from wastewater is achieved by various methods, such as bioadsorption, ion exchange, membrane filtration, reverse osmosis, chemical precipitation, electrochemical processes, photocatalysis, cementation (Gunatilake S.K., 2015).

Each of these methods has its own advantages and disadvantages. Unfortunately, some of these methods are difficult to use widely or expensive to apply. The use of the cementation method for the recovery of copper from metallic wastewater can be considered as a relatively simple, inexpensive and environmentally friendly method. Contamination of metal-treated water is a serious problem for many industrial sectors.

Tab. 1. Physico-chemical parameters of synthetic CuSO₄ solutions
 Tab. 1. Parametry fizyko-chemiczne syntetycznych roztworów CuSO₄

CuSO ₄ concentration	pH initial	ORP (mV)	EC (μS/cm)	TDS (mg/l)	Salinity (‰)
0.5%	3.6	+ 178.6	2480	1588	1.3
	2	+ 269	4570	2970.5	2.4
1%	3.4	+ 189.3	4250	2762.5	2.3
	2	+ 267.6	6190	4023.5	3.4
3%	3.0	+ 211.3	10290	6688.5	5.8
	2	+ 267.9	11910	7741.5	6.8

Tab. 2. Cu²⁺ values determined on the AAS ZEENIT 700 spectrometer
 Tab. 2. Wartości Cu²⁺ wyznaczone na spektrometrze AAS ZEENIT 700

Time hours	CuSO ₄ 0.5% pH=2.0	CuSO ₄ 0.5% pH=3.6	CuSO ₄ 1% pH=2.0	CuSO ₄ 1% pH=3.4	CuSO ₄ 3% pH=2.0	CuSO ₄ 3% pH=3.0
0	2092.19	2092.19	4184.38	4184.38	12553.14	12553.14
24	628.66	627.33	3187.86	3177.44	4841.17	4601.41
48	488.31	487.35	626.92	623.33	4654.42	1749.41
72	182.26	140.15	483.41	481.71	1841.82	952.12
96	32.81	16.84	91.76	181.65	323.8	904.85
120	10.14	6.51	16.03	19.41	175.5	310.04

There are many different techniques used to treat wastewater to reduce metal content. A common technique involves raising the pH of the wastewater to an alkaline level to induce precipitation of the metal. Although this method reduces the metal content of wastewater, the resulting solid sludge will require additional treatment (Moscatello N., Swayambhu G., Jones G.H., Jiale Xu, Ning Dai, Pfeifer B.A., 2018).

Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many of their ions are known to be toxic or carcinogenic (Fenglian Fu, Qi Wang, 2011). Copper has many practical uses in our society and is often found in coins, electric cables and pipes. However, too much copper can cause adverse health effects.

2. Materials And Methods

Cementation consists in the precipitation of metals from a solution of its salts by another electropositive metal (sacrificial metal) by spontaneous electrochemical reduction to its metallic state (Peng C., Liu Y., Bi J., Xu H., Ahmed A.S., 2011). The cementation method has several advantages, such as the recovery of metals in relatively pure metallic form, simple control requirements, low energy consumption and is generally a low cost process (Nassef E., El-Taweel Y.A., 2015). Cementation of copper on iron is done by a series of short-circuited electrochemical cells, in which electrons reduce the transfer of Cu²⁺ from the iron surface through the growing copper deposit. Copper ions are reduced from the surface of the copper deposit. Iron, which supplies electrons, is oxidized in the anodic places on its surface (EL-Ashtouky E.S.Z., Abdel A.M.H., 2013). However, it seems that cementing using an iron electrode is the simplest and most reasonable method for recovering copper. Therefore, it produces copper metallic sediments, which are suitable for metallurgical processes.

1.1 Equipment used

Determination of physico-chemical parameters

Using the WTW Multi 350i multiparameter, the following physico-chemical parameters were measured:

- electrical conductivity (EC);
- total dissolved solids (TDS);
- salinity;

- pH;
- redox potential (ORP).

Before the analyzes were performed, the apparatus was calibrated using standard solutions for pH and conductivity.

1.2 Determination of heavy metals

Heavy metals were analyzed by flame atomic absorption spectrometry (AAS-F) using the AAS ZEENIT 700 Analytik Jena apparatus. The device allows the analysis of the following heavy metals: Ni, Cd, Cr, Pb, Zn, Cu, Fe, using the lamp specific to each metal. The detection limit of the method is between 0.01–0.08 mg/l, depending on the metal. Prior to analysis, the water samples were acidified to pH 2 (using 65% HNO₃) and filtered.

1.3 Cementation method-use of iron electrode

Procedure: studying the scientific information presented in the specialized articles, regarding the cementation method for the recovery of copper from used solutions, one observes the following:

- the mode of work is specific to a laboratory work (small amounts of used copper solutions 0.1–10 l, using continuous mixing and sometimes heating).
- the influence of the pH of the used copper solution on the recovery yield or efficiency (natural pH was helped with 0.1 M H₂SO₄ solution up to pH 2).
- the working method designed for the experimental part simplifies the laboratory equipment (without agitation, without heating, with initial pH adjustment of CuSO₄ solutions prepared in the laboratory at a pH of 2, Fig. 1) and one sought to identify the optimal conditions for copper deposition in a reasonable time.

One prepared 3 solutions of different concentrations of CuSO₄ of 0.5%, 1%, 3% by dissolving the calculated amounts of CuSO₄*5H₂O for 250 ml volumetric flasks (stock solutions), (Table 1) and the parameters were measured with multiparameter WTW Multi 350i.

One monitored day by day, the changes of previously measured parameters, with WTW Multi 350i but also the amount of copper deposited (Fig. 2), along with determining the daily

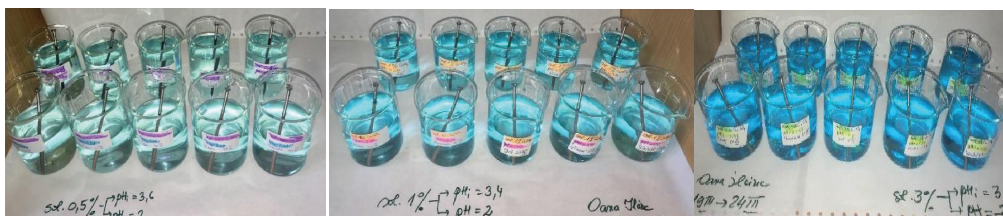


Fig. 1. Samples 3 solutions of different concentrations of CuSO_4 prepared for analysis

Rys. 1. Próbkę 3 roztworów o różnych stężeniach CuSO_4 przygotowane do analizy



Fig. 2. Samples with the amount of copper deposited on the iron, from different days of the experiment

Rys. 2. Próbkę z ilością miedzi osadzonej na żelazie, z różnych dni eksperymentu

Tab. 3. Yield values for the 3 solutions

Tab. 3. Wartości uzysków dla 3 eksperymentów

Concentration (%)	pH	Optime time (days)	η _{optimal}
0.5	3.6	3	95.23
	2	3	85.71
1	3.4	3	76.2
	2	4	97.62
3	3	3	86.83
	2	4	96.4

concentration of copper ions remaining in solution at AAS ZEE nit 700 spectrometer, so one could calculate the efficiency and daily efficiency of experiments (Table 2).

3. Results

One started the experiment by preparing 3 solutions of different concentrations, of 0.5% CuSO_4 , 1%, 3% by dissolving the calculated amounts of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ for 250 ml rated flasks. One monitored the changes in previously measured parameters with WTW Multi 350i but also the amount of copper deposited, along with determining the daily concentration of copper ions remaining in solution at the AAS ZEE nit 700 spectrometer, so one could calculate the daily efficiency and effectiveness of our experiments.

For each concentration solution prepared: 0.5% CuSO_4 , 1% CuSO_4 and 3% CuSO_4 were performed laboratory experiments at 2 different pH:

- the natural pH obtained by dissolving CuSO_4 in water;
- pH = 2 (adjustment with 0.1 M sulfuric acid solution).

The variation of salinity is observed, for the 3% pH 2 solution, which is fluctuating, reaching 6.8‰. The variation of the concentration of copper ions is observed, for the 3% solution (12553.14 mg/l) at pH 2, which is decreasing, reaching 175.5 mg/l. It is observed that after 4 days from the experiment, the concentration of copper ions reaches 323.8 mg/l, which gives us the possibility to identify an optimal time for the experiment (Fig. 3).

The synthesis yield is defined as the ratio between the practical mass obtained by copper powder (dry) and the terrorist mass (Călțaru M., Bădicioiu M., 2007).

It is observed that after 4 days the copper recovery efficiency stabilizes at 96.4%. It should be noted that after the first day of the experiment (24 h), the yield is almost 89% (Fig. 4). Which demonstrates the effectiveness of the iron waste used in the cementation method.

Table III shows yields over 95%, for all 3 optimal variants, but the time to obtain the optimal yield will differentiate the overall optimal variant, which one propose to be: concentration of 0.5%, at an initial pH of 3.6 after 3 days of experiment and yield of 95.23%.

4. Discussion

The results obtained for the variation of pH, EC, salinity, copper ion concentration and yield is the follow:

0.5% copper sulphate solution of initial pH = 3.6

The pH variation for the 5 days of the experiment is fluctuating, falling between 3.6–4.1 with an average of 3.88 (note that pH = 4.1 is obtained after 4 days). The variation of the EC ($\mu\text{S}/\text{cm}$) for the 5 days of the experiment is increasing, ranging between 2480 $\mu\text{S}/\text{cm}$ –2860 $\mu\text{S}/\text{cm}$, with an average of 2693.3 $\mu\text{S}/\text{cm}$ (note that EC = 2860 $\mu\text{S}/\text{cm}$ is obtained after 5 days). The variation of salinity (‰) for the 5 days of the experiment is increasing, ranging between 1.3–1.5‰, with an average of 1.4‰ (note that S = 1.5‰ is obtained after 5 days). The variation of the copper ion concentration (mg/l) for the 5 days of the experiment is decreasing from 2092.19 mg/l to 6.51 mg/l (on the 5th day) which demonstrates that in these conditions the method cementation also helps us in solving the problem of the concentration of copper ions in the used

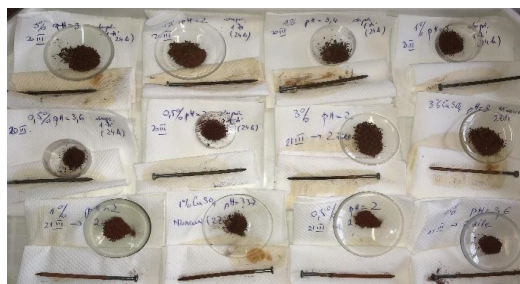


Fig. 3. Samples with the amount of copper deposited on the iron, from different days of the experiment
Rys. 3. Próbkę z ilością miedzi osadzonej na żelazie, z różnych dni eksperymentu



Fig. 4. The amount of copper powder obtained after one day of experiment
Rys. 4. Ilość miedzi otrzymanego po jednym dniu eksperymentu

industrial solution because after 5 days it reaches values below 10 mg/l (a decrease of about 322 times). The calculated synthesis yield is 95.23% after 3 days of experiment.

0.5% copper sulfate solution at adjusted pH = 2

The pH variation for the 5 days of the experiment is increasing, ranging between 2–3.8 with an average of 3.35 (note that pH = 3.8 is obtained after 3 days). The variation of the EC ($\mu\text{S}/\text{cm}$) for the 5 days of the experiment is decreasing starting from 4570–2960 $\mu\text{S}/\text{cm}$, with an average of 3370 $\mu\text{S}/\text{cm}$ (note that EC = 2960 $\mu\text{S}/\text{cm}$ is obtained after 2 days). The variation of salinity (‰) for the 5 days of the experiment is decreasing, starting from 2.4–1.5‰, with an average of 1.7‰ (note that S = 1.5‰ is obtained after 2 days). The variation of the concentration of copper ions (mg/l) for the 5 days of the experiment is decreasing from 2092.19 mg/l to 10.14 mg/l (on the 5th day), which demonstrates that in these conditions the cementation method also helps us in solving the problem of the concentration of copper ions in the used industrial solution because after 5 days it reaches a value of about 10 mg/l (a decrease of about 209 times). The calculated synthesis yield is 85.71% after 3 days of experiment.

Analyzing the data obtained for the two pH at the 0.5% CuSO_4 solution, it is observed that the optimal conditions for cementation would be for the initial pH = 3.6, because the yield is 95.23%, after 3 days of experiment.

1% copper sulphate solution at initial pH = 3.4

The pH variation for the 5 days of the experiment is fluctuating, falling between 3.4–3.77 with an average of 3.61 (note that pH = 3.77 is obtained after 3 days). The variation of the EC ($\mu\text{S}/\text{cm}$) for the 5 days of the experiment is increasing, ranging between 4250–5040 $\mu\text{S}/\text{cm}$, with an average of 4691 $\mu\text{S}/\text{cm}$ (note that EC = 5040 $\mu\text{S}/\text{cm}$ is obtained after 5 days). The variation of salinity (‰) for the 5 days of the experiment

is increasing, falling between 2.3–2.7‰, with an average of 2.51‰ (note that S = 2.7‰ is obtained after 5 days). The variation of the concentration of copper ions (mg/l), for the 5 days of the experiment is decreasing from 4184.38 mg/l to 19.41 mg/l (on the 5th day) which proves that in these conditions the cementation method it also helps us in solving the problem of the concentration of copper ions in the used industrial solution because after 5 days it reaches a value below 20 mg/l (a decrease of about 215 times). The calculated synthesis yield is 76.2% after 3 days of experiment.

1% copper sulphate solution at adjusted pH = 2

The pH variation for the 5 days of the experiment is increasing, ranging between 2–3.65 with an average of 3.12 (note that pH = 3.65 is obtained after 5 days). The variation of the EC ($\mu\text{S}/\text{cm}$) for the 5 days of the experiment is decreasing starting from 6190–5480 $\mu\text{S}/\text{cm}$, with an average of 5383.3 $\mu\text{S}/\text{cm}$ (note that EC = 5480 $\mu\text{S}/\text{cm}$ is obtained after 5 days). The variation of salinity (‰) for the 5 days of the experiment is decreasing, starting from 3.5–3‰, with an average of 2.9‰ (note that S = 3‰ is obtained after 5 days). The variation of the copper ion concentration (mg/l) for the 5 days of the experiment is decreasing from 4184.38 mg/l to 16.03 mg/l (in the 5th day) which proves that under these conditions the method cementation also helps us in solving the problem of the concentration of copper ions in the used industrial solution because after 5 days it reaches a value of about 16 mg/l (a decrease of about 261 times). The calculated synthesis yield is 97.62% after 4 days of experiment.

Analyzing the data obtained for the two pH at the 1% CuSO_4 solution, it is observed that the optimal conditions for cementation would be for adjusted pH = 2, because the yield is 97.62%, after 4 days of experiment.

Solution 3% copper sulfate initial pH = 3

The pH variation for the 5 days of the experiment is fluctuating ranging from 3–3.75 with an average of 3.42 (note that pH = 3.75 is get after 2 days). The variation of the EC ($\mu\text{S}/\text{cm}$) for the 5 days of the experiment is fluctuating, falling between 10290–11980 $\mu\text{S}/\text{cm}$, with an average of 11418 $\mu\text{S}/\text{cm}$ (note EC = 11980 $\mu\text{S}/\text{cm}$ is obtained after 5 days). The variation of salinity (‰) for the 5 days of the experiment is increasing, falling between 5.8–6.9‰, with an average of 6.46‰ (note that S = 6.9‰ is obtained after 3 days). The variation of the copper ion concentration (mg/l) for the 5 days of the experiment is decreasing from 12553.14 mg/l to 310.04 mg/l (on the 5th day) which demonstrates that under these conditions the method cementation also helps us in solving the problem of copper ion concentration in the industrialized solution because after 5 days it reaches a value of 310 mg/l (a decrease of about 40 times). The calculated synthesis yield is 86.83% after 3 days of experiment.

3% copper sulphate solution at adjusted pH = 2

The pH variation for the 5 days of the experiment is increasing, falling between 2–3.43 with an average of 2.96 (note that pH = 3.43 is obtained after 4 days). The variation of the EC ($\mu\text{S}/\text{cm}$) for the 5 days of the experiment is fluctuating starting from 11910–11960 $\mu\text{S}/\text{cm}$, with an average of 11421 $\mu\text{S}/\text{cm}$ (note that EC = 11960 $\mu\text{S}/\text{cm}$ is obtained after 5 days). The variation of salinity (‰) for the 5 days.

5. Conclusions

The cementation method can recover copper from industrial waste solutions. This study aimed to make a number of original contributions to the particularly complex field of recovery of copper from industrial wastewater by the method of cementation.

The best known reaction for obtaining copper in the laboratory is between iron and copper sulfate. This can be used to obtain copper by depositing it on the piece of metal iron inserted in the industrial water.

95.23% yield of obtaining copper powder indicates the optimal variant at the concentration of 0.5% with an initial pH of 3.6 after 3 days of experiment.

Experimentally it is possible to recover metallic copper powder from wastewater with low copper ion content, by the cementation method using a scrap iron electrode, without consuming other reagents or energy.

6. Acknowledgments

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Badania nad odzyskiwaniem miedzi z roztworów odpadów przemysłowych metodą cementacji

Artykuł dotyczy szczególnie złożonej dziedziny odzyskiwania miedzi ze ścieków przemysłowych. Celem badań eksperymentalnych jest odzyskanie proszku miedzi metalicznej ze ścieków o niskiej zawartości jonów miedzi metodą cementacji z użyciem elektrody złomowej oraz obliczenie wydajności cementacji miedzi, na którą mają wpływ następujące parametry: początkowe stężenia jonów miedzi, wartości pH i czas kontaktu. Receptury zostały eksperymentalnie zbadane metodą cementacyjną do odzyskiwania miedzi z przemysłowo stosowanych roztworów przy użyciu odpadów żelaznych, bez zużycia innych odczynników i energii. Opracowano receptury pracy i wybrano trzy różne stężenia: dla każdego roztworu o przygotowanym stężeniu: 0,5% CuSO₄, 1% CuSO₄ i 3% CuSO₄ oraz wykonano eksperymenty laboratoryjne dla dwu wartości pH (naturalne pH uzyskane przez rozpuszczenie CuSO₄·5H₂O w wodzie, pH = 2 (regulacja 0,1 M roztworem kwasu siarkowego). Optymalne warunki dla każdej receptury zostały określone na podstawie danych doświadczalnych uzyskanych z monitorowania każdego eksperymentu. Badania przeprowadzono na spektrometrze WTW Multi 350i i AAS ZEnit 700 Analytik Jena. Obliczenie wydajności otrzymywania miedzi dla każdego eksperymentu i dla każdej receptury łącznie, doprowadziły do wniosku, że optymalnym wariantem eksperymentu jest: stężenie 0,5%, przy początkowym pH 3,6 po 3 dniach doświadczenia, uzyskano wydajność 95,23%.

Słowa kluczowe: odzyskiwanie miedzi, oczyszczanie ścieków, metoda cementacji