


Article

Cavitation-Dispersion Method for Copper Cementation from Wastewater by Iron Powder

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Abstract: The circular economy for sustainable economic deployment is strongly based on the re-use of secondary products and waste utilization. In the present study, a new effective cementation method for recovering valuable metallic copper from industrial wastewater using Fe⁰ powders is reported. A high-speed mixer-disperser (HSMD) capable of providing a cavitation effect was used for the rapid intake, dispersion, and mixing of Fe⁰ powder in an acidic wastewater solution (pH ≈ 2.9) containing copper ions mainly in the form of CuSO₄. Three iron powders/particles were tested as the cementation agent: particles collected from industrial dust filters (CMS), water-atomized iron-based powder AHC100.29, and sponge-iron powder NC100.24. The effects of mixing regimes and related mixing conditions on the effectiveness of the Cu cementation process were evaluated by comparison between the HSMD and a laboratory paddle mixer. It was observed that the use of cavitation provided more efficient copper removal during the copper cementation process in comparison to the standard experiments with the propeller mixer. Under the cavitation regime, about 90% of copper was cemented in the first five minutes and the final copper removal of 95% was achieved using all three Fe⁰ powders after seven minutes of cementation. In comparison, only around 55% of copper was cemented in the first seven minutes of cementation using the traditional mixing method.

Keywords: cementation; copper removal; cavitation

1. Introduction

Copper is one of the most important non-ferrous metals due to its high thermal and electrical conductivity. It can be applied as an electrical and heat conductor, a building material, an alloying component, and in metal finishing, electroplating, plastics, fungicides, etching, etc. [1–4]. Increases in the rate of copper production and widespread demand for applications in many fields have led to a considerable increase of copper ions leaking into the ecosystem, particularly in industrial wastewater [1,4–6]. As a heavy metal, the presence of copper may cause hazardous effects on human health, even at low concentrations [7–9].

The United States Environmental Protection Agency (USEPA) allows a maximum contaminant level (MCL) of only 1.3 mg/L for the concentration of copper ions in industrial effluents. The standardized MCL in drinking water for copper is 0.25 mg/L [10–13]. Effective copper removal from wastewater has always been of great interest to researchers around the world. Cementation [14–17], adsorption [5,9,10,18,19], membrane filtration [20–22], electrodialysis [20,23], and photocatalysis [19,24] are the most common methods and techniques for the extraction of copper from wastewater. Each method and/or technology has its own advantages and disadvantages [25–29]. Nevertheless, the cementation process is considered to be the most economical and effective method to remove valuable and/or toxic metals from industrial wastewater [1]. This method reduces copper ions in the copper's salt-containing aqueous solution to its zero valent state at the interface of a more positive metal in the electromotive force series [14]. Low cost, low energy consumption, recovery of metals in pure metallic form, ease of control, simplicity of operation, and high efficiency make the cementation process most advantageous [1,30,31]. The most common cementation agents are iron and zinc [32]. The main disadvantage of the cementation technique is its excess sacrificial metal consumption [33].

Intensification of the cementation process has interested researchers in recent years. Nosier et al. has reported the use of ceramic for the enhancement of copper cementation under single-phase flow [17]. A bubble column reactor fitted with horizontal screens was used for copper removal from aqueous solutions [34]. A modified stirred tank reactor in combination with alcoholic additives increased the cementation rate of copper powder from wastewater containing CuSO₄ [35]. In his paper, Konsowa used a special jet reactor to cement copper on a zinc disc from a dilute copper sulfate solution [14].

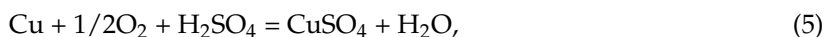
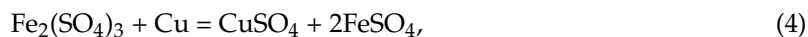
Ultrasonic cavitation is the well-known phenomenon in the ultrasonic cleaning method. In a liquid medium, the ultrasonic waves, generated by an electronic ultrasound generator and a special transducer suitably mounted under the bottom of a stainless-steel tank or directly to a metal cylinder (called a “horn”), produce compression and vacuum waves at a very high speed. Speed depends on the working frequency of the ultrasound generator. Normally, such apparatus operates at a frequency between 28 and 50 kHz. The pressure and vacuum waves in the liquid cause the phenomenon known as “ultrasonic cavitation”. However, this method is complicated for implementation on a commercial scale due to the low productivity and high cost of commercial ultrasonic devices. Another important factor is the risk to human health caused by long-term exposure to ultrasonic noise generated by ultrasound generators. In the present work, a rotational cavitation-generated device was employed to study the effect of cavitation on copper cementation from industrial wastewater.

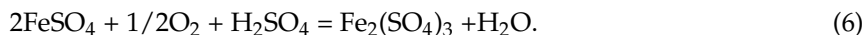
2. Theory

Cementation is an electrochemical process that leverages the difference between the standard electrode potentials of ions of the extracted metal and the cementing metal. The cementing metal should have a more negative standard electrode potential than the extracted metal. This process in acid media can be described by following Equations (1)–(3).

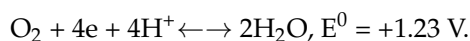
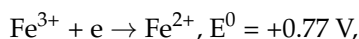
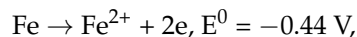
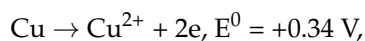


However, the following reactions occur simultaneously ((4)–(6)):

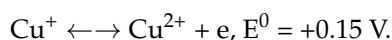
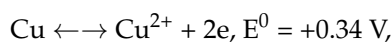
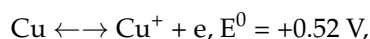




Standard electrode potentials of main species are given as follows [6]:



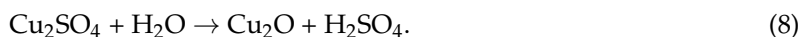
Reactions (4) and (5) reduce the amount of copper extraction in the cementation process. Also, in kinetic equilibrium, three following reactions occur simultaneously:



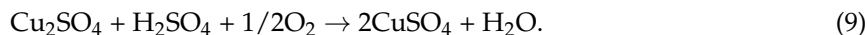
The speed and limit of copper dissolution is determined by steady equilibrium potential. Cuprous ions are unstable in sulfate solutions and are spontaneously transformed into divalent copper to form a powder according to disproportionation (Equation (7)):



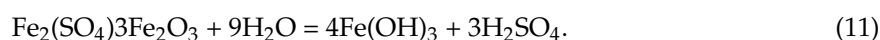
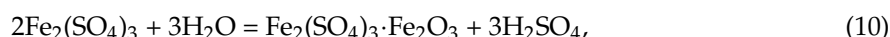
In neutral solutions, copper sulfate is hydrolyzed to form dark red crystals of copper oxide (Equation (8)):



In acidic solutions, oxidation with oxygen present in the solution is the main reaction (Equation (9)):



An insufficient amount of free sulfuric acid in solutions creates favorable conditions for the hydrolysis of iron ions.



Theoretically, the copper cementation process terminates when the concentration of copper ions in the solution decreases to a certain value, at which the electrode potential for copper is equal the electrode potential for iron. The system achieves the equilibrium state. The concentration of copper ions in the solution at equilibrium can be calculated from the Nernst Equations (12) and (13) [6]:

$$E_{\text{Fe}^{2+}/\text{Fe}} = E_{\text{Fe}^{2+}/\text{Fe}}^0 + \frac{RT}{zF} \ln a_{\text{Fe}^{2+}}, \quad (12)$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = E_{\text{Cu}^{2+}/\text{Cu}}^0 + \frac{RT}{zF} \ln a_{\text{Cu}^{2+}}, \quad (13)$$

If

$$E_{\text{Fe}^{2+}/\text{Fe}} = E_{\text{Cu}^{2+}/\text{Cu}}, \quad (14)$$

then

$$E_{\text{Fe}^{2+}/\text{Fe}}^0 + \frac{RT}{zF} \ln a_{\text{Fe}^{2+}} = E_{\text{Cu}^{2+}/\text{Cu}}^0 + \frac{RT}{zF} \ln a_{\text{Cu}^{2+}}, \quad (15)$$

where: E^0 is the standard electrode potential, a is ion activity, R is the gas constant, F is the Faraday constant, and z is the number of electrons participating in reaction.

The solution of this equation at 25 °C gives the following expression:

$$-0.44 + \frac{0.059}{2} \ln a_{\text{Fe}^{2+}} = 0.34 + \frac{0.059}{2} \ln a_{\text{Cu}^{2+}}, \quad (16)$$

$$\frac{a_{\text{Cu}^{2+}}}{a_{\text{Fe}^{2+}}} = 1.3 \times 10^{-27}. \quad (17)$$

At equilibrium, the concentration of copper ions in the solution is low ($C_{\text{Cu}^{2+}} = 1.3 \times 10^{-27}$), that is, cementation reaction can be considered as extending to the end. However, the thermodynamic equilibrium is not achieved due to kinetic difficulties. The mechanism of copper cementation can be represented by successive stages: delivery of ions to the cathode surface and removal of ions from the anode surface through a diffusion layer, discharge of copper ions to the cathode sections, and ionization of iron ions on the anodic sites (electrochemical conversion).

3. Materials and Methods

A high-speed cavitation-dispersion device (HSCD) (CORVUS Ltd., Riga, Latvia) and a paddle laboratory mixing device (LMD) EUROSTAR 40 digital (IKA, Staufen, Germany) were compared to determine the influence of mixing regimes and related parameters on the effectiveness of the copper extraction process. The duration of each test was 10 min. Samples were collected before and during the test after 1, 2, 3, 5, and 10 min. A total of 1500 mL of wastewater was used for every test.

Wastewater for treatment experiments was obtained from a European mining company. According to the non-disclosure agreement between the mining company and researchers, it is prohibited to reveal the source of wastewater. The chemical composition was provided by the supplier as listed in Table 1. The wastewater contained mainly copper ions in the form of CuSO_4 with $\text{pH} = 2.95$. Three different iron powders from Höganäs AB, Sweden were provided for cementation experiments: (1) iron particles collected from industrial dust filter (CMS) (Höganäs AB, Höganäs, Sweden); (2) water-atomized iron-based powder AHC100.29 (AHC); and (3) sponge-iron powder NC100.24 (NC). The particle size distribution and surface area of the powders are shown in Table 2.

The HSCD was used for Cu extraction experiments with the setup and principles demonstrated in authors' previous works as shown in Figure 1 [36–38]. As determined in the previous works [36–38], a linear speed over 24.13 m/s, which corresponds to 3847 rpm, is needed in order for the cavitation effect to appear in water media when HSCD is used. To ensure stable cavitation in all treated volumes, a rotor rotational frequency of 6000 rpm was applied. A reference laboratory mixer with an electric drive and a paddle-type stirrer was used (Figure 2). Nylon syringe filters (pore size of 0.45 μm , diameter of 25 mm, supplied by Cole-Parmer, Hamburg, Germany) were used with the aim of avoiding the presence of Fe^0 , Cu^0 , and other solid particles, and to terminate cementation reactions in collected solutions. Each experiment was repeated four times with the deviation in measurement results less than 5%. Surface area was determined by the Brunauer–Emmett–Teller (BET) analysis, using the surface area analyzer Quadrasorb SI-KR/MP (Anton Paar GmbH, Berlin, Germany) with nitrogen adsorption/desorption at 77K.

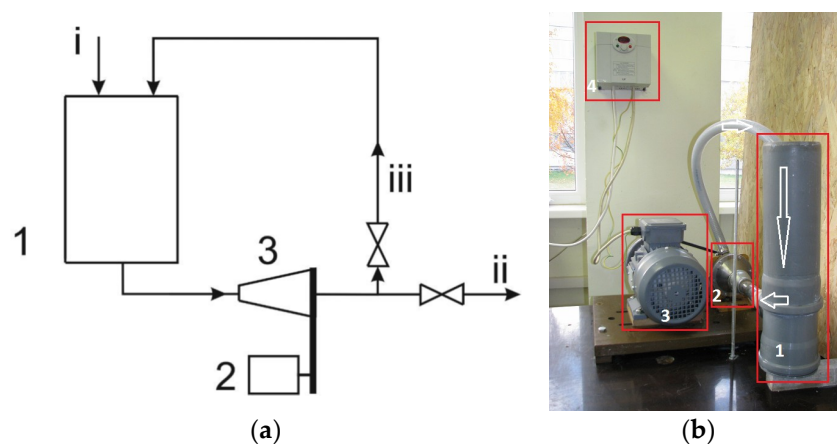


Figure 1. Scheme of the experimental setup for Cu^{2+} -containing wastewater treatment. Principal scheme (a) 1—container for suspension; 2—engine; 3—mixer-disperser; i—supply components to be mixed; ii—suspension output; iii—recycle stream. General view (b) 1—container for suspension; 2—mixer-disperser; 3—engine; 4—engine rpm control unit. Arrows indicate suspension circulation directions.

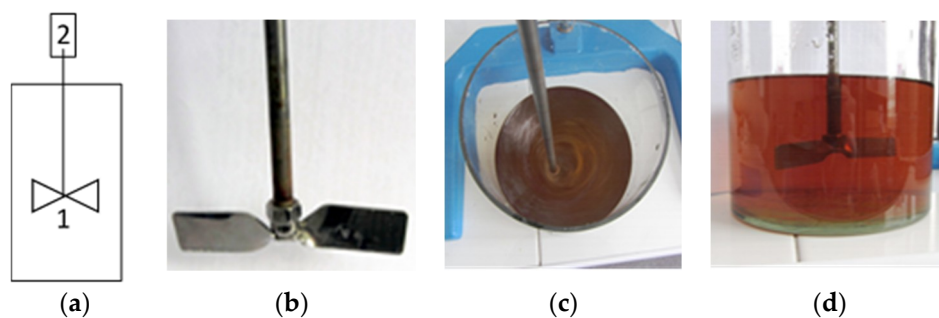


Figure 2. Experimental setup for control experiment of a propeller-type sitter. (a) Scheme of process volume with a propeller-type sitter (1), and a laboratory mixer with electric drive (2). (b) Propeller-type sitter view. (c) Sitter axis located asymmetrically to the vessel. (d) Sitter location in processed wastewater volume.

Table 1. Physicochemical parameters of the wastewater sample.

Parameter	Value	Unit
pH *	2.95	-
Copper (Cu) *	750 ± 10	mg/L
Lead (Pb)	0.250	mg/L
Sulfate ions (SO_4^{2-})	20.0	g/L
Cyanide ions (CN^-)	<0.050	mg/L
Chromium ions (Cr^{6+})	≥ 0.005	mg/L
Nickel (Ni)	≥ 4.000	mg/L
Mercury ions (Hg^+)	≥ 0.005	mg/L
Nitrate ions (NO_3^-)	<0.010	mg/L
Fe (II+III) *	6600 ± 100	mg/L
Concentration of other cations: Al^{3+} , Mg^{2+} , Zn^{2+}	<300	mg/L
* determinate by RTU laboratory.	-	-

Table 2. Physical properties of iron powders—CMS: iron particles collected from industrial dust filter; AHC100.29: water-atomized iron-based powder; NC100.24: sponge-iron powder.

Parameter	CMS	AHC 100.29	NC 100.24
Particle size >150 μm	0%	6%	1%
Particle size 150–45 μm	47%	70%	80%
Particle size <45 μm	53%	24%	19%
Specific surface area, m^2/g	0.67 ± 0.07	0.78 ± 0.1	0.73 ± 0.1

The stoichiometric amount of Fe^0 powder needed for cementation tests was calculated according to reaction (1) and the initial concentration of Cu^{2+} . It was found that 0.441 g/L of iron powder was necessary. On the other hand, taking into account simultaneous chemical reactions (2)–(4), four times the excess of the stoichiometric amount of iron powder was proposed and tested, corresponding to the ratio between the amount of iron powder and the solution volume of 1.764 g/L. Figure 3 shows a photograph of iron powder AHC 100.29 with sponge-like morphology. For microstructural characterization, optical imaging was carried out by the optical digital microscope VHX-2000 (Keyence Corporation, Osaka, Japan) equipped with lenses VH-Z20R/W and VH-Z500R/W. Metal concentrations in solutions were analyzed by the atomic absorption spectrometer GBC 932plus (GBC Scientific Equipment Ltd., Dandenong, Australia).

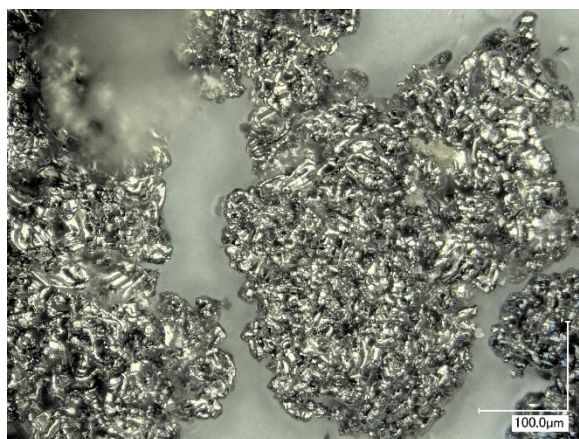


Figure 3. Picture of sponge-like surface structure of AHC 100.29.

4. Results and Discussion

As shown in Figures 4 and 5, cavitation dispersion provided more effective copper cementation from wastewater by Fe^0 powders than the traditional mixing method using propellers. Using the high-speed mixer-disperser (HSMD), the copper concentration in wastewater decreased rapidly in first five minutes and achieved the steady state in only seven minutes, when about 95.9% of copper was cemented. Increasing the cementation duration to ten minutes did not result in a significant increase in cementation efficiency. Although the copper concentrations remaining in wastewater when three types of Fe^0 powders were used varied slightly in the first 5 min of cementation, the final copper concentration after 10 min cementation with all three powders was almost identical, at about 31 mg/L. Therefore, it is more economical and ecological to use the powder from dust filters in practice. In contrast, the copper cementation using the conventional propeller sitter proceeded more slowly than the cementation using the HSMD and achieved only 53%–55% efficiency in the first five minutes of cementation for all three types of Fe^0 powder. After that, the cementation process slowed down, with cementation efficiency varying from 61.5% for AHC powders to 69.2% for NC powders after ten minutes. It was also observed that the temperature of wastewater during cementation using the HSMD increased to about 35 °C after 7 min, while the temperature of wastewater during

cementation using the propeller stirrer remained unchanged, at 18 °C. It was probable that the increase in cementation temperature also contributed to some increase in the copper cementation efficiency by the cavitation-dispersion method.

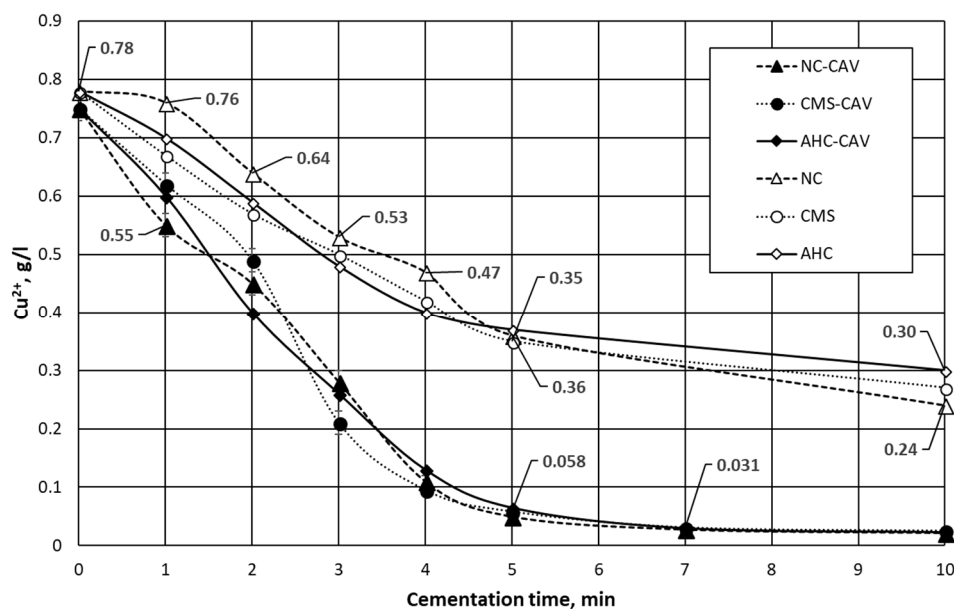


Figure 4. Dependence of Cu^{2+} concentration in the waste water, depending on the treatment time and used setup. NC-CAV: powder NC 100.24 with cavitation; CMS-CAV: powder CMS with cavitation; AHC-CAV: powder AHC 100.29 with cavitation; NC: powder NC 100.24 without cavitation; CMS: powder CMS without cavitation; AHC: powder AHC 100.29 without cavitation.

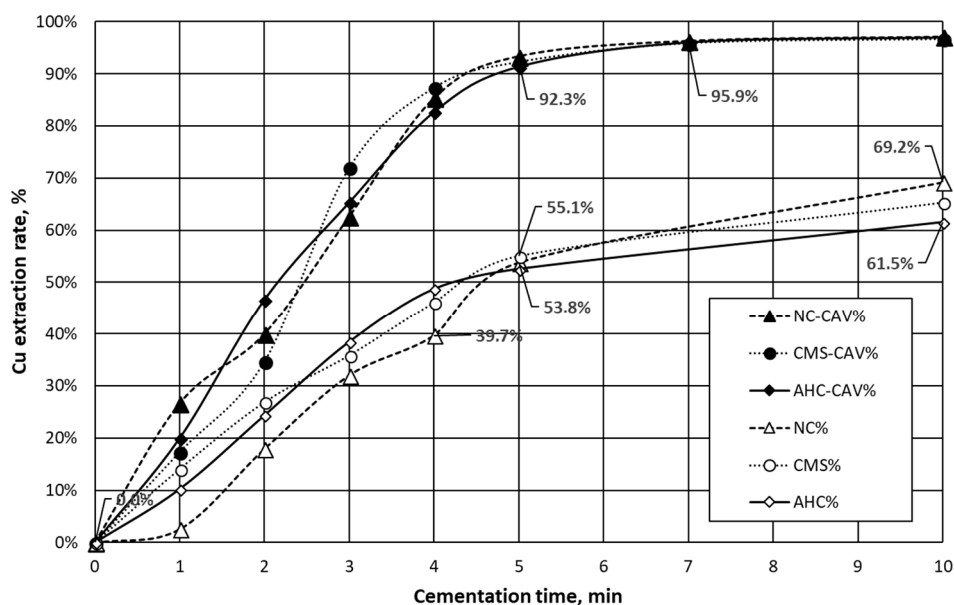


Figure 5. Dependence of the copper extraction rate, depending on the treatment time and setup used.

As described in Section 2, the reduction of Cu^{2+} to Cu^0 occurs on Fe^0 surface, which will be gradually covered by a layer of cemented Cu^0 . During the first five minutes of cementation, the opened Fe^0 surface was quite large, so cementation proceeded quickly. After that, cementation slowed down due to decreased accessible Fe^0 surface on which Cu^{2+} ions can be cemented. This behavior was observed during cementation using all three types of Fe^0 powders under both non-cavitated and cavitated cementation conditions. As shown in Table 2, all three Fe^0 powders had similar specific

surfaces, so in general, copper cementation courses using these Fe^0 powders followed similar trends (Figures 4 and 5).

Figure 6 shows the original NC 100.24 Fe^0 powders and their cemented particles obtained under the traditional mixing regime and the cavitation regime. Under the traditional mixing regime, Fe^0 powders were covered by cemented Cu^0 . Some of them are agglomerated, probably by bridging of cemented Cu^0 , making the resulting Fe^0 particles bigger than the original ones (Figure 6b). The cavitated samples consisted of some small particles with particle size ranging from 10 to 30 μm (Figure 6c). The majority of particles had particle size ranging from 50 to 100 μm , much smaller than the original particle size of 150 μm (Table 2). The formation of smaller particles and the reduction in particle size of the majority of original Fe^0 particles were probably the results of the cavitation effects, which caused newly cemented Cu^0 to rip off the Fe^0 surface, creating small Cu^0 particles and allowing additional cementation on the newly opened Fe^0 surface. Together with increased diffusion of Cu^{2+} ions to Fe^0 surfaces and/or through the pores of cemented Cu^0 on Fe^0 surfaces, the copper cementation process quickened during the cavitation regime. The other explanation for the formation of smaller particles in cavitated samples is that some of the Fe^0 particles broke down during cavitation, leading to increased specific surface and increased copper cementation efficiency.

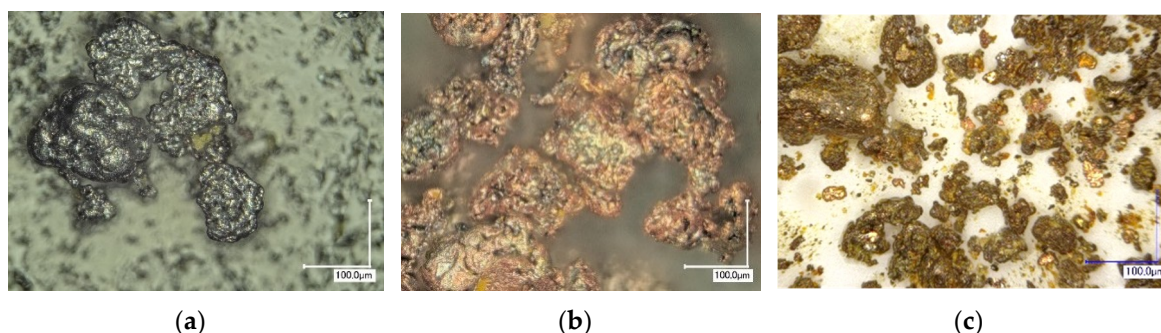


Figure 6. (a) NC 100.24 Fe powder particles before cementation; (b) NC 100.24 Fe powder particles after cementation at 10th minute, without cavitation treatment; (c) NC 100.24 Fe powder particles after cementation at 10th minute, with cavitation treatment.

The commercial cementation process usually operates the flows at 100–300 m^3/h . In order to implement the studied cavitation cementation method, repetition of the cavitation treatment using tanks can be envisaged. Figure 7 shows the following proposed commercial application scheme: Cu^{2+} contaminated waste water and Fe^0 powder are continuously fed in to a tank (1) with a paddle mixer (2), the mixture flows through the HSMD (3), during cavitation treatment, Fe^0 particles are cemented with Cu^0 (i), and then separated and de-agglomerated (ii). The set-up has a multiple number (n) of set tanks, mixers, and HSMD (4). At the end of the process, the suspension with Fe^0 and Cu^0 flows through a magnetic separator (5) for unreacted Fe^0 separation, which is returned to the extraction process via the reactor (1) for mechanical separation by filtration or sedimentation (6) of Cu^0 . According to a common electrochemical Equation (18), it is also possible to extract Cd, In, Tl, Co, Ni, Sn, Pb, Bi, Cu, Hg, Ag, and Au metals.



where N^{n+} is the reduced metal ion (metal with a higher standard potential value), and M^0 is metal that carries cementation (metal with a lower standard potential value).

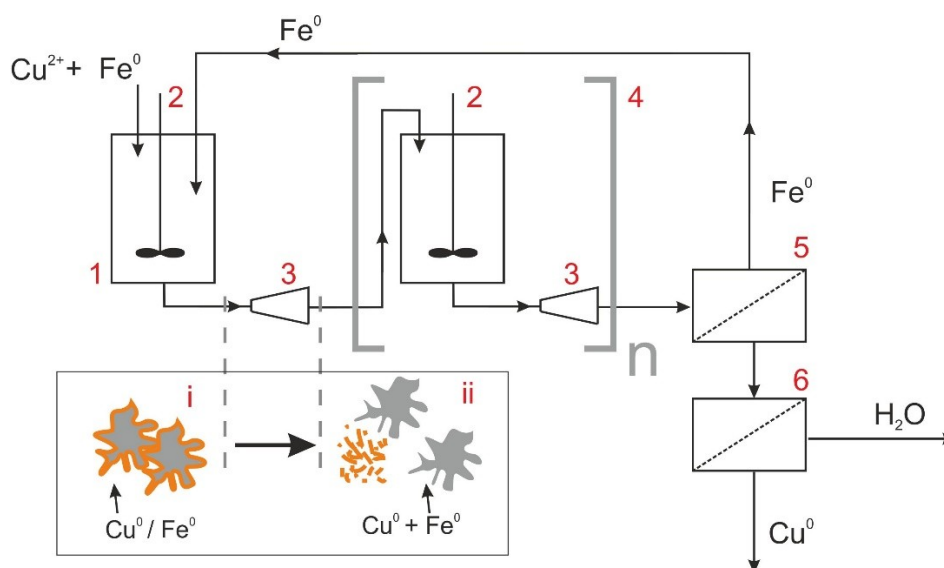


Figure 7. Principal scheme for commercial implementation for Cu extraction from mining waste water: 1—container for suspension; 2—paddle mixer; 3—mixer-disperser; 4—a set of tanks, mixers, and HSMD; 5—magnetic separator; 6—mechanical filter; i—Cu cemented on Fe particles before the cavitation; ii— cemented Cu and Fe particles after the cavitation; Arrows indicating flow directions.

5. Conclusions

Using a high-speed mixer-disperser (HSMD) as the mechanical cavitation source, it is possible to achieve copper extraction from mining wastewater with around 40% higher cementation efficiency, in a significantly faster time than by using the traditional mixing method. After seven minutes, over 95% of copper was cemented on Fe^0 powders by applying the HSMD. Morphology and iron powder origins do not play a significant role in metal extraction by the cementation process. The investigated cementation process improvement could be foreseen as a route for obtaining fine powders of copper and other metals (e.g., Cd, In, Tl, Co, Ni, Sn, Pb, Bi, Cu, Hg, Ag, and Au). It could also be used at the industrial scale for mining and metallurgical wastewater purification.

Author Contributions: A.S., J.B., V.M., A.P. and J.B. conceptualized and designed the experiments; A.S., J.B., J.O. and A.P. performed the experiments; A.S., J.B., V.M. and J.O. analyzed the data; A.P. contributed reagents, materials, analysis, and necessary tools; H.V., A.S. and J.O. prepared the original draft; H.V. and P.N. reviewed and completed the final manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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