

Techno-Economic Feasibility for Water Purification from Copper Ions

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ABSTRACT

The main direction of the industrial development of Ukraine is the solving of the environmental pollution problems under the conditions of preservation of natural resources through complex use of raw materials with involvement of industrial wastes. The developed technology is intended for galvanic, accumulator, machine-building, mine and other enterprises, the wastewater from which contains ions of heavy metals. Heavy metal ions are extremely dangerous toxic substances because of a cumulative effect on aquatic organisms. In order to remove copper ions from aqueous solutions, the chemical precipitation with lime is used. The choice of reagent is associated with its cheapness. The most effective reagent precipitation of copper ions in the form of hydroxide occurs when the pH is raised to 10. In this work, the influence of sludge, which is formed as a result of water purification from copper ions, on the properties of cement was investigated. The effect was evaluated on the following properties: normal density of cement, hardening time, compressive strength at the age of 2 and 28 days and water separation coefficient. This allowed us to develop effective ways to their disposal. The developed method provides: a high degree of metal removal (up to 98-99%); simplicity of technological process; small capital and operating costs; complex technology of wastewater treatment process. Thus, the results of the study will contribute to the creation of low-waste and non-waste technologies for waste processing and disposal.

Keywords: industrial development, heavy metals, removal of copper, reagent methods, hardening time properties of cement, compressive strength properties

INTRODUCTION

Today, the reserves of freshwater, which are especially needed by people, are insignificant and exhaustive. In many parts of the planet, these resources are lacking and insufficient for irrigation, industrial needs, drinking and other household needs. More and more industries have focused on the highly efficient water utilization (Jia et al. 2016). In the chemical industry, in the manufacturing of galvanic elements, printing, leather and fur products, the release of heavy metal ions happens (Buzlyo et al. 2018, Naidu et al. 2019, Kolesnyk et al. 2020).

The application of environmentally unreliable technologies in industry leads to an increase in the content of heavy metal ions in wastewater.

Such metals can be iron, cadmium, chromium, copper, cobalt, nickel, manganese, molybdenum, zinc, tin, mercury, lead, and others. Heavy metal ions are toxic and carcinogenic; moreover, unlike organic substances, they are not biodegradable and can be accumulated in living organisms. Thus, they result in a hazard to living organisms as well as causing serious health problems in the human beings (Awual et al. 2013, Wang et al. 2014, Fazzo et al. 2017).

Pollution of the hydrosphere by these pollutants is one of the most serious problems of our time. Therefore, it is important to deepen the research on wastewater treatment from heavy metal ions for technical and drinking purposes, to find the most effective methods with the subsequent development of integrated technologies

(Chowdhury et al. 2016, Malik et al. 2019, Vardhan et al. 2019).

For strict control over the discharge of heavy metals into the environment, it is necessary to use relatively inexpensive, affordable methods of their removal. It is important to achieve a significant decrease in the discharge of insufficiently treated wastewater into water bodies, to create closed production cycles of water supply by developing schemes for reuse of treated wastewater, to improve deep treatment technologies and to reconstruct the existing treatment plants using more efficient processes and devices (Trus et al. 2019 a, Radovenchyk et al. 2021).

Nowadays, different physicochemical methods are used to treat wastewater from heavy metal ions, the implementation of which requires the use of special equipment, materials and chemicals. The most widely used methods are reagent (Gomelya et al. 2014, Hargreaves et al. 2018.), ion exchange (Zewail et al. 2015, Hu and Boyer 2018), sorption (Biela et al. 2016, Kyrii et al. 2018, Halysh et al. 2020a, Halysh et al. 2020 b), electrochemical (Trokhymenko et al. 2020, Chen et al. 2018), and membrane extraction (Zheng et al. 2018, Trus et al. 2020).

Currently, the reagent method is most widely used in treatment plants. The method involves adding different reagents into the sewage effluents, resulting in the conversion of toxic compounds into low-toxic with their further precipitations (Gomelya et al. 2014). CaCO_3 is used as the precipitation reagent (Li et al. 2016). A significant advantage of the process is that the moisture content of the filtrate residues is much lower (less than 50%) than when using lime neutralization (more than 80%), which offers a potential reduction in the amount of sludge in wastewater treatment (Li et al. 2017, Li et al. 2020). However, this reagent is too stable so it needs to be activated (Zeng et al. 2020, Wang et al. 2019). In addition, activated antigorite (Lei et al. 2019), and dolomite (Hu et al. 2020), as well as mechanochemical activation of serpentine (Li et al. 2020, Huang et al. 2017), and magnetite (Han H. et al. 2016, Trus et al. 2019 b) are employed.

Lime, lime water and ferrite are widely used to precipitate heavy metals. The application of the ferritization method allows achieving a high degree of water purification, which prevents the discharge of contaminated wastewater into reservoirs and reduces water consumption through the use of treated water in the circulating water supply system. When the temperature rises above

60°C, the duration of the process is 20–30 minutes, lowering the temperature to 30°C leads to an increase in the duration of the process over an hour. Lime is a quite affordable reagent, in addition, the reaction of precipitation of copper ions takes place at normal temperature; thus, there is no need to spend extra energy to heat the solutions. The main disadvantages of reagent methods are the formation of large amounts of wet sludge and the absence of methods for their effective disposal, the need for additional facilities for their storage or disposal, which can lead to secondary water pollution (Trus et al. 2019).

Copper is one of the most common and dangerous pollutants of the environment. The industrial discharges and the corrosion of copper pipelines and other structures, which are used in water supply systems, are the main sources for water pollution with copper ions (Deyab 2018, Vasyliov et al. 2019, Vorobyova et al. 2019). It is known that the intake of heavy metals, even in relatively small doses, reduces immunity, increases susceptibility to infections, stimulates the development of allergic, autoimmune and cancer diseases (Fu et al. 2020, Dorne et al. 2011, Cortés et al. 2021). Copper also shows allergenic, immunogenic and other effects. The excessive concentrations of copper adversely affect plant organisms (Järup 2003, Ohsawa 2009, Rehman et al. 2018).

The MPC of copper in sanitary water bodies is 0.1 mg/dm³, in the water of fishery reservoirs – 0.001 mg/dm³. Despite the high degree of copper removal from water (99–99.5%), the residual concentration of heavy metals in purified water does not always meet the sanitary standards for discharge into reservoirs for cultural and domestic purposes. In this regard, the technological scheme of wastewater treatment from heavy metals often consists of two processes – reagent treatment followed by flotation.

MATERIALS AND METHODS

Materials

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and lime $\text{Ca}(\text{OH})_2$ of analytical grades were used throughout the work. In order to study the physical and mechanical properties of the composites, we used cement of I-500 type of the following mineralogical composition, wt.%: C_3S – 57,10, C_2S – 21,27, C_3A – 6,87, C_4AF – 12,19.

Study of the effect of reagent consumption on copper ions precipitation

In wastewater, copper can remain in ionic form and in the form of complex compounds. In this study, the concentration of copper ions in the initial solution was 1–100 mg/dm³, pH = 6.9. The most effective removal copper from aqueous solutions in the form of hydroxides is achieved at pH = 8.5–10.0. The reagent consumption was expected to increase the pH.

After treatment with reagent, water was left to precipitate copper hydroxide during 60 min, then it was filtered and the residual content of copper ions in water was determined, and the iodometric determination was used (Brescia et al. 2012). The efficiency (Z) of copper ions removal was calculated by the formula:

$$Z = \frac{C_0 - C_f}{C_0} \cdot 100, \%$$

where: C_0 – initial concentration, mg/dm³;
 C_f – final concentration, mg/dm³.

Water treatment was carried out according to a statistical 22-factorial design, which is shown in Table 1.

The variables studied were initial concentration of copper ions (X_1) and reagent consumption (X_2). The model of the process can be described by a second-order polynomial:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_1X_2 + b_4X_{12} + b_5X_{22}$$

where: Y is a response factor (efficiency of copper ions removal, %);

b_0 – $b_{1,2,3,4,5}$ are regression coefficients.

The variance analysis was carried out with MINITAB 17 software and the response was constructed in MATLAB software. All experiments were performed three times and the average value is given. The study was performed at 20–25°C.

Utilization of sludge in the composition of cement

Reagent water purification produced a large amount of sludge, which was subject to

dehydration and drying. As a result, Cu(OH)₂ in a solid powdered form was obtained and utilized as chemical additives in the composition of cement.

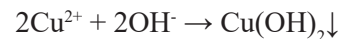
The precipitates were introduced into the composition of the cement in the amount of 0.5–1.5 wt.% by co-mixing the components in a laboratory ball mill for 10 minutes. Such properties of cement composites as normal density, hardening time, the compressive strength and water separation coefficient were determined.

RESULTS AND DISCUSSION

Study of the effect of reagent consumption on copper ions precipitation

During the water treatment with reagent methods, the contaminants are separated from the solution in the form of precipitates, which are then filtered or centrifuged. After that, the purified solution can be discharged or reused in the technological processes.

Lime was chosen as the reagent for water treatment due to economic reasons. When lime is added, copper ions precipitate in the form of hydroxides ($K_{sp}(Cu(OH)_2 \downarrow) = 5.6 \cdot 10^{-20}$. Solubility = $2.7 \cdot 10^{-6}$ mol/dm³ (0.17 mg Cu/dm³):



The application of an alkaline reagent raises the pH, which reduces the solubility of copper ions. When the pH increases from 8.5 to 10.0, copper is removed more efficiently in the form of hydroxides. The results of the research at different initial Cu²⁺ concentration in solution and lime consumption are shown in Table 2.

As can be seen from Table 2, the lime consumption has a significant impact on copper removal efficiency. The increase in the efficiency of copper ions removal from the aqueous solution with increasing consumption of the reagent is associated with an increase in pH, resulting in the formation and precipitation of copper hydroxide. The view of the second-order model of normalized variables for factors X1 and X2

Table 1. 22-factorial design for copper ions precipitation

Factor	Levels		
	(-1)	(1)	(0)
Initial concentration of copper ions, mg/dm ³	2	100	51
Reagent consumption, mg-eq/dm ³	5.4	10.0	7.7

Table 2. Effect of process parameters on Cu²⁺ removal efficiency

X1	2	2	2	100	100	100	51
X2	5.4	7.7	10.0	5.4	7.7	10	7.7
Y	99.9	99.9	99.9	46.4	73.2	99.9	92.6

with statistically significant coefficients is the following:

$$y = 101.51 - 0.9296 \cdot X_1 - 0.16458 \cdot X_2 - 0.0025198 \cdot X_1^2 + 0.11868 \cdot X_1 \cdot X_2 - 0.0047259 \cdot X_2^2$$

The model fitted very well with the experimental data as R²-value is close to 1. 3D-surface response was plotted to investigate the interactions of main effects on efficiency of copper removal in detail (Fig. 1).

The greatest efficiency of copper removal was achieved during the application of lime in the quantity of 10 mg-eq per 1 dm³ of water solution with copper ions concentration 100 mg/dm³. In Table 3, the optimal values of lime consumption for water treatment with different initial concentrations of copper ions as well as the cost of the technology are shown.

The process of precipitation of copper in the form of hydroxide has many advantages such as simple implementation technique, low cost, pH is easy to control. However, large volumes of sludge are formed during the treatment, which must be processed.

Utilization of sludge in the composition of cement

Nowadays, from an ecological point of view, it is important to solve the problem of utilization or practical application in various solid wastes in different industries, as well as to increase the recycling and reuse of illiquid wastes (Skiba et al. 2018). Therefore, a method of efficient utilization of the formed precipitate in the composition of cements was developed (Martínez-Cruz et al. 2021).

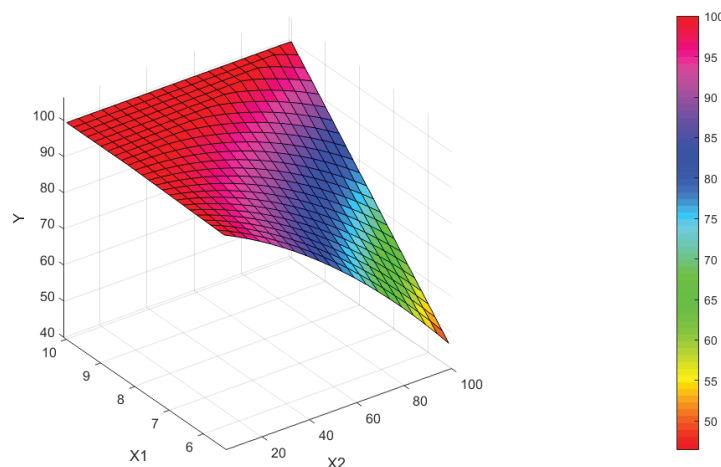


Figure 1. 3D-surface response for the efficiency of copper removal

Table 3. Optimal values of lime consumption for water treatment with different initial concentrations of copper ions

Concentration of Cu ²⁺ , mg/dm ³	Lime consumption, mg/dm ³	Cost of the technology for water treatment, \$/m ³
1.00	4.30	41.14
2.00	4.80	46.28
5.00	5.40	51.42
10.00	6.50	61.71
20.00	7.60	72.00
50.00	9.20	87.42
100.00	10.00	95.14

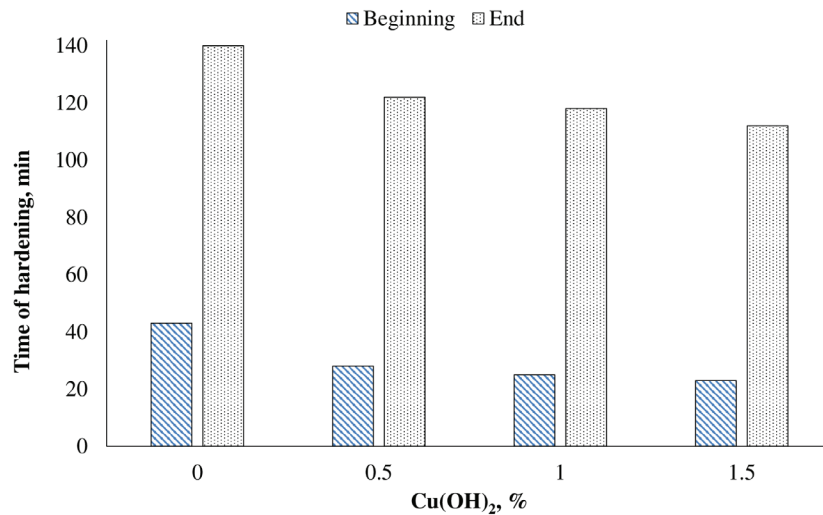


Figure 2. Hardening time properties of cement with Cu(OH)₂ formed during water treatment

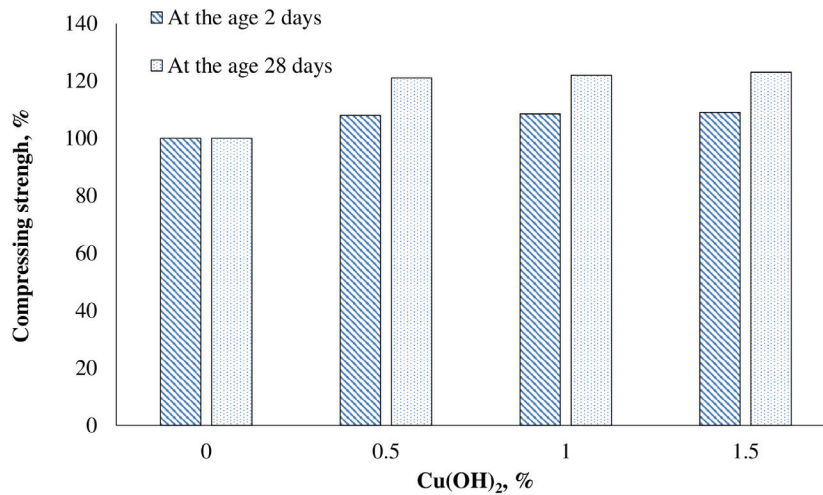


Figure 3. Compressive strength properties of cement with Cu(OH)₂ formed during water treatment

According to the State standards of Ukraine, not more than 5 wt.% of additives can be used in the composition of cement. The effect of copper hydroxide formed during water purification on the physicochemical properties of cement is shown in Figures 2 and 3. The precipitate was added into the cement in the amount of 0.5, 1.0 and 1.5 wt.%.

Copper hydroxide significantly accelerates hardening. According to the results, copper hydroxide increases the strength of the cement samples after 2 days of hardening by 8% and after 28 days of hardening by 27%. The normal density of cement and cement with precipitated copper hydroxide was 30%. The addition of the basic salt does not affect this value. Similarly, no effect was observed on the water removal from the cement slurry. Therefore, the precipitate formed

during the water purification, which consists of hydroxides, can be recommended for use in the composition of cement as chemical additives that regulate hardening and accelerate the hardening of cement. The developed scheme of complex technology of purification of aqueous solutions from copper ions is presented in Figure 4.

After reagent purification, if necessary, it is possible to apply a subsequent purification on the nanofiltration membrane, which increases the degree of the removal of Cu²⁺ ions to 99.6% (Trus et al. 2020).

CONCLUSIONS

1. Copper hydroxide, which is formed during the purification of water, was utilized as an additive

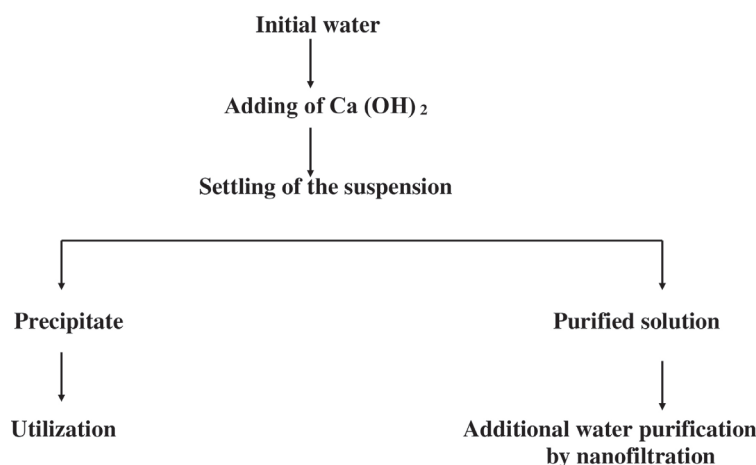


Figure 4. Scheme of complex technology of aqueous solutions purification from copper ions

in cement of I-500 type. The sludge was added into the cement and their effect was evaluated according to the indicators of normal density, hardening time, strength and water removal according to the methods for small samples.

2. The precipitates based on hydroxides increase the strength of cement and do not affect water removal, so they are suitable for the use in cements as chemical additives.
3. The economically feasible technology of complex purification of aqueous solutions from copper ions using reagent methods with utilization of the formed precipitates as a part of building materials was developed.

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