

Reagent precipitation of copper ions from wastewater of machine-building factories

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Abstract. The article presents the results of reagent removal of copper ions from wastewater of machine-building factories. The urgency of the study is conditioned by the widening of the range of effective reagents through the implementation of industrial waste. The investigation covers mineralogical and fractional composition of chalk enrichment waste. In the work, the conditions of thermal activation of chalk enrichment waste used for reagent removal of copper ions from wastewater were elaborated. It was shown that the thermal activation of waste facilitates the increased treatment efficacy up to the set sanitation, hygiene and technological standards.

1. Introduction.

The main source of copper in natural water is wastewater of chemical, metallurgical, machine-building and electroplating industries [1–4]. The reason of copper presence in wastewater is corrosion of copper pipelines and other facilities of a water supply system. The maximum allowable concentration of copper in sanitary and household water bodies is 0.1 mg/l (Limiting Harmful Index is general sanitary), while in fishery waters it is 0.001 mg/l. Excess copper has harmful effect on endotherms, causes acute poisoning of humans and animals, has a wide range of toxic effects with a variety of clinical signs [5].

Heavy metals from wastewater can be removed by a bunch of methods, of which the reagent treatment is most frequently used [6–12].

2. Materials and Methods.

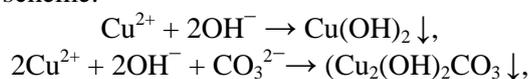
The object of study is model wastewater with copper ion concentration from 0.5 up to 1.5 g/l. Model wastewater was prepared by dissolving a sample of copper sulphate pentahydrate in distilled water. The other object of study was the oversize fraction of chalk particles larger than 2 mm with the wetness of 34.7%.

The total content of active calcium and magnesium (CaO+MgO) in water extract was determined by titrimetry by 1N solution of hydrochloric acid. The content of active magnesium oxide (MgO) was determined by trilonometry. The mass concentration of copper was determined by colorimetry with sodium dimethylthiocarbamate. The XRD analysis of chalk waste ground in agate mortar and compacted into a tablet was performed on the DRON-3 diffractometer with X-ray tube BSV-27(Cu). The fractional composition was determined by wavelength X-ray fluorescence analysis on the ARL 9900 spectrometer.



3. Results and Discussion

According to literature sources, the reagent precipitation of copper ions as hydroxide or hydroxycarbonate follows the scheme:



The solubility product of copper hydroxide is $8.3 \cdot 10^{-20}$, while that of basic copper carbonate is $1.7 \cdot 10^{-34}$. In this connection, copper ions are reasonable to be precipitated as basic carbonate. Thus, the solution of the neutralizing reagent must contain both hydroxide ions (OH^-) and carbonate (CO_3^{2-}) ions.

The reagent feedstock is the waste of chalk enrichment with the fractional composition presented in Table 1.

Table 1. Waste fractional composition

Waste component	CaO	SiO ₂	MgO	AlO	FeO	NaO
Content [%]	97	0.97	0.35	0.29	0.22	0.31

The implementation of the waste in the initial condition to remove copper ions from model solutions with the concentrations from 0.5 to 1.5 mg/dm³ allowed reaching the purification degree from 36 to 55%, which is insufficient regarding the sanitary and hygiene standards.

To increase the purification degree, the reagents were prepared by burning the chalk waste (thermal activation) at different temperatures from 600 to 900 °C. The choice of temperature interval is conditioned by the decomposition beginning temperature of CaCO₃ of 600 °C; however, the reaction is incomplete and slow. Total decomposition of CaCO₃ occurs at approximately 900 °C. The decomposition of MgCO₃ begins at 400 °C and complete decomposition starts from 710 °C.

Important components of chemical precipitation of copper ions are calcium and magnesium compounds. Each produced specimen after burning was analysed for the content of total active calcium and magnesium, and active calcium. The results are in Fig. 1. Evidently, the increase of chalk burning temperature facilitates increased total content of CaO+MgO, and active CaO. The maximum values are reached after burning chalk at 700–1000 °C.

Simultaneously, pH of the water extract was established for the specimens of thermally activated reagents since this indicator is an important factor of reagent precipitation of metal ions. According to literature, pH of copper ion precipitation beginning is 3.8; the end value is 6.02. The average copper precipitation pH is 5.3. According to Fig. 1, the required pH is reached when using reagents produced by burning at 700–900 °C.

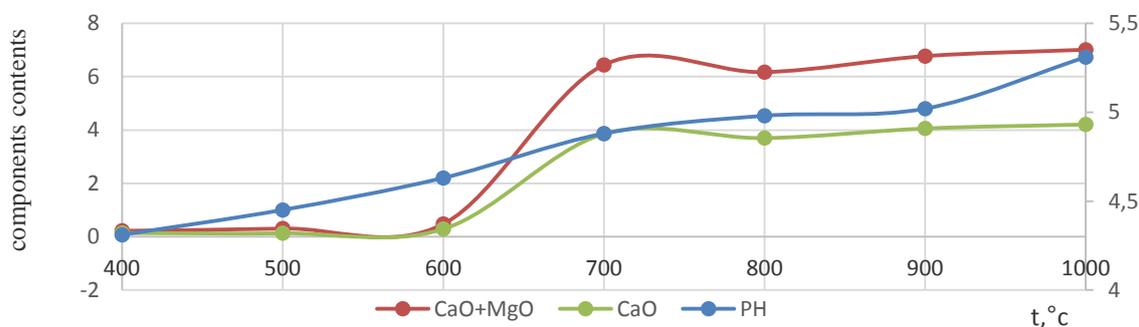


Figure 1. The dependence of total content of CaO+MgO, pH of medium and active calcium on chalk burning temperature

Figs. 2 and 3 present X-ray diagrams of unburnt chalk specimens and those burnt at 800 °C.

The comparative analysis of the diagrams in Figs. 2 and 3 shows that the intensity of diffraction maxima, which are characteristic for the following minerals: calcite CaCO_3 ($d, (\text{\AA}) = 3.043; 1.916; 1.879$); dolomite CaMgCO_3 ($d, (\text{\AA}) = 2.853; 2.290; 2.099$) and magnetite MgCO_3 ($d, (\text{\AA}) = 2.853; 1.629$), decreases. And at the same time, the intensity of diffraction maxima increases, which is characteristic for the following minerals: $\text{Ca}(\text{OH})_2$ ($d, (\text{\AA}) = 4.793; 2.63; 1.93; 1.79$) and $\text{Mg}(\text{OH})_2$ ($d, (\text{\AA}) = 4.77; 2.365; 1.79$).

Thus, the thermal treatment of chalk waste specimens allows obtaining the reagent containing at the same time carbonates and hydroxides of calcium and magnesium, which in its turn is a condition of effective precipitation of copper ions from the solution.

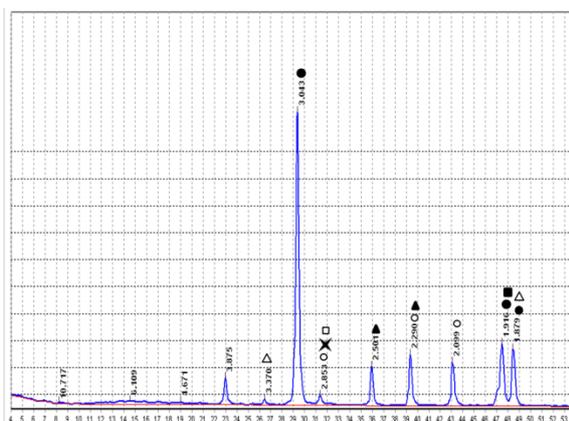


Figure 2. XRD analysis of chalk waste specimen

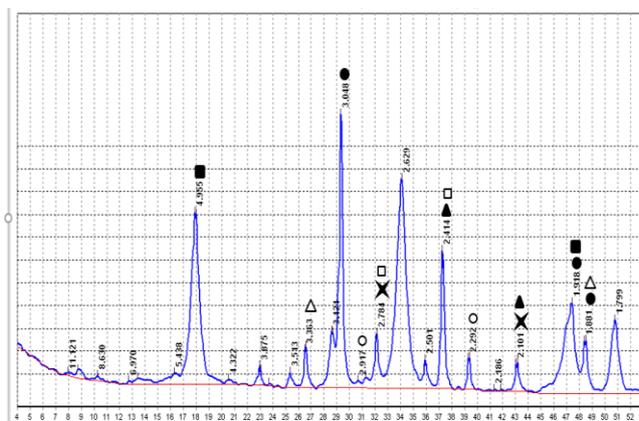
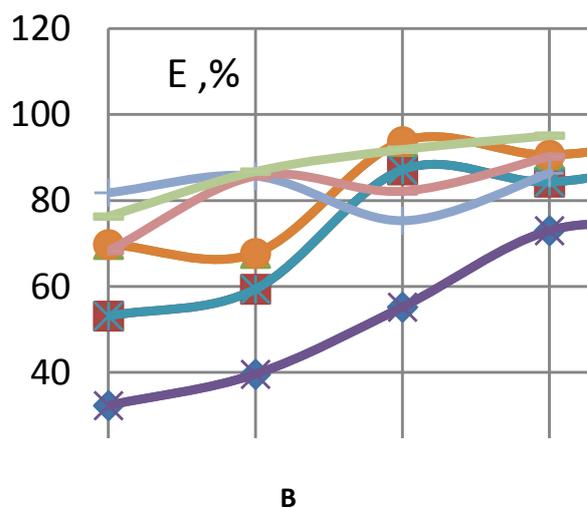
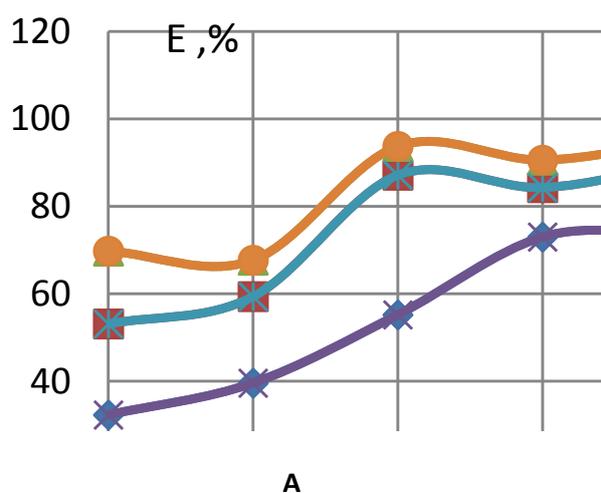
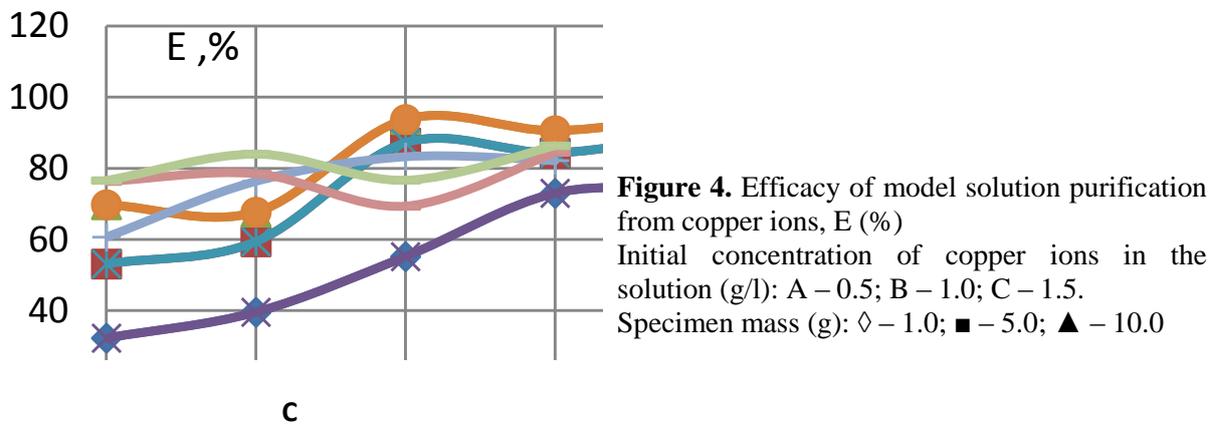


Figure 3. XRD analysis of the reagent burnt at $800 \text{ }^\circ\text{C}$

The testing was done with model solutions containing copper ions with the concentration from 0.5 to 1.5 g/dm^3 . The dependencies of purification efficacy on the mass of thermally activated reagents and initial concentrations of model solutions were obtained.





Obviously, the reagent mass increase from 1 up to 10 g per 100 ml of the treated solution facilitates the increase of a purification degree. The optimum burning temperature of chalk specimens to produce reagents varies from 700 to 900 °C. The application of reagents thermally activated at those temperatures for copper-containing wastewater treatment allows reaching the purification degree of 65–98%.

4. Conclusion.

Thus, the study results have shown that the thermal activation of chalk waste allows obtaining the reagent capable of effective precipitation of copper ions from treated solution and can be implemented for deep purification of industrial wastewater, including machine-building industry.

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