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Studies Regarding the Copper Ions Removal from Waste Waters

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Abstract: Waste waters resulted from industry usually contain heavy metals salts. During the neutralization process with sodium hydroxide and sodium carbonate these salts are transformed in compounds such as insoluble hydroxides or basic salts. The precipitation process represents one of the most used methods for the removal of heavy metals from waste waters. In the present paper are presented studies on the removal of copper ions from waste waters resulted from industry through precipitation, using 15% NaOH and 20% Na_2CO_3 solutions as precipitation agents. The studies were carried out on synthetic solutions containing copper in various concentrations (5, 10 and 15 g Cu^{2+}/L). Several aspects of the precipitation process were studied: the dependence of the pH of the reaction mass on the volume of precipitation agent, the evolution of the volume of suspensions in time and the dependence on the pH of the residual concentration of copper ions. The optimum pH value for the removal of cooper ions from the waste waters for both precipitation agents is 7. For all initial copper ions concentrations, pH = 7 assures residual concentrations smaller than the maximum value admitted by the legislation. The copper ions removal using the 20% Na_2CO_3 solutions was also studied on a pilot installation. Copper residual concentration decreased with installation functioning time; the installation went into constant conditions after ~300 minutes; a constant residual concentration of ~1.1 mg Cu^{2+}/L was reached.

Keywords: waste water, copper removal, precipitation method

1. Introduction

Waste waters resulted from industry usually contain heavy metals salts. During the neutralization process with sodium hydroxide and sodium carbonate these salts are transformed in compounds such as insoluble hydroxides or basic salts. The precipitation process represents one of the most used methods for the removal of heavy metals from waste waters.

The solubility of the precipitation products and therefore the removal degree of heavy metals from the waste water depends on the value of the pH, on the initial concentration of metallic ions in the solution, on the nature of precipitation agent and also on the nature and concentration of other chemical species which are present in the solution.

The most important physical and chemical phenomena which lead to the removal of heavy metals through precipitation are: hydrolysis, formation of the precipitate, flocculation and sedimentation. Due to the complex phenomena which take place at the precipitation of heavy metals, in the first stages a large number of various compounds, having an undefined stoichiometry, is formed. Some of them precipitate immediately as solid matter, and the others build up a colloidal solution. For the same reasons instead a crystallized product, an amorphous gelatinous mass is obtained.

The precipitation of metallic ions does not take place at a certain pH value, but in a wide pH range. The beginning and the end of the precipitation process are well marked on the titration curves [1-7].

In the present paper are presented studies on the removal of copper ions from waste waters resulted from industry through precipitation, using sodium hydroxide and sodium carbonate as precipitation agents.

2. Experimental

The studies were carried out on synthetic solutions with various concentrations of copper ions (5, 10 and 15 g Cu^{2+}/L). The composition of synthetic solutions is similar to the composition of waste waters resulted from industry. As precipitation agents a 15% NaOH solution and respectively a 20% Na_2CO_3 solution were used.

The neutralizations curves were registered by treating samples of 100 mL from the synthetic solutions with increasing quantities of the precipitation agent. The values of pH were measured up to 11, using a Denver 250 pH-meter.

After precipitation, the samples were filtered. The residual concentrations of copper ions in the solutions were determined by means of atomic absorption spectrometry, using a VARIAN SpectrAA 110 spectrophotometer.

The removal of copper ions from waste waters was also studied on a pilot installation.

3. Results and discussion

In order to determine the optimum conditions for the removal of copper ions from waste waters, it was studied: the dependence of the pH of the reaction mass on the volume of precipitation agent, the evolution of the volume of suspensions in time, the dependence on the pH of the residual concentration of copper ions in the solutions.

3.1. Dependence of the pH of the reaction mass on the volume of precipitation agent

Figures 1 and 2 present the experimental data regarding the dependence of the pH of the reaction mass on the volume of precipitation agent (neutralization curves).

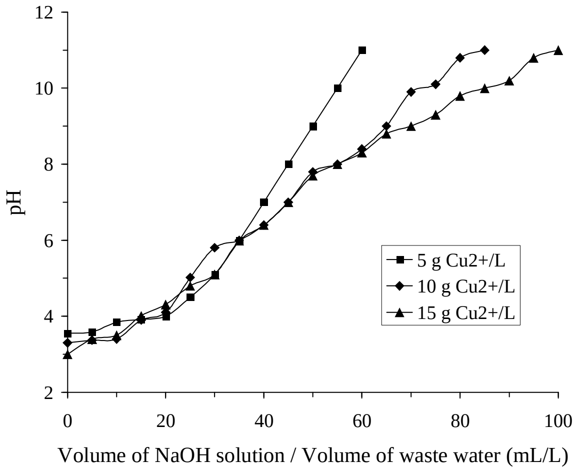

Figure 1. Dependence of the pH of the reaction mass on the volume of 15% NaOH solution

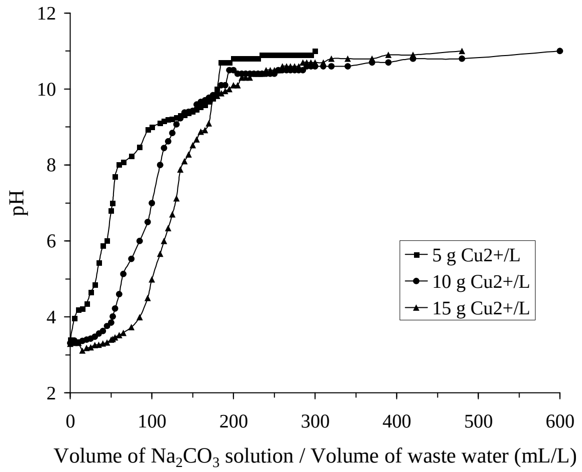

Figure 2. Dependence of the pH of the reaction mass on the volume of 20% Na_2CO_3 solution

From the neutralization curves one observes that the pH of the reaction mass depends on the volume of precipitation agent.

Figure 1 shows that at the neutralization with NaOH solution, for all initial concentrations, at the beginning the pH of the reaction mass slowly increases up to ~4; after that the increase is almost linear. One also notice that as copper ions initial concentration increases, the volume of NaOH solution required for the precipitation of copper and to reach the final pH = 11 increases.

Figure 2 shows that when the Na_2CO_3 solution was used, for the initial concentrations of copper ions of 10 and 15 g/L, the pH of the reaction mass increased slowly with the volume of precipitation agent up to ~4. After that, the increase was almost linear up to ~9, for all studied copper ions concentrations. As the volume of the precipitation agent further increases, the increase of the pH slows down until reaches the value ~11.

3.2. Evolution in time of the volume of suspensions

Figures 3-8 illustrate the evolution in time of the volume of suspensions resulted in the precipitation process at various values of the pH of the reaction mass (pH = 6, 7, 8, 9, 10 and 11).

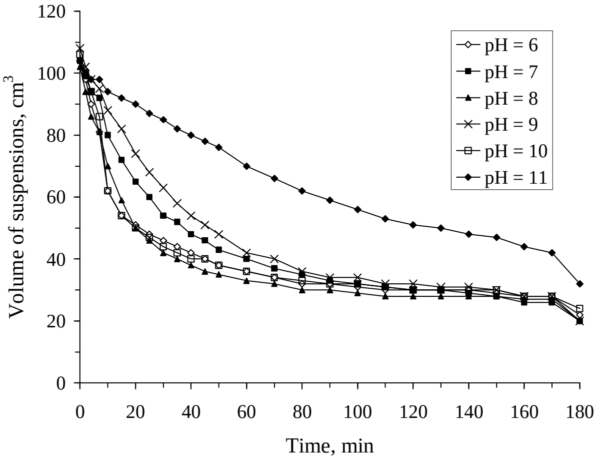

Figure 3. Evolution in time of the volume of suspensions, for the waste water containing 5 g Cu^{2+} /L, precipitation agent 15% NaOH solution

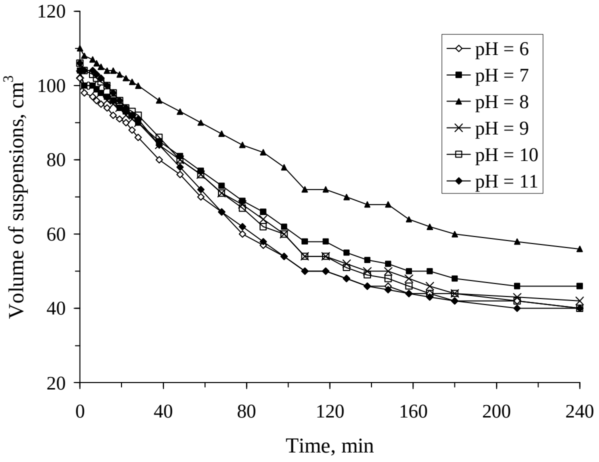

Figure 4. Evolution in time of the volume of suspensions, for the waste water containing 10 g Cu^{2+} /L, precipitation agent 15% NaOH solution

Figures 3-5 show that at the precipitation with NaOH solution, the volume of suspensions increases as the copper ions initial concentration increases. One may also notice that the sedimentation rate decreases with the increase of initial concentration: for the solution with an initial concentration of 5 g Cu^{2+}/L, the volume of suspensions remains constant after 50 minutes; for the solution containing 10 g Cu^{2+} /L, after 100 minutes and for the solution containing 15 g Cu^{2+} /L, after 200 minutes.

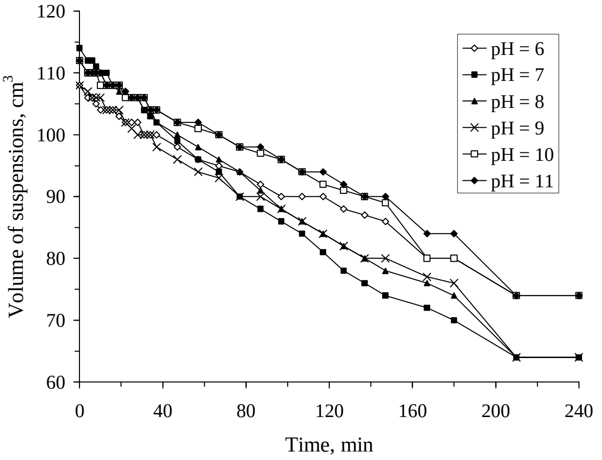

Figure 5. Evolution in time of the volume of suspensions, for the waste water containing 15 g Cu^{2+} /L, precipitation agent 15% NaOH solution

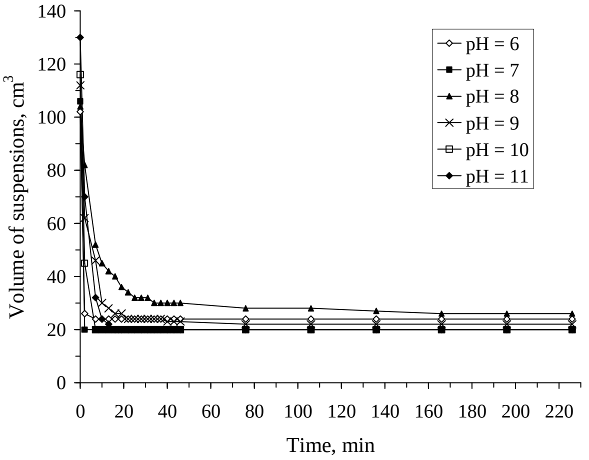

Figure 6. Evolution in time of the volume of suspensions, for the waste water containing 5 g Cu^{2+} /L, precipitation agent 20% Na_2CO_3 solution

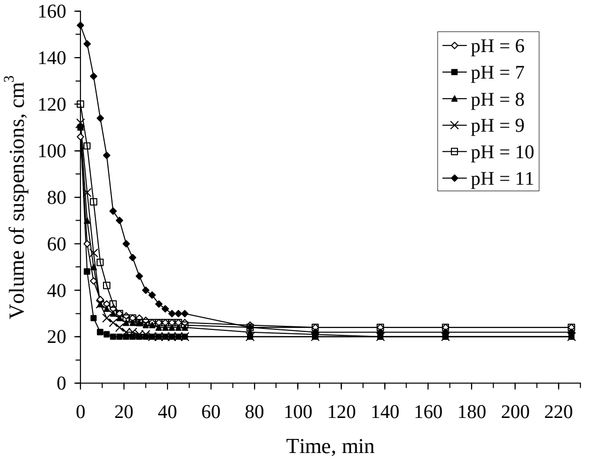

Figure 7. Evolution in time of the volume of suspensions, for the waste water containing 10 g Cu^{2+} /L, precipitation agent 20% Na_2CO_3 solution

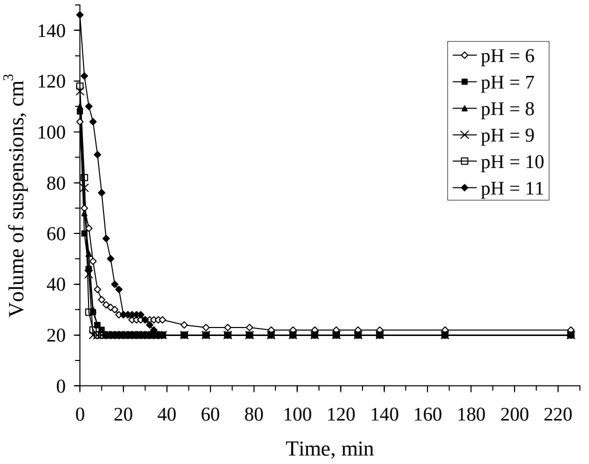

Figure 8. Evolution in time of the volume of suspensions, for the waste water containing 15 g Cu^{2+} /L, precipitation agent 20% Na_2CO_3 solution

From the experimental data presented in Figures 6-8, one may observe that when the 20% Na_2CO_3 solution is used as precipitation agent, the volume of suspensions resulted in the precipitation process does not depend on the initial concentration of copper ions in the solutions. The volume of suspensions remains constant after 50 minutes, a shorter period than the period required when using NaOH solution.

3.3. Dependence of copper ions residual concentration on the pH

The experimental results regarding the dependence of copper ions residual concentration on the pH are presented in Figures 9 and 10.

According to the experimental data obtained using the 15% NaOH solution, the residual concentration of copper ions decreases with the increase of pH and also with the increase of initial concentration.

When the 20% Na_2CO_3 solution is used as precipitation agent, the residual concentration of copper ions decreases for all initial concentration with the increase of pH up to pH = 7. In the pH range 8-11 the residual concentration increases, due to the fact that the precipitates are re-dissolving.

One may consider that the optimum value for the removal of copper ions from the waste waters is pH = 7, for both precipitation agents. One may also notice that when the NaOH solution is used as precipitation agent, the residual concentrations are smaller than those reached using the Na_2CO_3 solution. For both precipitation agents the residual concentrations are smaller than 1.1 mg/L, the maximum value admitted by the legislation for the disposal of waste waters into the sewerage system [8].

Although the NaOH solution is more efficient for the removal of copper ions, it is more expensive than the Na_2CO_3 solution. An other disadvantage is the fact that the precipitates formed using the NaOH solution are difficult to settle and filter. Since the precipitates obtained using the Na_2CO_3 solution are easy to settle, filter and wash, we recommend the use of this precipitation agent for the removal of copper ions from waste waters.

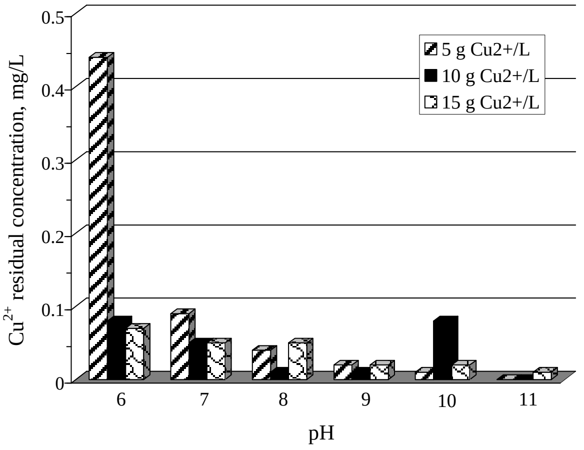

Figure 9. Dependence of copper ions residual concentration on the pH, using as precipitation agent the 15% NaOH solution

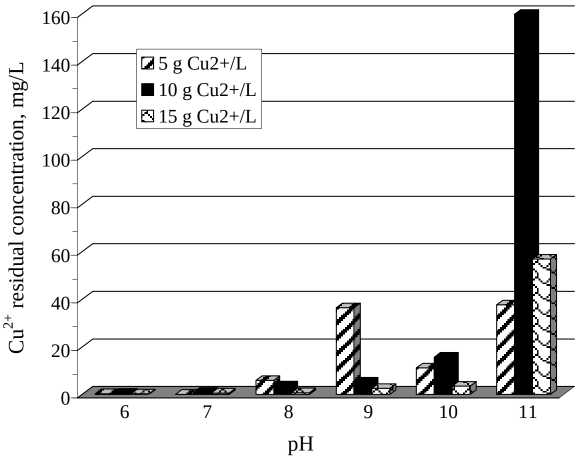

Figure 10. Dependence of copper ions residual concentration on the pH, using as precipitation agent the 20% Na_2CO_3 solution

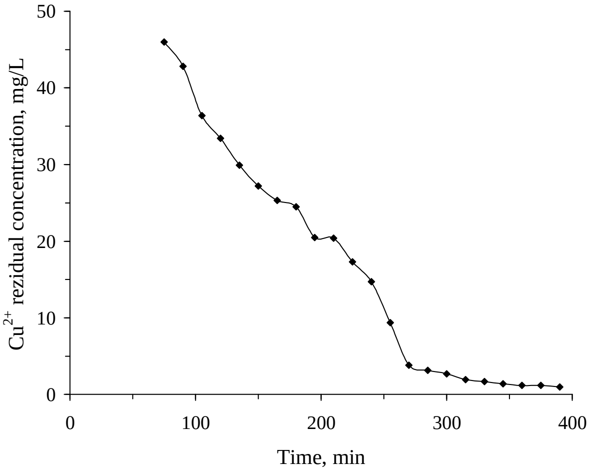

Figure 11. Evolution in time of copper residual concentration in the pilot installation

The removal of copper ions was also studied on a pilot installation; a solution containing 2.5 g Cu^{2+}/L with a flow of 3.2 L/h was used; the flow of 20% Na_2CO_3 solution was of 0.23 L/h; the pH of the reaction mass was maintained around the optimum value of 7, determined before. Figure 11 illustrates the evolution in time of copper residual concentration.

Figure 11 shows that copper residual concentration decreases with installation functioning time, up to ~200 minutes. In this moment, the pilot installation is going into constant conditions and a constant residual concentration of ~1.1 mg Cu^{2+}/L is reached.

4. Conclusions

The studies presented in the paper were carried out in order to determine the optimum conditions for copper ions removal from waste waters.

Synthetic solutions with various concentrations of copper ions (5, 10 and 15 g Cu^{2+}/L) were used. As precipitation agents a 15% NaOH solution and respectively a 20% Na_2CO_3 solution were used.

In order to find the optimum conditions, it was determined the dependence of copper ions residual concentration on pH, copper ions initial concentration and the nature of precipitation agent which was used.

The neutralization curves showed that the pH of the reaction mass depends on the volume of precipitation agent. As copper ions initial concentration increases, the volume of NaOH solution required for the precipitation of copper and to reach the final pH = 11 increases.

At the precipitation with NaOH solution, the volume of suspensions increases and the sedimentation rate decreases with the increase of initial concentration. When the 20% Na_2CO_3 solution was used as precipitation agent, the volume of suspensions resulted in the precipitation process did not depend on the initial concentration of copper ions in the solutions. The volume of suspensions remains constant after 50 minutes, a shorter period than the one required when using NaOH solution.

For both precipitation agents, copper ions residual concentration depends on the pH of the reaction mass. For both precipitation agents the optimum value is pH = 7, which assures residual concentrations smaller than the maximum value admitted by the legislation.

We recommend the use of 20% Na_2CO_3 solution as precipitation agent also because is less expensive than the NaOH solution. We also found that he precipitates obtained using the Na_2CO_3 solution are easier to settle, filter and wash.

At the removal of copper ions from waste water on the pilot installation, using 20% Na_2CO_3 solution as precipitation agent. Copper residual concentration decreases with installation functioning time; the installation went into constant conditions after ~300 minutes; a constant residual concentration of ~1.1 mg Cu^{2+}/L was reached.

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