

Removal of Cu(II) from Wastewaters Using Impregnated Resin

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Abstract: The paper presents studies on the removal of copper from wastewaters with high copper ions content resulting from galvanizing process. In the first step of the purification process, copper ions were precipitated using a 10 M NaOH solution as precipitation agent. By increasing the pH of the Cu(II) solutions up to 12, the residual concentration of copper ions reached the values required for the discharge in sewerage and in water resources. Taking into account that this pH value does not allow the discharge, the solution resulting from the precipitation process at pH 8 was submitted in the second step to an advanced treatment using as adsorbent material an Amberlite XAD-7 resin impregnated with di-2(ethyl-hexyl) phosphoric acid. To establish the conditions for the adsorption process was studied the influence of contact time and of adsorbent dosage on the efficiency of copper ions removal from the solution. The maximum efficiency of ~ 98% was reached after 90 min for an adsorbent dosage of 0.3g:25 mL. The residual concentration of copper ions was ~0.1 mg/L, value that allows the discharge in the sewerage and even in water resources.

Keywords: copper, wastewater, XAD-7, impregnated resin, adsorption, DEHPA

1. Introduction

Nowadays heavy metals are among the most important pollutants in source and treated water and are becoming a severe public health problem. Industrial and municipal wastewaters frequently contain metal ions. The heavy metal ions are stable and persistent environmental contaminants, since they cannot be degraded and destroyed [1-5]. Conventional chemical treatment methods including precipitation, solvent extraction, ion exchange, adsorption, electrochemical recovery, membrane separation and other techniques are frequently used for their removal from environmental matrices. These techniques may be ineffective or uneconomical because of several technical and environmental constraints [6].

The recovery of metal ions from dilute solutions using solvent impregnated resins (SIR) has been proposed as a technological alternative to solvent extraction techniques [7-10].

One of the most important properties of impregnated materials is their easy processing which allows their use in many applications [11, 12].

The studies presented in paper aim the removal of copper ions from wastewaters with high copper ions content resulting from galvanizing process, in view of discharge in sewerage or in water resources. In the first step of the purification process, copper ions were precipitated using a 10 M NaOH solution as precipitation agent. In the second step, the solution resulting from the precipitation process was submitted to an advanced treatment using as adsorbent material an Amberlite XAD-7 resin impregnated with di-2(ethyl-hexyl) phosphoric acid.

2. Experimental

The wastewater resulting from galvanizing process was analyzed in order to determine its copper ions content and its pH value.

In order to establish the conditions for copper removal through precipitation, samples of 100 mL wastewater were treated with 10 M NaOH solution until various final pH values of the suspensions were reached: 4, 6, 8, 10 and 12. The suspensions were filtered and the residual concentration of copper ions in the resulting solutions was determined by means of atomic absorption spectrometry, using a Varian SpectrAA-280 FS spectrophotometer. The pH value of the samples was measured using a Denver Instrument pH-meter.

In view of discharge, the solutions resulting from the precipitation process were submitted in the second step to an advanced treatment using as adsorbent material an Amberlite XAD-7 resin impregnated with di-2(ethyl-hexyl) phosphoric acid (DEHPA).

The conditions for the adsorption process were established by varying the adsorbent dosage (S:L ratio = 0.1 g:25 mL; 0.2:25 mL and 0.3:25 mL) and the contact time (15, 30, 45, 60, 90 and 120 min). The samples were shaken with 150 strokes/min using a Shaker Bath – Julabo SW23. After contact time elapsed, the samples were filtered and the residual concentration of copper ions in the resulting solutions was determined through atomic absorption spectrometry.

3. Results and Discussion

The analysis of the initial wastewater sample showed that it presented a high copper ions concentration (10 g/L) and a pH value of 1.7. These results show that the wastewater cannot be discharged in water resources or in sewerage. In order to reach the discharge conditions this wastewater should be submitted to a purification process.

3.1. Studies on the removal of Cu(II) through precipitation

The experimental data regarding the dependence of the pH of the suspensions on the volume of precipitation agent are presented in Fig. 1. In Fig. 2 and Fig. 3 is given the dependence of the residual concentration and the degree separation of Cu(II) on the final pH of the suspensions.

Figure 1 shows that as the volume of precipitation agent added to the wastewater sample increases up to 7 mL NaOH/100 mL sample, the pH of the reaction mass also increases slowly up to ~7. For volumes of precipitation agent between 7 and 9 mL/100 mL sample, the pH value increases rapidly up to ~11. For volumes of precipitation agent between 9 and 12 mL/100 mL sample, the pH value remains practically unchanged.

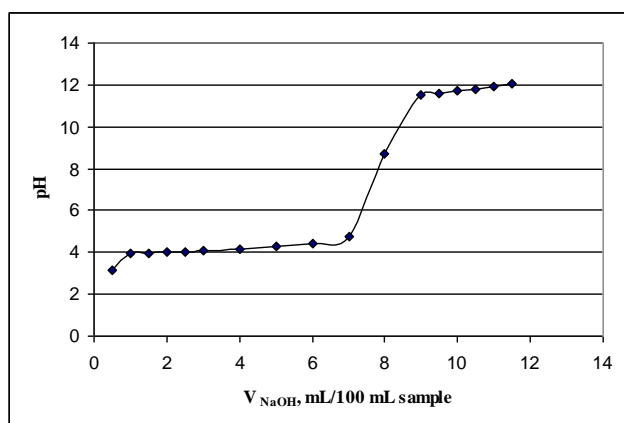


Figure 1. Dependence of pH of the suspension on the volume of precipitation agent

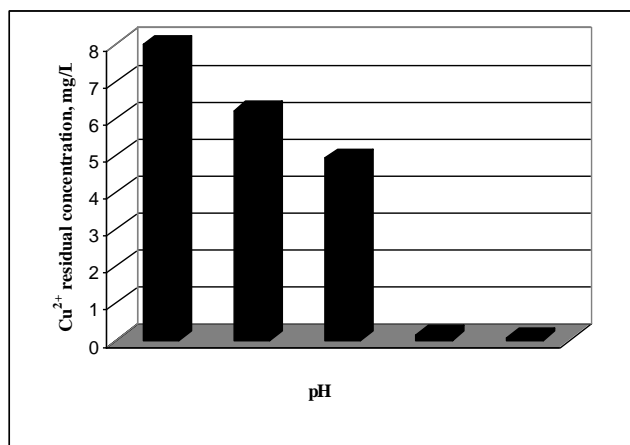


Figure 2. Dependence of Cu(II) residual concentration on final pH value

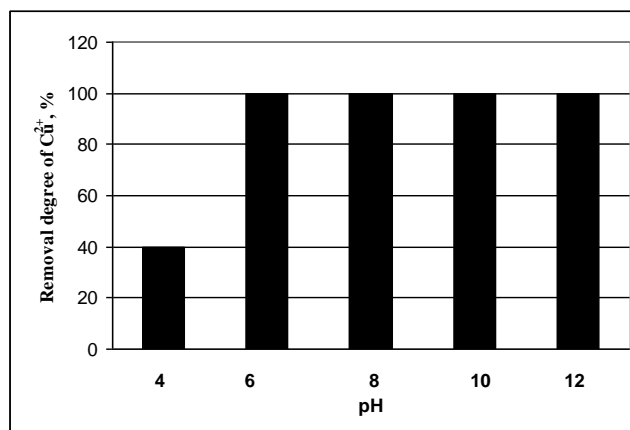


Figure 3. Dependence of removal degree of Cu(II) on final pH value

From data presented in Fig. 2 and Fig. 3 one may notice that the residual concentration of Cu(II) decreases and the removal degree of Cu(II) increases as the final pH of the suspensions increases. At pH 12 the residual concentration of copper ions was of 0.07 mg/L, which is smaller than the maximum permitted values by the Romanian legislation for the discharge in the sewerage (0.2 mg Cu²⁺/L) and close to the value for the discharge in water resources (0.1 mg Cu²⁺/L). Even if the residual concentration reached at pH 12 was under the maximum permitted values, this pH value does not allow the discharge. The same legislation specifies that the pH of the discharged water should be in the range 6.5 – 9. In the sample treated at pH 8 the residual Cu(II) concentration was ~5 mg/L, much higher than the permitted values. In view of discharge, the subsequent studies aimed the advanced removal of copper ions from this solution through adsorption on DEHPA-impregnated XAD-7 resin.

3.2. Studies on the removal of Cu(II) through adsorption on DEHPA-impregnated XAD-7 resin

Figure 4 illustrates the influence of contact time between the Cu(II) solution and the adsorbent material on the efficiency of the adsorption process, for various adsorbent dosages.

The efficiency of the adsorption process (the removal degree of copper ions from the solution) was calculated using the following equation:

$$\eta = \frac{C_i - C_{res}}{C_i} 100 \quad (1)$$

where C_i and C_{res} are the initial and the residual concentrations of Cu(II), respectively.

Experimental data presented in Fig. 4 show that the efficiency of the adsorption process increases as the contact time increases up to 90 min, for all adsorbent dosages. As contact time further increases, the efficiency remains the same. The maximum efficiency of ~99% was reached for all adsorbent dosage. In this situation, the residual concentration of copper ions was ~0.1 mg/L, value which allows the discharge in the sewerage and even in water resources.

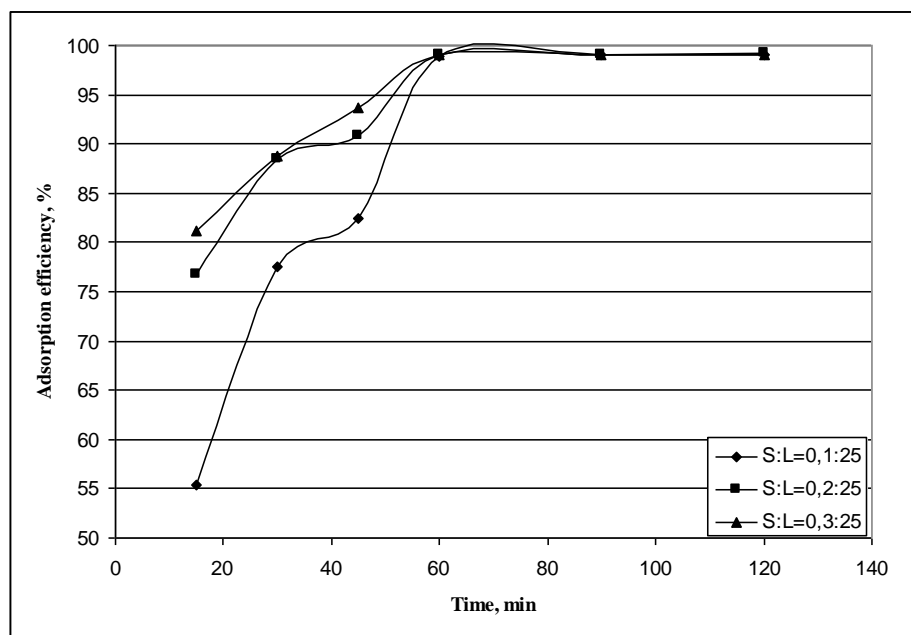


Figure 4. Dependence on the contact time of the efficiency of Cu(II) adsorption on XAD7-DEHPA, for various adsorbent dosages

4. Conclusions

The paper presents studies on the removal of copper from wastewaters with high copper ions content resulting from galvanizing process, in view of discharge in sewerage or in water resources.

In the first step of the purification process, copper ions were precipitated using a 10 M NaOH solution as precipitation agent. The wastewater samples were treated with the precipitation agent until various final pH values of the suspensions were reached: 4, 6, 8, 10 and 12. In the solution treated at pH 12, residual concentration of copper ions reached the values required for the discharge in sewerage and in water resources, but this pH value does not allow the discharge.

In view of discharge, the solution resulting from the precipitation process at pH 8 and containing 5 mg Cu²⁺/L was submitted in the second step to an advanced treatment using as adsorbent material an Amberlite XAD-7 resin impregnated with di-2(ethyl-hexyl) phosphoric acid. To establish the conditions for the adsorption process was studied the influence of contact time (15, 30, 45, 60, 90 and 120min) and of adsorbent dosage (S:L ratio = 0.1 g:25 mL; 0.2:25mL and 0.3:25mL) on the efficiency of copper ions removal from the solution. The maximum efficiency of ~ 99% was reached after 90 min for all adsorbent dosage. The residual concentration of copper ions was ~0.1 mg/L, value that allows the discharge in the sewerage and even in water resources.

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