STUDIES ON THE PURIFICATION OF WASTEWATERS WITH HIGH NICKEL IONS CONTENT

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ABSTRACT
The paper presents studies on the removal of nickel from wastewaters with high nickel ions content resulting from galvanizing process. In the first step of the purification process, nickel ions were precipitated using a 10 M NaOH solution as precipitation agent. By increasing the pH of the Ni^{2+} solutions up to 11, the residual concentration of nickel 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 9 was submitted in the second step to an advanced treatment using as adsorbent material an Amberlite XAD-4 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 nickel ions removal from the solution. The maximum efficiency of ~ 94% was reached after 90 min for an adsorbent dosage of 0.3 g:25 mL. The residual concentration of nickel ions was ~0.5 mg/L, value that allows the discharge in the sewerage and even in water resources.

KEY WORDS: nickel, wastewater, XAD-4, impregnated resin, adsorption, DEHPA

INRODUCTION

Nickel is widespread in soil and plants. Nickel ore is mainly found in the form of sulphides, silicates and arsenide. Among the most toxic nickel compounds is nickel-carbonyl, which is a colorless liquid with a smell of soot and high volatility. This compound is used in industry to produce nickel alloys and some special steels resistant to corrosion and high temperatures; in nickel-plate baths; in the operations of metallization of contacts in electrical circuits. Nickel-carbonyl is also used to extract pure metal from ore and as catalyst in the plastics industry [1-6].
The rapid development of leading industries generated a huge demand for new materials with controlled properties. Of great importance in materials chemistry is getting some smart materials such as materials that react to environmental changes, because they open the way for new technologies. One of the most important properties of functionalized / impregnated materials is their easy processing which allows their use in many applications [7, 8].
The studies presented in paper aim the removal of nickel ions from wastewaters with high nickel ions content resulting from galvanizing process, in view of discharge in sewerage or in water resources. In the first step of the purification process, nickel 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-4 resin impregnated with di-2(ethyl-hexyl) phosphoric acid.

MATERIALS and METHODS

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

In order to establish the conditions for nickel 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: 6, 7, 8, 9, 10, 11 and 12. The suspensions were filtered and the residual concentration of nickel 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-4 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 and 0.3:25) and the contact time (15, 60, 90, 120 and 240 min). The samples were shaken with 150 strokes/min using a Shaker Bath – Kutesz Tip 609/A (Hungary). After contact time elapsed, the samples were filtered and the residual concentration of nickel ions in the resulting solutions was determined through atomic absorption spectrometry.

RESULTS

The analysis of the initial wastewater sample showed that it presented a high nickel ions concentration (43.6 g/L) and a pH value of 4.63. 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.

1. Studies on the removal of Ni^{2+} 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 is given the dependence of the residual concentration of Ni^{2+} on the final pH of the suspensions.

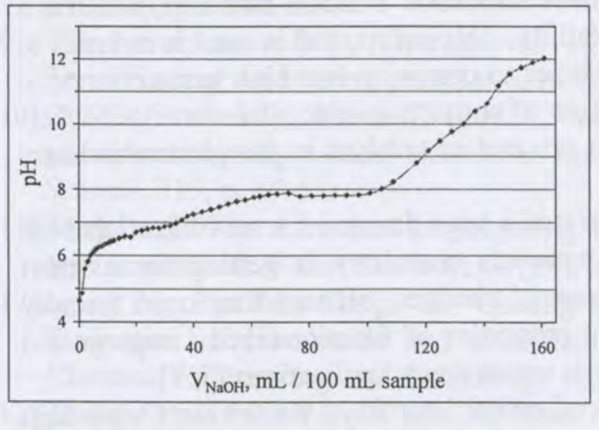

Fig. 1. Dependence of pH of the suspension on the volume of precipitation agent

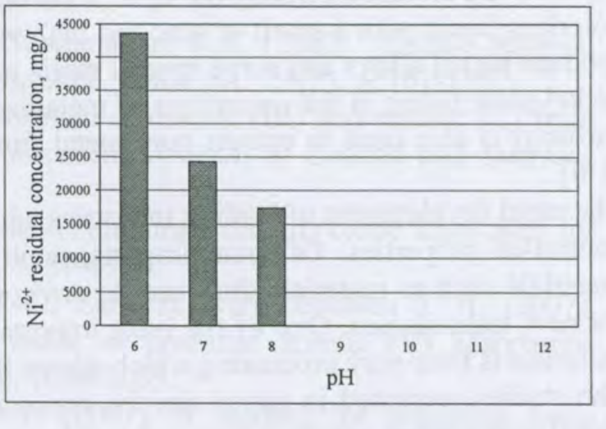

Fig. 2. Dependence of Ni^{2+} residual concentration on final pH value

Fig. 1. shows that as the volume of precipitation agent added to the wastewater sample increases up to 75 mL NaOH/100 mL sample, the pH of the reaction mass also increases up to ~8. For volumes of precipitation agent between 75 and 100 mL/100 mL sample, the pH value remains practically unchanged. As the volume of precipitation agent further increases, the pH of the suspensions increases also up to 12.

From data presented in Fig. 2 one may notice that the residual concentration of Ni^{2+} decreases as the final pH of the suspensions increases. At pH 11 the residual concentration of nickel ions was of 0.57 mg/L, which is smaller than the maximum permitted values by the Romanian legislation for the discharge in the sewerage (1 mg Ni^{2+}/L) and close to the value for the discharge in water resources (0.5 mg Ni^{2+}/L). Even if the residual concentration reached at pH 11 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 9 the residual Ni^{2+} concentration was ~10 mg/L, much higher than the permitted values. In view of discharge, the subsequent studies aimed the advanced removal of nickel ions from this solution through adsorption on DEHPA-impregnated XAD-4 resin.

2. Studies on the removal of Ni^{2+} through adsorption on DEHPA-impregnated XAD-4 resin

Fig. 3 illustrates the influence of contact time between the Ni^{2+} 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 nickel ions from the solution) was calculated using the following equation:

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

where C_i and C_{res} are the initial and the residual concentrations of Ni^{2+}, respectively.

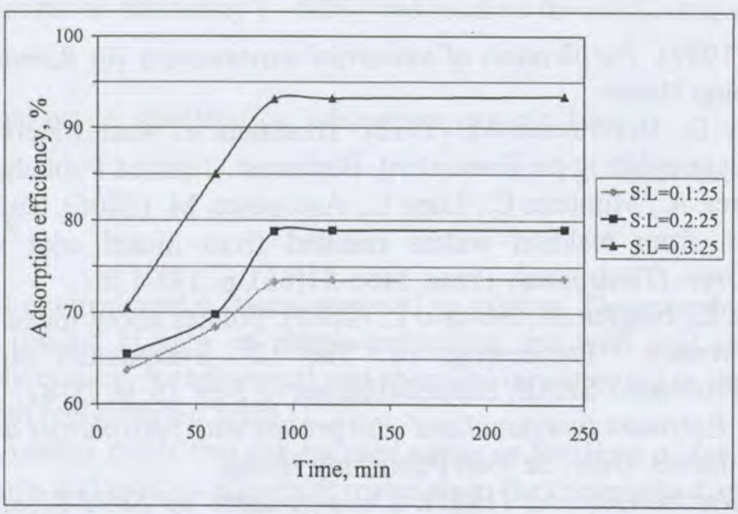

Fig. 3. Dependence on the contact time of the efficiency of Ni^{2+} adsorption on DEHPA-XAD-4, for various adsorbent dosages

Experimental data presented in Fig. 3 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 ~ 94% was reached for an adsorbent dosage of 0.3:25. In this situation, the residual concentration of nickel ions was ~0.5 mg/L, value which allows the discharge in the sewerage and even in water resources.

CONCLUSIONS

The paper presents studies on the removal of nickel from wastewaters with high nickel ions content resulting from galvanizing process, in view of discharge in sewerage or in water resources.
In the first step of the purification process, nickel 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: 6, 7, 8, 9, 10, 11 and 12. In the solution treated at pH 11, residual concentration of nickel 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 9 and containing 10 mg Ni^{2+}/L was submitted in the second step to an advanced treatment using as adsorbent material an Amberlite XAD-4 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, 60, 90, 120 and 240 min) and of adsorbent dosage (S:L ratio = 0.1 g:25 mL; 0.2:25 and 0.3:25) on the efficiency of nickel ions removal from the solution. The maximum efficiency of ~ 94% was reached after 90 min for an adsorbent dosage of 0.3 g:25 mL. The residual concentration of nickel ions was ~0.5 mg/L, value that allows the discharge in the sewerage and even in water resources.

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