

Čištění a recyklace odpadních vod z galvanizovny pro povrchovou úpravu automobilových součástí

Treatment and recycling of wastewater from a galvanizing plant for surface treatment automotive components

Dušek L., Šiška B., Korbel E.

Ústav environmentálního a chemického inženýrství FCHT, Univerzita Pardubice,

libor.dusek@upce.cz

Summary

The work summarizes the experimental results of the separation of zinc and nickel ions from real process and waste waters of the galvanic operation. It can be stated that alkaline precipitation with hydroxides is no longer a sufficient separation process for reliable compliance with emission limits for zinc and nickel, mainly due to the high salinity of the water and the amphoteric behavior of zinc. Sulfide precipitation is very effective, but it poses a safety risk due to the possible release of toxic sulfane. Organic precipitants based on dialkyldithiocarbamates (DDTC) appear to be effective, which are effective but require strict pH control. In addition, they pose a risk of toxic by-products. The optimal solution appears to be two-phase precipitation, where primary alkaline precipitation is followed by final purification using the trisodium salt of trimercapto-s-triazine (TMT), which is highly effective, does not require additional pH adjustment, and reliably ensures that the required limits of 0,15 mg/l Ni^{+2} and 1,5 mg/l Zn^{+2} are achieved. The costs of secondary precipitation ranged from 0,08-1,0 Euro/m³ and depended on the initial concentration of Ni^{+2} (0,2 -5 mg/l) and Zn^{+2} (2,0 - 20 mg/l)

Key words

Zinc and nickel precipitation process, alkaline, sulfide and complex dithiocarbamate precipitation, trisodium trimercapto-s-triazine and its insoluble metal complexes

We have already addressed the issue of zinc separation in industrial wastewater and process waters using various methods in previous publications [1-4]. The present contribution contains a summary of the findings obtained during laboratory verification of the reduction of zinc and nickel concentrations in selected process and waste streams of a galvanizing plant using precipitating agents.

A comparison of alkaline, sulfide and complex dithiocarbamate precipitation with the precipitation process using the trisodium salt of trimercapto-s-triazine (TMT) shows that the remediation limit (for zinc 1.5 mg/l and nickel 0.15 mg/l) cannot be achieved by simple alkaline precipitation. In the case of Ni^{2+} ions, this is excluded at $\text{pH} \approx 10.0$, and for Zn^{2+} ions, the limit can only be met in the case of low-saline waters. At pH above 10.5, it is theoretically possible to meet the remediation limit for nickel, but amphoteric zinc already forms water-soluble complexes, which preclude achieving the remediation limit. On the other hand, alkaline precipitation is cheap and, about the optimally selected pH value in the precipitation reactor, is also maximally effective. In contrast, sulfide precipitation meets the remediation limits for both metals with a margin but is relatively expensive and mainly there is a risk of

developing toxic and strongly smelling sulfane.

The application of dialkyldithiocarbamates (DDTC) in the form of Metalsorb is suitable for the precipitation of nickel and zinc, the precipitant is relatively selective, however, it is necessary to ensure precise dosing and complete pH control. Precipitation must take place at $\text{pH} \approx 6.5\text{--}7.0$. With regard to the price of the reagent, two-phase precipitation after cheap alkaline and pH adjustment is advantageous. Then it is possible to achieve concentrations of $c_{\text{Zn}} < 0.1 \text{ mg/l}$ and $c_{\text{Ni}} < 0.1 \text{ mg/l}$. However, in the case of pH above 9, DDTC decomposes into toxic carbon disulfide, which can then hydrolyze back into sulfane. The method requires very strict pH control. Precipitation using TMT appears to be optimal, especially when applied after the previous alkaline precipitation as a two-phase precipitation process. Then the high dose of TMT is greatly reduced, and therefore the operating costs for the expensive reagent. Moreover, the precipitation in the second phase takes place at the same pH as the previous alkaline precipitation, which is also the optimal pH to ensure maximum efficiency and selectivity of precipitation using TMT.

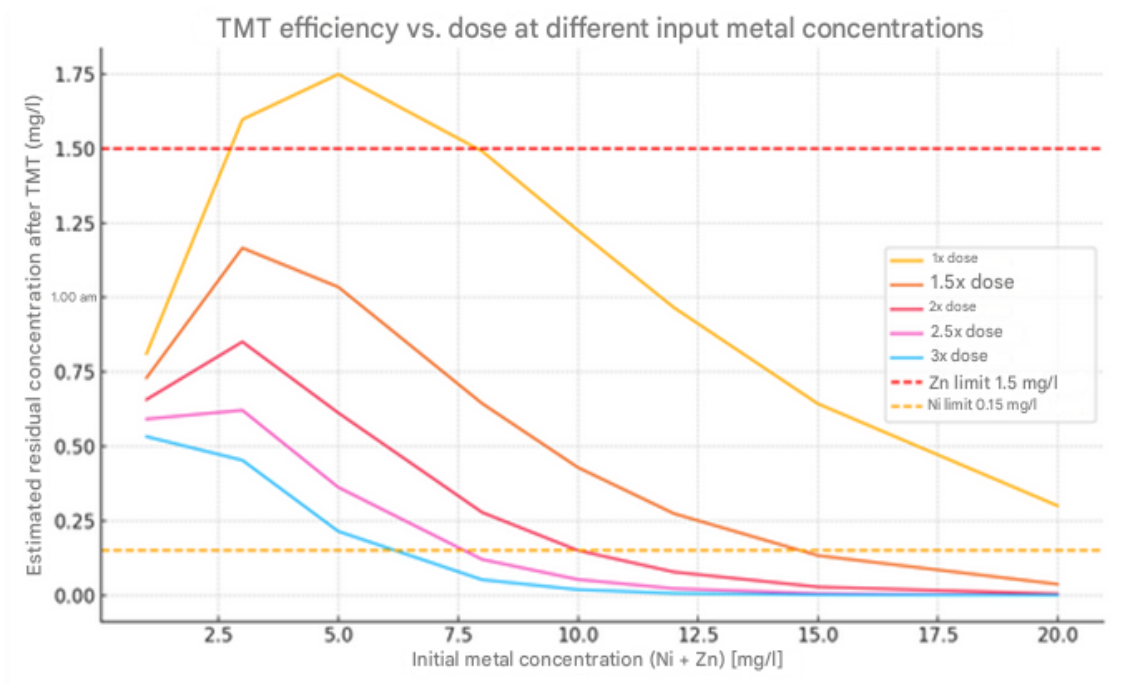


Figure 1. Efficiency of precipitation of Zn^{2+} and Ni^{2+} ions using the commercial TMT reagent depending on the multiple of the theoretical dose and the initial total molar concentration of both metals including the permitted emission limits of the galvanic operation.

Acknowledgements: This work was made possible by the financial support of the project SGS_2025_002 within the framework of the specific university research fund provided by the Ministry of Education, Youth and Sports of the Czech Republic.

References

- [1] Dušek L., Kočanová V., Novotný L. 37th International Conference on Modern Electrochemical Methods, 2017, pp.31-34..

- [2] Kočanová V., Cuhorka J., Dušek L., Mikulášek P., *Application of nanofiltration for removal of zinc from industrial wastewater*, Desalination and Water Treatment, 2017, 75, p. 342-347.
- [3] Dusek, L., Karásková, A., Kočanová V., Novotný L., Mikulášek P., *Galvanostatic removal of zinc using copper cathode from waste waters of a viscose production*, Journal of Electroanalytical Chemistry, 2020, 864, p. 11406.
- [4] Kuchtová G., Herink P., Chýlková J., Mikulášek P., Dušek L., *From lab-scale to pilot-scale treatment of real wastewater from the production of rayon fiber*, Process Safety and Environmental Protection, 2023, 171, 834-846.