NATURAL ZEOLITE CLINOPTILOLITE AND ITS SODIUM FORM IN TREATMENT OF ZINC-CONTAMINATED WATER – HOW EFFECTIVE ARE THEY?

Ivona Nuić, Sara Jurkić, Ivana Zelić, Marin Ugrina, Marina Trgo*
Faculty of Chemistry and Technology, University of Split, Ruđera Boškovića 35, 21000 Split, Croatia
*E-mail: ivona@ktf-split.hr

ABSTRACT

The present study provides a comparison of chemical precipitation and sorption using natural zeolite clinoptilolite and its modified homoionic form for zinc removal from simulated wastewaters. The main goal was to define the appropriate treatment method depending on initial zinc concentration. Therefore, the treatment of zinc-contaminated waters containing 100 and 500 mg Zn/L was firstly performed by sorption using natural zeolite (NZ) and its modified sodium form (Na-NZ). Afterwards, the treatment of zinc-contaminated waters was carried out by chemical precipitation using milk of lime suspension. Based on the obtained results, initial zinc concentration at which a particular method is effective in order to meet criterion for zinc discharge was defined.

Key words: natural zeolite, cost-effective wastewater treatment, sorption, chemical precipitation.

INTRODUCTION

There are many available methods for removal of toxic heavy metals from wastewaters such as chemical precipitation, ion exchange, adsorption, oxidation-reduction, flocculation, membrane techniques etc. Each of them has certain advantages and limitations. An appropriate method for wastewater treatment should be effective, but also low-cost, simple and easy applicable. The introduction of chemicals should be avoided or minimized to prevent secondary pollution. It is also desirable that applied method do not generate large amounts of hazardous waste. According to the literature, the most effective method for removal of high heavy metals concentrations is chemical precipitation. On the other hand, sorption is more suitable for removal of lower heavy metals concentrations, whereby avoiding rapid saturation of the sorbent material, and thus unprofitability [1-4]. However, questions arise - what means lower or high metal concentrations? Where is the line when one method becomes ineffective compared to other? In some studies, it is considered that the metal concentration higher than 1000 mg/L is adequate for the application of the chemical precipitation, while other studies reported lower concentrations, around 500 mg/L or even lower [4,5]. What is the threshold concentration of heavy metal for choosing sorption as an appropriate treatment method? Therefore, this research aimed to give the answers on aforementioned questions and offered optimal solution for treatment of zinc-contaminated water. Sorption of zinc was performed using low-cost environmentally friendly natural zeolite clinoptilolite, as well as its modified homoionic sodium form. Namely, homoionic form improves the zeolite sorption properties and increases its efficiency since sodium ions from zeolite structure are the easiest to exchange with surrounding metal cations compared to magnesium, calcium or potassium [6,7]. Chemical precipitation was carried out using milk of lime suspension as cost-effective precipitant to achieve pH approximately 9.5 which is, according to the literature the optimal for the removal of most heavy metal ions, including zinc [4,8]. Finally, the development of effective methods of wastewater treatment with the simultaneous use of economically and ecologically acceptable materials, is a priority in sustainable wastewater management.

EXPERIMENTAL

Materials

For purposes of this research the natural zeolite clinoptilolite (CEC=1.42 meq/g) from the Zlatokop mine in Serbia was used as low-cost sorbent for treatment of zinc-contaminated waters. The natural zeolite was washed, dried, crushed and then sieved into fractions of different sizes. The fraction of particle size 0.56-1.00 mm was chosen for this experiment. One part of prepared natural zeolite (NZ) was modified in order to increase its sorption properties. The modification to homoionic sodium form (Na-NZ) was done using sodium chloride solution (NaCl, 2 mol/L) according to the procedure described previously [9].

For chemical precipitation of zinc, the milk of lime suspension was used as low-cost precipitant. The milk of lime suspension with a concentration of 4 g/L was prepared by mixing the technical lime containing 94.3% of $Ca(OH)_2$ and tap water, resulting in final pH of 12.65.

The simulated wastewaters containing zinc in concentrations of 100 and 500 mg/L were prepared by dissolving zinc(II) nitrate hexahydrate salt, $Zn(NO_3)_2 \cdot 6H_2O$ in ultrapure water.

Sorption of zinc using natural zeolite samples

The zinc sorption from a simulated wastewaters containing 100 and 500 mg Zn/L was carried out by batch mode on a laboratory shaker (Heidolph Unimax 1010) at 230 rpm for 24 h at room temperature in solid/liquid ratio 1/100, using zeolite samples NZ and Na-NZ. After contact time of 24 h, the suspensions were filtered and the residual equilibrium zinc concentrations were determined by means of atomic absorption spectrophotometry, AAS (PinAAcle 900F).

Chemical precipitation of zinc using milk of lime suspension

The chemical precipitation of zinc in the form of zinc hydroxide, $Zn(OH)_2$, was performed in two stirred (Heidolph RZR 2041) reaction tanks. Zinc precipitation was initiated by adding the milk of lime suspension in small portions to the zinc-contaminated wastewaters containing 100 and 500 mg Zn/L until reaching the pH value of 9.5. Then, both suspensions were filtered and the residual zinc concentration in the filtrates were determined using AAS.

RESULTS AND DISCUSSION

The results of residual zinc concentrations ($c_{residual}$) after treatment of zinc-contaminated wastewaters by sorption and chemical precipitation are presented in Figure 1. Based on the residual zinc concentrations, the removal efficiency of zinc by sorption and chemical precipitation was calculated according to the equation:

$$\alpha = [(c_{initial} - c_{residual})/c_{initial}] \cdot 100 \qquad (1)$$

where α is removal efficiency (%), $c_{initial}$ are the initial zinc concentrations (mg/L) in simulated wastewaters, while $c_{residual}$ are residual zinc concentrations (mg/L) after sorption or chemical precipitation. Calculated removal efficiencies are presented in Figure 2.

According to the results in Figure 1 it can be observed that sorption of zinc onto NZ and Na-NZ resulted in very high residual concentrations (51.5 and 3.36 mg/L for lower initial zinc concentration, while 353.0 and 193.2 mg/L for higher initial zinc concentration). These values are considerably above the maximum prescribed value of 2 mg/L for zinc discharge into the surface waters or into the sewage system [10]. However, Na-NZ showed significantly better sorption properties compared to the NZ [7], for both initial zinc concentrations, especially for the lower one. Residual concentration reduced almost 30 times compared to the initial one and was very close to the discharge limit. These results justifying eco-friendly and economically modification of natural zeolite using harmless sodium chloride. Still, for the examined experimental conditions, sorption cannot be recommended as appropriate single-step method for effective removal of zinc concentrations higher than 100 mg/L. Contrary, treatment of both zinc-contaminated waters containing 100 and 500 mg/L by chemical precipitation at pH=9.5 showed successful removal with the residual zinc concentrations (0.13 and 0.31 mg/L) in conformity with industrial discharge standards.

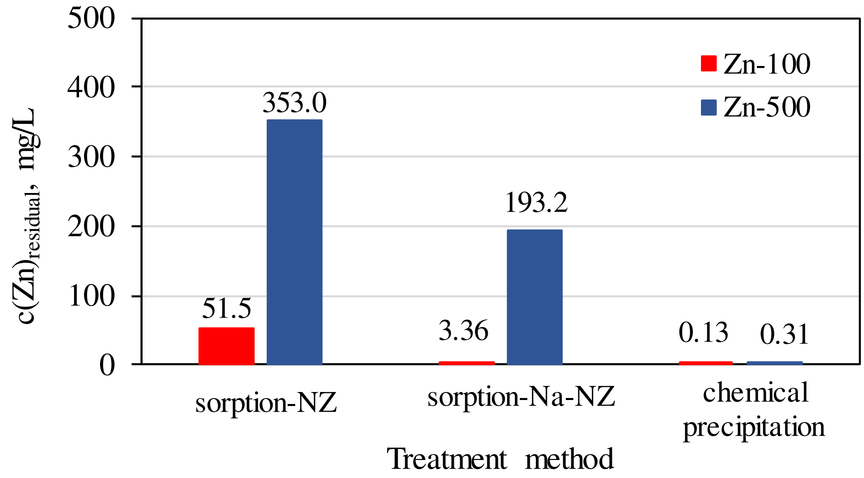

Figure 1. Residual zinc concentrations after treatment of zinc-contaminated waters by sorption on the NZ, Na-NZ and by chemical precipitation.

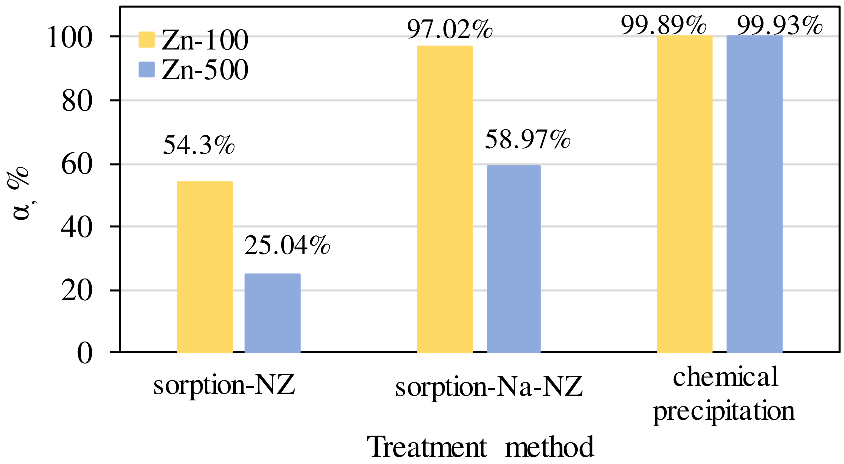

Figure 2. Efficiency of zinc removal by sorption and chemical precipitation.

According to the results in Figure 2, the efficiency of zinc removal by sorption onto NZ was 54.30% for lower initial zinc concentration, and 25.04% for higher initial zinc concentration, while onto Na-NZ values were higher, 97.02% and 58.97%, respectively. Also, sorption efficiency was higher for the lower zinc content, which was expected.

Efficiency of chemical precipitation was extremely high (99.89% and 99.93%), indicating the advantage of choosing this method compared to the sorption for examined initial zinc concentrations of 100 and 500 mg/L.

CONCLUSION

Removal of zinc below discharge limits by sorption onto natural zeolite and its homoionic sodium form from simulated wastewaters containing 100 and 500 mg Zn/L was not achieved, indicating single-step sorption as not suitable method for zinc content ≥ 100 mg/L, for examined experimental conditions. Chemical precipitation at pH=9.5 enabled successful removal of zinc from both simulated wastewaters, with residual concentrations below the discharge criterion of 2 mg/L, indicating the chemical precipitation as method of choice for zinc concentrations ≥100 mg/L. Nevertheless, for choosing the most appropriate method, future research should consider the amount of generated waste after wastewater treatment. The limitation of chemical precipitation and sorption is generation of sludge or zinc-saturated zeolite, which represent hazardous waste that must be disposed of properly. Since waste disposal represents an additional cost in wastewater treatment, it should be taken into account when choosing the optimal method of water treatment, thus respecting the principles of circular economy and sustainable development.

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