# APPLICATION OF THE YOON-NELSON MODEL AND THE REACTOR THEORY FOR PACKED BEDS ON ZINC UPTAKE ON CLINOPTILOLITE

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## ABSTRACT

The column method of zinc removal onto the 80 mm fixed bed depth of natural zeolite has been used. The experimental results for the breakthrough curve have been fitted to the Yoon-Nelson empirical kinetic model and excellent agreement has been observed. The modelled curve has been derived in order to define the mass transfer mechanism using the reactor theory for packed beds. It can be observed that up to the inflection point on the breakthrough curve the mass transfer through the aqueous phase governs the rate, while after the inflection point the diffusion through particles governs the overall rate. The time corresponding to the inflection increases proportionaly with the increase of bed depth. The change of bed depth does not affect the mass transfer mechanism through the bed. The results are compared with results for the system at the 40 mm zeolite bed depth.

Keywords: zeolite, zinc, Yoon-Nelson model, reactor theory for packed beds.

## INTRODUCTION

The use of natural zeolites as adsorbents and ion exchangers has been becoming an important alternative method for removal of heavy metals from wastewaters. The experimental performance in the column provides multiple repetitions of service and regeneration cycles, which provides for multiple use of the same zeolite sample. Based on the experimental results, it is possible to predict the behaviour of zeolite at defined experimental conditions. For this purpose several kinetic empirical models are indicated in literature and used for plotting of predicted breakthrough curves. This paper examines the application of the Yoon-Nelson model on experimental breakthrough curves in order to evaluate its possible use in prediction of the shape and position of breakthrough curves for some chosen experimental conditions [1-4]. The reactor theory for packed beds has been applied to the equation of the curve obtained by the Yoon-Nelson model and the description of mass transfer through the liquid phase and solid zeolite particles has been obtained [5].

## EXPERIMENTAL

The sample of natural zeolite (particle size 0.6-0.8 mm) originates from the Vranjska Banja deposit and contains >80% clinoptilolite. Experiments were performed in a glass column (the inner diameter of 12 mm) filled with the zeolite sample up to 80 mm. The solution of zinc ions with concentration of 1.083 mmol Zn/l passed through the bed with the flowrate of 1ml/min using the down-flow mode. During experiments, effluents were collected and concentrations of zinc were determined complexometrically. The results for the bed depth of 80 mm have been compared with previously obtained results for the system at the 40 mm zeolite bed depth [6,7].

## RESULTS AND DISCUSSION

*Modelling of the experimental breakthrough curve*. The experimental results of zinc removal from aqueous solutions are presented by the breakthrough curve in Figure 1. The experimental points in Figure 1 have been tested by following Yoon-Nelson empirical kinetic model [1]:

$$t = \tau + \frac{1}{k_{YN}} \ln \left(\frac{c}{c_o - c}\right) \qquad (1)$$

where:

$k_{YN}$ – the Yoon-Nelson rate constant, $h^{-1}$; t - time, h; $\tau$ - time when $c/c_o \approx 0.5$, h; c - concentration of Zn in the effluent, mmol/l; $c_o$ - initial concentration of Zn, mmol/l.

For a symmetrical breakthrough curve, the quantity of zinc bound at time $\tau$ equals half of the removal capacity, and is calculated as a function of initial concentration and flow rate:

$$q = \frac{c_o \cdot Q \cdot \tau}{m} \qquad (2)$$

where:

q - removal capacity, mmol/g; Q - flowrate, l/h; m - mass of zeolite fixed bed, g.

Equation (1) has been solved by nonliear regression analysis and the values of $\tau$, removal capacity q and the Yoon-Nelson rate constant $k_{YN}$ have been calculated. For chosen values of time t in Equation (1), using the calculated values of $\tau$ = 63.135 h, q = 0.695 mmol Zn/g zeolite and $k_{YN}$ = 0.251 $h^{-1}$, the modelled curve has been obtained and shown by line in Figure 1. The modelled curve shows excellent agreement with the experimental points, therefor the Yoon-Nelson model provides a mathematical correlation which describes experimental points.

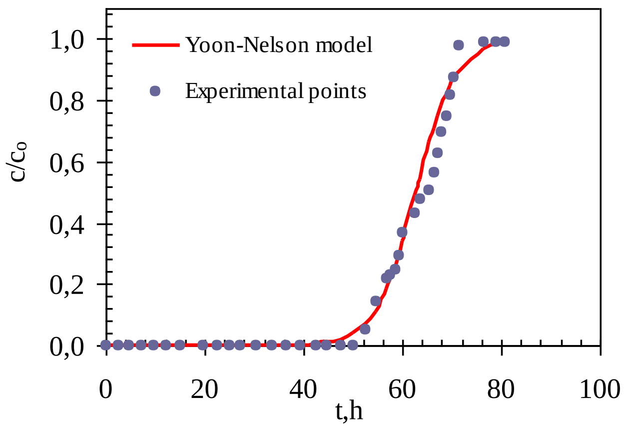


Figure 1. Experimental points and modelled breakthrough curve for removal of Zn onto a 80 mm fixed bed depth.

*Application of the reactor theory for packed beds.* In order to introduce mass transfer in the fixed bed of zeolite it has been necessary to apply the wave pattern model [5] which is suitable for mass transfer in the plug flow reactor and is described by the equation:

$$\left[\frac{\partial c}{\partial t}\right]_o = -\nu \frac{\partial c}{\partial Z} + D\frac{\partial^2 c}{\partial Z^2} - \rho \frac{1-P}{P}\frac{\partial q}{\partial t} \qquad (3)$$

where:

v - interstitial velocity, m/s; Z - distance along the flow path from some covenient reference, m; D - coefficient of dispersion for the porous media at velocity v, $m^2/s$; P - porosity of zeolite particle, -; $\rho$ - dry density of zeolite, $g/cm^3$; q - quantity of Zn bound at time t, mmol/g.

Equation (3) is a basic mathematical formulation for the packed bed reactor. It says that the rate of change of concentration of zinc ions within slice $\Delta Z$ depends on the transport flux into the slice by advection/convection and dispersion, minus the flux carried out by same transport mechanisms, minus the rate of uptake to the zeolite particles. The described mass balance through fixed bed can be presented as follows:

$$\begin{pmatrix}\text{net rate of} \\ \text{change of Zn} \\ \text{concentration}\end{pmatrix} = \begin{pmatrix}\text{net convection/} \\ \text{advection}\end{pmatrix} + \begin{pmatrix}\text{net} \\ \text{dispersion}\end{pmatrix} - \begin{pmatrix}\text{uptake of Zn} \\ \text{into}\end{pmatrix} \quad (4)$$

Equation (3) cannot be solved mathematically, and includes two basic rate control mechanisms; particle kinetics and advection kinetics which are responsible for mass transfer through the packed bed.

If zinc ions are delivered to the zeolite particle faster than is its uptake rate, particle kinetics controls the rate of zinc removal. When zinc removal is limited by the transport through the aqueous phase by advection/convection and dispersion, none of zinc ions making contact with the external surface of zeolite solid particles is rejected [5]. Which of these rate controlling steps governs mass transfer along the bed is shown in Figure 2.

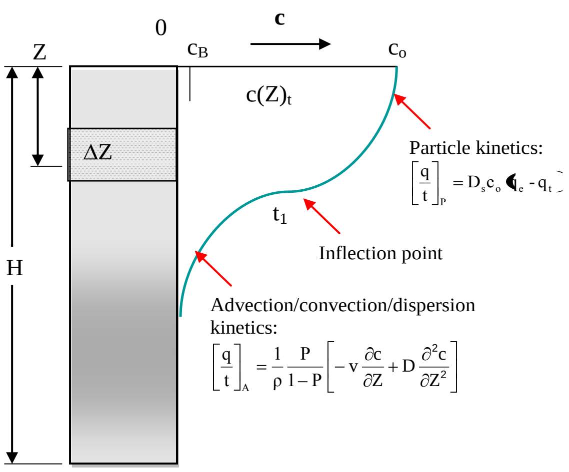


Figure 2. Illustration of the concentration profile and model components showing zones of influence of the governing kinetic equation. Note: $D_s$-diffusion coefficient through zeolite particle, $q_e$-amount of Zn bound onto zeolite at equilibrium, $q_t$-amount of Zn bound onto zeolite at time t [5].

The concentration profile along the flow path Z (Figure 2) shows the inflection point which indicates a change of mechanism. Right of the inflection point particle kinetics governs mass transfer, while to the left of the inflection point advection/convection/ dispersion governs mass transfer. To define the time when the mechanism changes it is necessary to derive the modelled breakthrough curve by the Yoon-Nelson model in Figure 1, e.g. $d(c/c_o)/dt = f(t)$. The derived curve is presented in Figure 3 and compared with the breakthrough curve by the Yoon-Nelson model. The derived curve (Figure 3) shows three parts; the first is the increase of the process rate, the second $d(c/c_o)/dt = 0$ and rate is constant, and the third is the decrease of the process rate.

The inflection point of the breakthrough curve appears at t ≈ 63 h and overlaps with the maximum of its derivation curve. This maximum indicates the change of the mass transfer mechanism, which is in correlation with rate controlling mechanisms explained in Figure 2. Based on the two main mechanisms, it can be assumed that from the beginning of the process up to the inflection point mass transfer rate is governed by the advection kinetics, around the inflection point the particle kinetics become more significant, and finally control the overall rate till the exhaustion point. After the inflection point the transfer rate becomes slower, probably due to the diffusion through zeolite particles. This has been confirmed by the calculation of quantity of zinc ions bound onto the fixed bed as the service cycle progresses, and Figure 4 compares these values for bed depths H = 80 mm and H = 40 mm. From the beginning of the process the quantity of bound zinc increases linearly and after the time corresponding to the inflection in Figure 3, becomes slower. When the bed depth increases twice, the time corresponding to the inflection point also increases twice, from 31 min to 63 min. It is evident that bed depth doesn't affect the mechanism of zinc uptake.

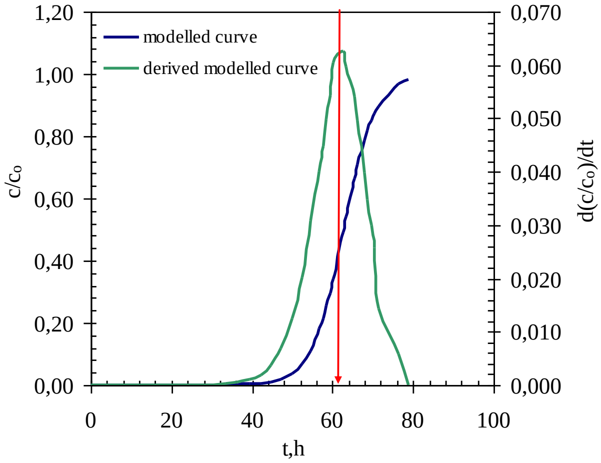


Figure 3.Comparison of the modelled curve and its derived form.

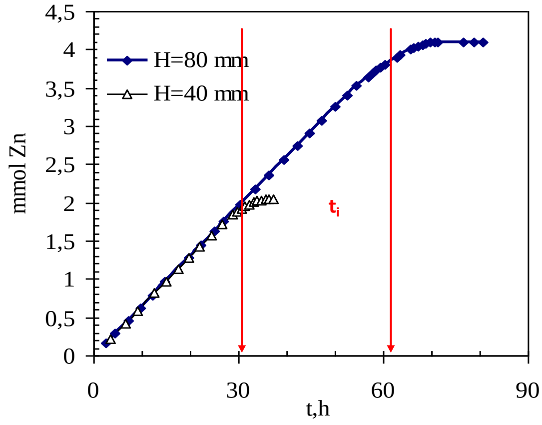


Figure 4. Comparison of quantity of zinc ions bound onto the zeolite bed during the service cycle for different bed depths.

## CONCLUSION

The application of the Yoon-Nelson kinetic empirical model has shown excellent agreement with the experimental breakthrough curve, so that this model can be used for prediction of curves. The derivation of modelled curves provides insight into mass transfer through the zeolite fixed bed. The application of the reactor theory for packed beds makes it possible to define the mass transfer mechanism. Up to the inflection point on the breakthrough curve, the mass transfer through the aqueous phase governs the rate, while after the inflection point the diffusion through particles governs the overall rate. The increase of bed depth from 40 mm to 80 mm does not change the mechanism of mass transfer, but only prolongs the time corresponding to the inflection on the breakthrough curve.

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## REFERENCES

[1] Y.H. Yoon and J. H. Nelson, *Am. Ind. Hyg. Assoc. J.*, 1984, **45**, 509-516.

[2] S.H. Lin and C.Y. Huang, *J. Environ. Eng.*, 2000, 802 - 806.

[3] Z. Aksu, *Process. Biochem.*, 2005, **40**, 997-1026.

[4] H. H. Tran and F. A. Roddick, *Water Res.*, 1999, **33**, 3001-3011.

[5] D. Hendricks, *Water Treatment Unit Processes*, Taylor and Francis Group, Boca Raton, 2006, 767-859.

[6] A. Galić, Final exam, Faculty of Chemistry and Technology, University of Split, 2008.

[7] G. Slavić, Final exam, Faculty of Chemistry and Technology, University of Split, 2008.