APPLICATION OF THE THOMAS MODEL AND THE REACTOR THEORY FOR PACKED BEDS ON ZINC UPTAKE ON CLINOPTILOLITE

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ABSTRACT

The experimental breakthrough curves of zinc removal onto the 40 mm fixed bed depth of natural zeolite have been obtained. The results have been fitted to the Thomas 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 seen 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.

Keywords: zeolite, zinc, Thomas model, reactor theory for packed beds.

INTRODUCTION

Removal of heavy metals onto the fixed bed of natural zeolite containing clinoptilolite has shown some advantages over the batch method. One of them is consecutive performance of several service cycles and regeneration cycles on the same fixed bed of zeolite. The choice of dimensional properties such as the zeolite sample particle size, column diameter and particularly the bed depth are most important for successful removal. Based on experimental results it is possible to predict the behaviour of zeolite at defined experimental conditions. For this purpose several kinetic empirical models, such as Bohart-Adams, Clark, Thomas, Wolborska and Yoon-Nelson, can be used for plotting of predicted breakthrough curves. This paper examines the application of the Thomas model on experimental breakthrough curves in order to evaluate its possible use in prediction of 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 Thomas 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) originated from the Vranjska Banja deposit and contained >80% clinoptilolite. The aqueous solution of zinc ions has been prepared by dissolving $Zn(NO_3)_2 \times 6H_2O$ in ultrapure water to obtain the concentration of 1.083 mmol Zn/l. Experiments were performed in a glass column (the inner diameter of 12 mm) filled with the zeolite sample up to 40 mm [6]. The solution passed through the bed with the flowrate of 1ml/min using the down-flow mode. After the service cycle, the regeneration cycle was performed with the solution of $NaNO_3$. During experiments, effluents were collected and concentrations of zinc were determined complexometrically.

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 the Thomas empirical kinetic model [1-4]:

$$\frac{c}{c_o} = \frac{1}{1 + \exp\left[\frac{k_{Th} \cdot q \cdot m}{Q} - k_{Th} \cdot c_o \cdot t\right]} \qquad (1)$$

where:
c – concentration of Zn in the effluent, mmol/l
c_o – initial concentration of Zn, mmol/l
k_{Th} – the Thomas rate constant, l/(mmol h)
Q – flowrate, l/h
m – mass of zeolite fixed bed, g
t - time, h
q – removal capacity, mmol/g.

Equation (1) is solved by nonlinear regression analysis and the removal capacity q and Thomas rate constant k_{Th} have been calculated. For chosen values of time t in Equation (1), using the calculated values of q = 0.706 mmolZn/g zeolite and k_{Th} = 0.491 l/(mmol h), the modelled curve has been obtained and shown by line in Figure 1. The modelled curve shows excellent agreement with the experimental points, therefore the Thomas model provides a mathematical correlation which describes experimental points.

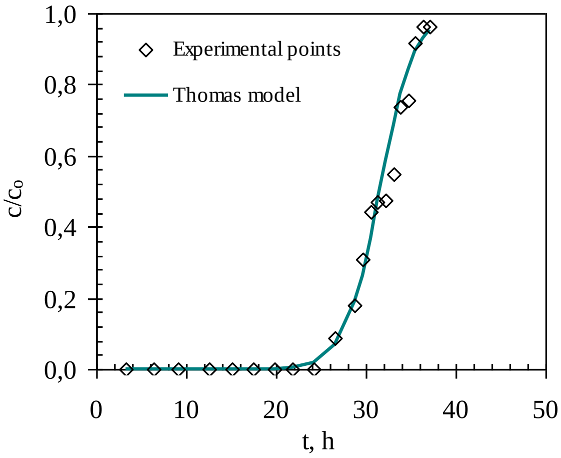

Figure 1. Experimental points and the modelled breakthrough curve for removal of Zn onto a fixed zeolite bed.

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:

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

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

Equation (2) is a basic mathematical formulation for the packed bed reactor. It says that the rate of change of concentration of zinc ions within slice ΔZ depends on the transport flux into the slice by advection/convection and dispersion, minus the flux carried out by the same transport mechanisms, minus the rate of uptake to the zeolite particles. The described mass balance through the fixed bed can be presented as follows:

$$\left(\begin{array}{c}\text{net rate of}\\ \text{change of Zn}\\ \text{concentration}\end{array}\right) = \left(\begin{array}{c}\text{net convection/}\\ \\ \text{advection}\end{array}\right) + \left(\begin{array}{c}\text{net}\\ \\ \text{dispersion}\end{array}\right) - \left(\begin{array}{c}\text{uptake of Zn}\\ \\ \text{into}\end{array}\right) \qquad (3)$$

Equation (2) 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 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. Which of these rate controlling steps governs mass transfer along the bed is shown in Figure 2.

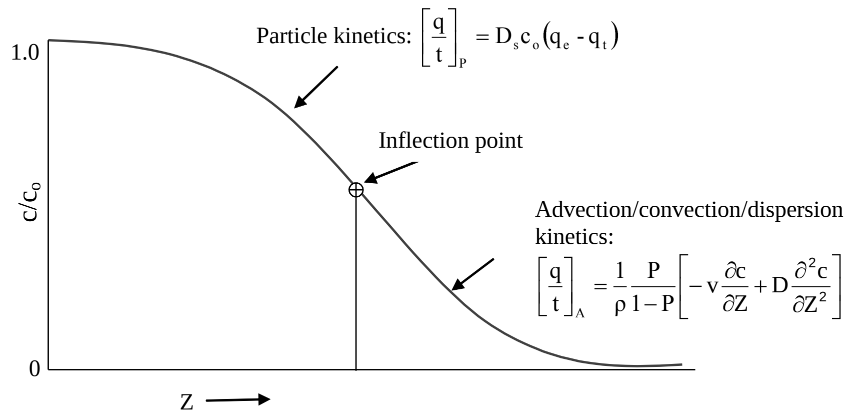

Figure 2. Illustration of the concentration profile and model components showing zones of influence of the governing kinetic equations. Note: D_s-diffusion coefficient through zeolite particle, q_e-amount of Zn bound onto zeolite at equilibrium, q_t-amount of Zn bound onto zeolite at time t [5].

The concentration profile along the flow path Z (Figure 2) shows the inflection point which means a change of mechanism. Left of the inflection point, the particle kinetics governs mass transfer, while to the right 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 Thomas 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 Thomas 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 the rate is constant, and the third shows the decrease of the process rate. The inflection point of the breakthrough curve appears at t = 31 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 the 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 inflection point the mass transfer rate is governed by the advection kinetics, around the inflection point the particle kinetics become more significant, and finally controls the overall rate till the exhaustion point. This has been confirmed by the calculation of quantity of zinc ions bound onto the fixed bed as the service cycle progresses (Figure 4). 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. It is evident that after the inflection point the transfer rate becomes slower, probably due to the diffusion through zeolite particles.

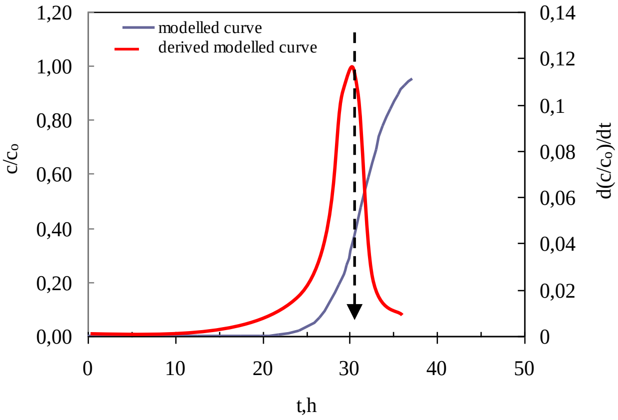

Figure 3. Comparison of the modelled breakthrough curve and its derived form.

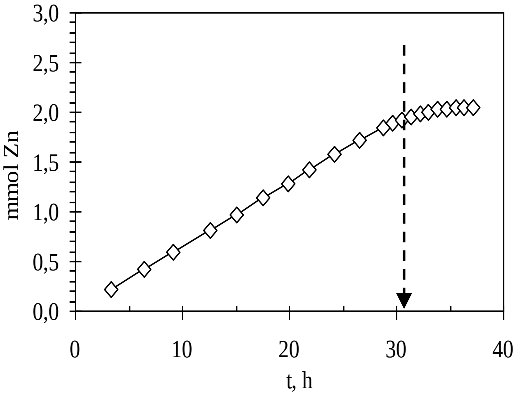

Figure 4. Quantity of zinc ions bound onto the zeolite bed during the service cycle.

CONCLUSION

Zn ions have been successfully removed from aqueous solutions using the column method. The application of the Thomas kinetic empirical model has shown excellent agreement with the experimental breakthrough curve, so this model can be used for prediction of breakthrough 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 aqueous phase governs the rate, while after the inflection point the diffusion through particles governs the overall rate.

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