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## **MODELLING OF ZINC(II) EXTRACTION FROM MODEL HYDROCHLORIC ACID SOLUTIONS IN HOLLOW FIBER MODULES**

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The recovery of zinc(II) from model hydrochloric acid solutions in hollow fiber modules was studied. It was found that zinc(II) could be removed from these model solutions by 80% and 40% tributyl phosphate in kerosene. A steady-state and an unsteady-state models of zinc(II) extraction in hollow fiber modules were formulated and experimentally verified. The proposed advanced mathematical model describes the system with high accuracy. The presented models of mass transfer in hollow fibre modules much better described the process of zinc(II) extraction than the model showed previously (Torz et al., 2002). The analysis of the experimental data and theoretical calculations showed that the kinetics of the mass transfer process was limited by the diffusion of species in the membrane's pores.

*Key words: hollow fiber module, extraction, hot-dip galvanizing, modelling*

### INTRODUCTION

The problem of recovery of metal ions from waste waters has been increasingly important in recent years. Traditional technologies of solute recovery like ion-exchange, adsorption, precipitation or solvent extraction are usually low-efficient or generate secondary pollution problems. Among new methods proposed for removing of toxic ions liquid membranes have been particularly promising (De Gyves and de San Miguel, 1999). The methods comprise the advantages of solvent extraction (high selectivity and distribution coefficient) at the same time enabling to overcome typical extraction's drawbacks (loss of extractant due to dispersion, emulsification).

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Solvent extraction as well as membrane techniques have been proposed for the recovery of zinc(II) from spent hydrochloric acid solutions (Regel et al., 2001, Kirschling et al., 2001). Such solutions, produced in hot-dip zinc galvanizing plants, generate a serious environmental and technological problems due to high toxicity of zinc and the presence of large amounts of iron in the waste stream. Recent studies has led to the selection of tributyl phosphate as a selective extractant enabling to remove zinc(II) ions. However, TBP is a weak extractant and therefore has to be used as a concentrated solution. Its using in high concentrations produces many potential problems like extractant's loss due to solubility in aqueous phase, formation of a second organic phase, emulsification. The problems could be avoided if the extractant was immobilised in a membrane. Since flat-sheet membranes offer low mass transfer area, recent interests have focused on hollow fiber modules. The modules usually operate in a two-phase mode with one phase passing through the lumen side and the other through the shell side. The interface is located in the membrane's pores. The efficiency of the extraction in the module depends on the distribution coefficient of solute and hydrodynamics. Several mathematical models of the batch process have been presented in literature (Escalante et al., 1998). In this paper a steady-state and an unsteady-state models of zinc(II) extraction in hollow fiber modules were formulated and verified.

## EXPERIMENTAL

The composition of model aqueous phase was chosen to resemble spent pickling solutions from galvanizing plants (Kirschling et al., 2001):  $[Zn^{2+}] = 20 \text{ g/dm}^3$ ,  $[H^+] = 0.54 \text{ mol/dm}^3$ ,  $[Cl^-] = 5 \text{ mol/dm}^3$ . The model solution did not contain iron since the selected extractant, which was tributyl phosphate diluted with kerosene (40% and 80%), did not exhibit affinity towards Fe(II) ions extraction. All used inorganic chemicals (P.O.Ch. Gliwice) were of pure for analysis grade; TBP (Fluka or Sigma Aldrich) had the original purity of 97%.

Prior to membrane experiments zinc(II) distribution coefficient for different TBP concentrations (0-100%) was found in a dispersive system. Equal volumes of both phases were shaken in separatory funnels for two hours and equilibrium zinc(II) concentrations were determined.

Membrane extraction experiments were carried out in an one-module system (Fig. 1). The system was comprised of a hollow fibre module (Liqui-Cel 2.5×8" X30 and X50 for 80% and 40% TBP, respectively), two tanks with ideal mixing (a magnetic stirrer was used when the flowrates were small), flowrate and pressure regulatory valves. A 0.5-bar overpressure was kept at the aqueous phase side to avoid the forming of dispersion. Geometrical parameters for the modules and tanks were collected in Table 1.

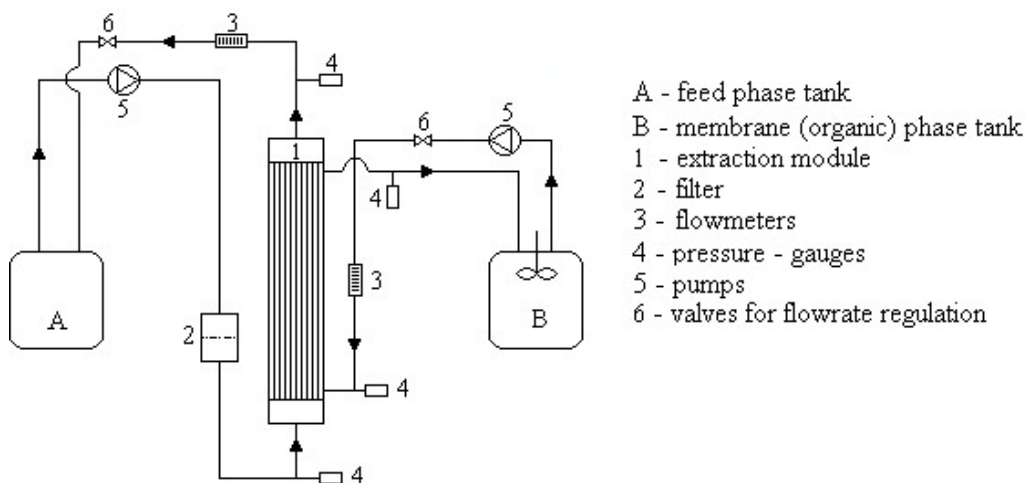


Fig. 1. Experimental extraction set-up

Table 1. Geometrical parameters for the Liqui-Cel Extra-Flow 2.5×8" X30 and X50 modules and tanks

Parameter	80% TBP system with X30 modules	40% TBP system with X50 modules
Fibre internal diameter	240 $\mu\text{m}$	220 $\mu\text{m}$
Fibre wall thickness	30 $\mu\text{m}$	40 $\mu\text{m}$
Effective pores size	0.03 $\mu\text{m}$	0.04 $\mu\text{m}$
Porosity	40%	40%
Effective fibre length	15 cm	15 cm
Effective surface area	1.4 $\text{m}^2$	1.4 $\text{m}^2$
Tubeside volume	145 ml	145 ml
Shellside volume	195 ml	400 ml
O-rings material	Viton	Karlez
Feed phase tank volume	400 ml	1315 ml
Organic phase tank volume	200 ml	1200 ml

## RESULTS

Preliminary equilibrium experiments showed that zinc(II) distribution coefficient for the fixed zinc(II) concentration (20  $\text{g}/\text{dm}^3$ ) and the volumetric ratio of phases 1:1 depended highly on the TBP concentration when TBP content was higher than 50% (Fig. 2). Below this value the extractant was practically saturated with zinc(II). Two

concentrations of tributyl phosphate were selected for membrane experiments: 40% ( $m_{Zn} < 0.5$ ) and 80% ( $m_{Zn} \approx 2$ ).

Typical zinc(II) concentration profile for membrane experiments was presented in Fig. 3. The solute concentration variation was strong in the first period of experiments since the driving force of the process was high. When the zinc(II) concentration approached its equilibrium value the curves reached plateau. Similar profiles were observed for HCl concentration in the 80% TBP system; the extraction of 1 mole of zinc(II) was accompanied by the transfer of ca. 1.2 mole of HCl. However, when the concentration of extractant was 40%, only negligible amount of HCl was transferred from the aqueous phase.

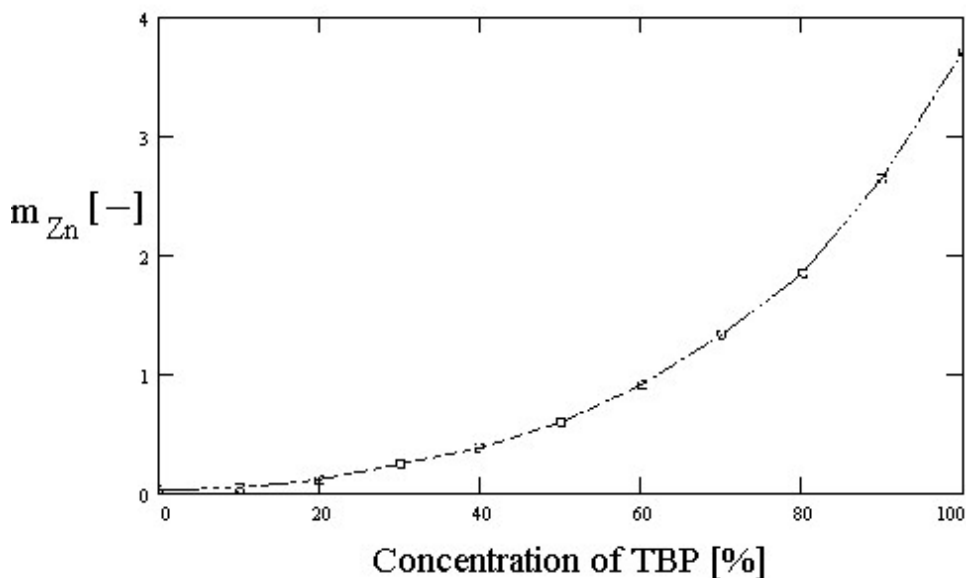


Fig. 2. The dependence of zinc(II) distribution coefficient on the volumetric concentration of TBP

#### MODELLING OF MASS TRANSFER

In our previous paper (Torz et al., 2002) a simplified mass transfer model based on a driving force defined as the difference between actual and final zinc(II) concentrations was presented. Despite satisfactory results of fitting to experimental data the model could be regarded as artificial because the definition of real driving force of the mass transfer process should take into account the difference between actual activities (usually approximated as concentrations) of the solute in both phases.

If at a fixed time the solute concentration could be considered constant in a given phase, which is true when the residence time in any part of the installation is short, then a general model equation could be expressed as:

$$-V_w \cdot \frac{dC_{Zn}}{dt} = K_1 \cdot \frac{A_m}{Q_w} \cdot (C_{Zn} - C_{Zn}^*) \quad (1)$$

where:  $A_m$  - mass transfer area,  $C_{zn}$  - actual zinc(II) concentration in the feed phase,  $K_1$  - average mass transfer coefficient,  $Q_w$  - aqueous phase volumetric flowrate,  $V_w$  - volume of the aqueous phase,  $t$  - time.

Here, the driving force of mass transfer was defined as the difference of actual zinc(II) concentrations, because:

$$C_{Zn}^* = \frac{C_{Zn(o)}}{m_{Zn}} \quad (2)$$

where:  $C_{zn(o)}$  - actual zinc(II) concentration in the organic phase,  $m_{zn}$  - zinc(II) distribution coefficient.

To integrate the model equation an additional mass balance equation was introduced:

$$C_{Zn(o)} = (C_{Zn,i} - C_{Zn}) \cdot \frac{V_w}{V_o} \quad (3)$$

For the initial condition  $t = 0$ ,  $C_{zn} = C_{zn,i}$  the solution was:

$$C_{Zn}(t) = \frac{V \cdot C_{Zn,i}}{1 + V} + \frac{C_{Zn,i}}{1 + V} \cdot \exp\left[-K_1 \cdot \frac{A_m}{V_w} \cdot (1 + V) \cdot t\right] \quad (4)$$

where  $V = \frac{V_w}{V_o \cdot m_{Zn}}$ .

Table 2. Mass transfer coefficients  $K_1$  and  $K_2$  in 40% TBP extraction system

$Q_w \times 10^3$ [m <sup>3</sup> /min]	$Q_o \times 10^3$ [m <sup>3</sup> /min]	$K_1 \times 10^7$ [m/s]	$K_2 \times 10^7$ [m/s]
1.7	2.0	1.0	1.0
1.9	2.0	1.0	1.0
3.3	2.0	1.1	1.1
4.5	2.0	1.1	1.0
4.8	2.0	1.1	1.1
5.6	2.0	1.1	1.1
3.8	0.7	0.9	0.9
3.8	0.3	0.9	0.9

The only parameter to be fitted was the average mass transfer coefficient  $K_1$ . Its values, calculated using the least square method, were collected in Tables 2 and 3. As shown in Fig. 3, the fitting of the model equation (4) to experimental data was satisfactory; no significant discrepancies were observed in the whole experimental region.

Table 3. Mass transfer coefficients  $K_1$  in 80% TBP extraction system

$Q_w \times 10^3$ [m <sup>3</sup> /min]	$Q_o \times 10^3$ [m <sup>3</sup> /min]	$K_1 \times 10^7$ [m/s]
1.6	0.5	2.9
2.4	0.5	3.0
4.0	0.5	3.9
2.4	0.6	3.9
2.4	1.0	5.5
2.4	1.6	6.1

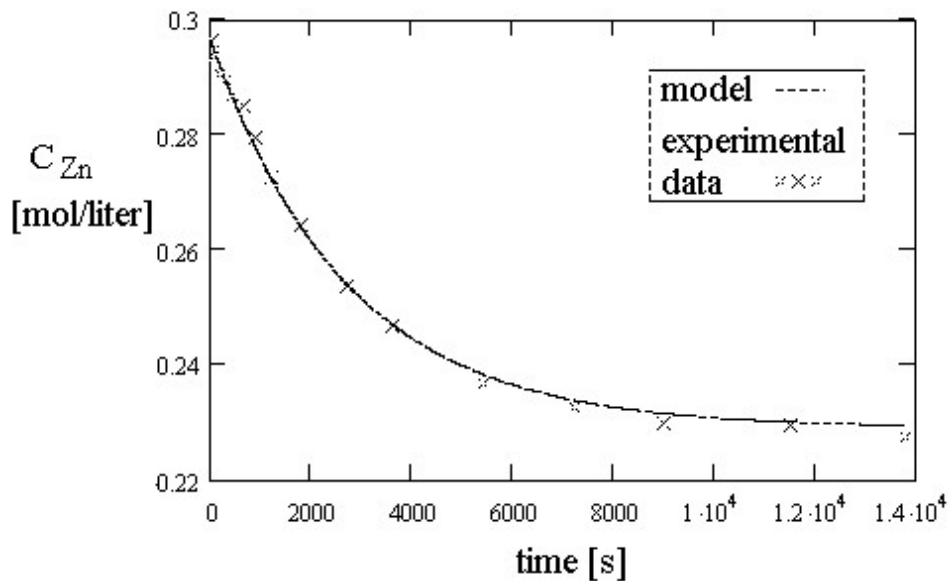


Fig. 3. Experimental concentration profile of zinc(II) in the feed phase and theoretical results from the fitting of model equation (4) (40% TBP,  $Q_w = 1.9 \times 10^{-3}$  m<sup>3</sup>/min,  $Q_o = 2 \times 10^{-3}$  m<sup>3</sup>/min)

As mentioned before, the model equation (1) was built on the presumption of negligible variations of zinc(II) concentration at a fixed time in a given phase. In such an approach no differentiation between module and tanks was introduced and thus the

mathematical description was simplified. To improve the precision of modelling, the solute concentration changes in tanks and modules were described by separate equations. The concentration of zinc(II) in the module varied both with time and with axial position. A mass balance resulted in the following equations for lumen side and shell side, respectively:

$$-\frac{V_w^m}{Q_w \cdot L} \cdot \frac{\partial C_{Zn}}{\partial t} - \frac{\partial C_{Zn}}{\partial t} = \frac{A_m}{Q_w \cdot L} \cdot K_2 \cdot (C_{Zn} - C_{Zn}^*) \quad (5)$$

$$\frac{V_o^m}{Q_o \cdot L} \cdot \frac{\partial C_{Zn(o)}}{\partial t} - \frac{\partial C_{Zn(o)}}{\partial t} = \frac{A_m}{Q_o \cdot L} \cdot K_2 \cdot (C_{Zn} - C_{Zn}^*) \quad (6)$$

where: L - effective length of the fibres,  $V^m$  - volume of the lumen side (subscript w) or shell side (subscript o).

If the assumption of an ideal mixing in the tanks was valid, then the concentration changes of zinc(II) in both reservoirs with time could be expressed by two differential equations:

$$\frac{dC_{Zn}}{dt} = \frac{Q_w}{V_w^t} \cdot [C_{Zn}(L) - C_{Zn}] \quad (7)$$

$$\frac{dC_{Zn(o)}}{dt} = \frac{Q_o}{V_o^t} \cdot [C_{Zn(o)}(L) - C_{Zn(o)}] \quad (8)$$

where:  $V^t$  - volumes of tanks.

A set of initial and boundary conditions was introduced:

$$\begin{aligned} t = 0 \quad C_{Zn} &= C_{Zn,i} \quad C_{Zn(o)} = 0 \\ z = L \quad C_{Zn} &= C_{Zn}(L) \quad C_{Zn(o)} = C_{Zn(o)}(L) \end{aligned}$$

The model given by equations (5) - (8) constituted a set of differential and partial differential equations over two domains. To solve it, the implementation of a numerical method was necessary. The model was solved by means of gPROMS software. A special procedure made it possible to introduce discontinuities caused by the volume depletion due to sampling. The average mass transfer coefficients  $K_2$  were calculated by the least square method. Their values for 40% TBP system were collected in table 2.

Exemplary results of fitting to experimental data were shown in Fig. 4. The fitting was better than the one obtained from the simplified model, and proved a superior precision of modelling. However, the comparison of average mass transfer coefficients  $K_1$  and  $K_2$  for 40% TBP system (Table 2) showed that the respective values were almost identical. Therefore, the complicated and time-consuming model was not solved for 80% TBP system. The simplified model proved to be sufficient for evaluating kinetics of the process.

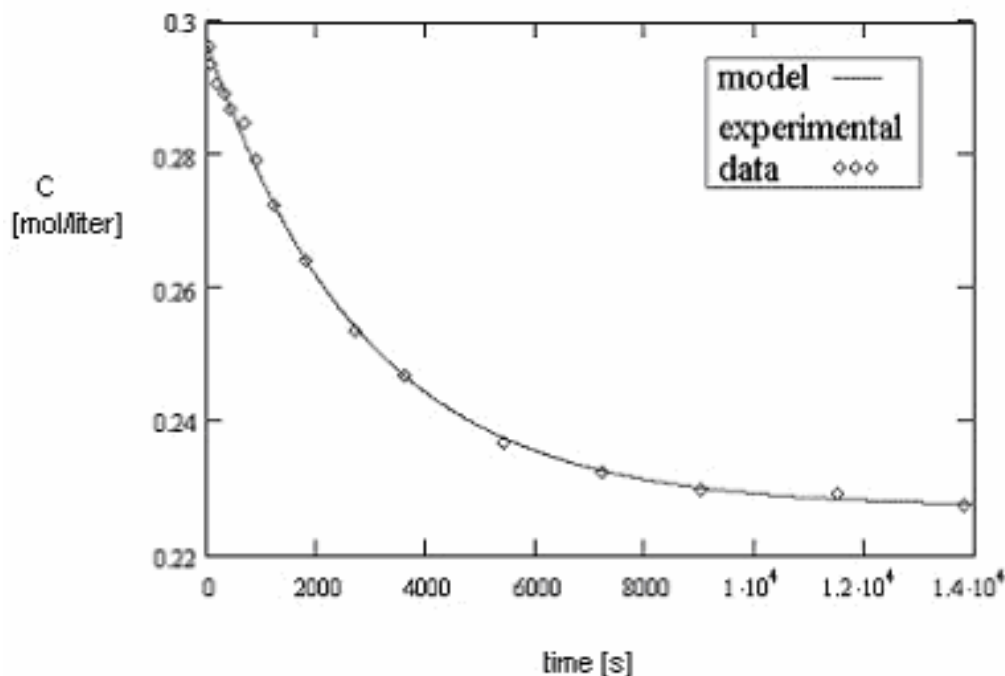


Fig. 4. Experimental concentration profile of zinc(II) in the feed phase and theoretical results from the fitting of model equations (5) - (8) (40% TBP,  $Q_w = 1.9 \times 10^{-3} \text{ m}^3/\text{min}$ ,  $Q_o = 2 \times 10^{-3} \text{ m}^3/\text{min}$ )

## DISCUSSION AND CONCLUSIONS

The presented models of mass transfer in hollow fibre modules much better described the process of zinc(II) extraction than the model showed previously (Torz et al., 2002) based on an artificial driving force. The model curves covered the experimental data well, although the only parameter to be fitted was mass transfer coefficient.

Although the precision of modelling was improved when the process was considered as an unsteady-state, with zinc(II) concentration varying both with time and axial position in the module, the mass transfer coefficients were almost identical to those obtained from the simplified model.

The variation of mass transfer coefficients with flowrates for 80% TBP system (Table 3) suggested that the concentration of extractant was high enough to enable an increase of zinc(II) flux with the increase of flowrates. The kinetics of the process was improved when either aqueous phase or organic phase flowrate was increased. However, the hydrodynamics on the shell side (organic) phase exerted stronger influence on the process kinetics within the investigated flowrates' range.



While the zinc(II) flux could be increased in the 80% TBP system, such phenomenon was not observed in the 40% TBP system. As shown in table 2, practically no variation of mass transfer coefficients with either flowrates occurred. The obtained flux of zinc(II) was maximal within the investigated range of flowrates. Therefore, it might be concluded that the kinetics of the mass transfer process was limited by the diffusion of species in the membrane's pores.

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**Torz M., Alejski K., Szymanowski J.**, *Modelowanie ekstrakcji cynku(II) z modelowych roztworów kwasu solnego w modułach z włóknami kapilarnymi*, Physicochemical Problems of Mineral Processing, 37 (2003) 97-105 (w jęz. ang.).

W pracy przedstawiono wyniki badań ekstrakcji cynku(II) z modelowych roztworów kwasu solnego w modułach z włóknami kapilarnymi. Stwierdzono, że cynk(II) może być usuwany z badanych, modelowych roztworów przy pomocy zarówno 40%, jak i 80% roztworów fosforanu tributyłu w nafcie. Sformułowano i eksperymentalnie zweryfikowano model matematyczny procesu uwzględniający pracę w stanie ustalonym, jak i nieustalonym. Zaproponowany złożony model matematyczny opisuje pracę modułu z dużą dokładnością. Rozpatrywany model transportu masy w modułach z włóknami kapilarnymi opisuje proces znacznie dokładniej niż model opracowany wcześniej (Tórz et al., 2002). Analiza wyników eksperymentalnych oraz obliczeń teoretycznych pokazuje, że kinetyka transportu masy jest limitowana dyfuzją w porach membrany.