

COMMUNICATION

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KINETICS OF SEA WATER DESULFATION ON A WEAK ANION EXCHANGE RESIN

NOTATIONS

- a — area of the transfer surface, cm^2/cm^3 ,
- a_l — area of the liquid phase boundary, $\text{cm}^2/\text{cm}_r^3$,
- a_p — area of the solid phase boundary, $\text{cm}^2/\text{cm}_r^3$,
- C — total solution concentration, eq/dm^3 ,
- C_0 — feed solution or sea water concentration, eq/dm^3 ,
- \bar{C} — exchange capacity of the resin, eq/dm_r^3 ,
- d — average particle diameter, cm ,
- D_l — liquid $\text{SO}_4^{=}/\text{Cl}^-$ ion interdiffusivity, cm^2/s ,
- F_l — liquid flow rate, dm^3/h ,
- F_s — solid flow rate, dm_r^3/h ,
- h — mean bed height, cm ,
- h_z — height of exchange zone, cm ,
- HTU — height of transfer unit, cm ,
- k_l — liquid mass transfer coefficient, cm/s ,
- k_p — solid mass transfer coefficient, cm/s ,
- K_G — overall mass transfer coefficient, cm/s ,
- K_L — overall mass transfer coefficient based on liquid concentrations, cm/s ,
- K_p — overall mass transfer coefficient based on solid concentrations, cm/s ,
- m — constant in eq. (8),
- n — concentration factor, i.e. ratio between regenerant and feed solution concentration; constant in eq. (8),
- NTU — number of transfer units,
- N_{Re} — Reynolds number for porous systems = $F_l d / 6(1-\epsilon) v_s$,
- N_{Sc} — Schmidt number = v / D_l ,
- N_{Sh} — Sherwood number = $k_l d / D_l$,

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- S — column cross-sectional area, cm^2 ,
 t — time, s,
 V — volume of solution, dm^3 ,
 v — volume of resin, dm_r^3 ,
 X — sulfate equivalent fraction in solution,
 X_0 — sulfate equivalent fraction in sea water,
 X_i — sulfate equivalent fraction in solution at the liquid-solid interface,
 X^* — sulfate equivalent fraction in solution at equilibrium,
 Y — sulfate equivalent fraction in resin,
 Y_0 — sulfate equivalent fraction in resin equilibrated with sea water,
 Y_i — sulfate equivalent fraction in resin at the liquid-solid interface,
 Y^* — sulfate equivalent fraction in resin at equilibrium,
 a — constant in eq. (9),
 ϵ — void fraction in the column,
 ν — kinematic viscosity of sea water, cm^2/s .

1. INTRODUCTION

A process for sea water desulfation by exchange on a fixed bed of a weak anion resin in chloride form has already been reported [3]. The resin was Kastel A-102/812 by Montedison S.p.A. It has a polyacrylic matrix, H^{ary} and I^{ary} amino groups, and it is characterized by a particular high selectivity towards sulfate ions. This resin was expressly developed for such a process on the basis of thermodynamic considerations on the selectivity performances of many anion resins with different functional groups. The study was carried on to investigate the resin dynamic performances by means of the breakthrough profile analysis, in order to evaluate the fundamental kinetic coefficients and the other parameters of the process useful for design calculations,

2. EXPERIMENTAL

Fig. 1 shows the $\text{SO}_4^{=}$ breakthrough curves at different flow rates in the desulfation of sea water on a fixed bed of the same resin, regenerated with a NaCl solution.

Natural sea water was used, previously dealkalized at a pH of 3.5.

The performances of the resin were found strictly dependent on liquid-solid mass transfer kinetics. As shown by fig. 2, the slopes of these curves at the same X value lie on a straight line of equation

$$\frac{dX}{dt} = A(F_l/S)^{0.5}, \quad (1)$$

where A is a function of X and represents the slope of the breakthrough curve at unitary flow rate.

Within the investigated F_l/S range (0.111-0.788 cm/s), at $X = X_0/2$, it results $A = 1.279 \times 10^{-4} \text{cm}^{-0.5} \text{s}^{-0.5}$.

Equation (1), as previously reported [1], enables the breakthrough curve for a given flow rate to be deduced from any other known one.

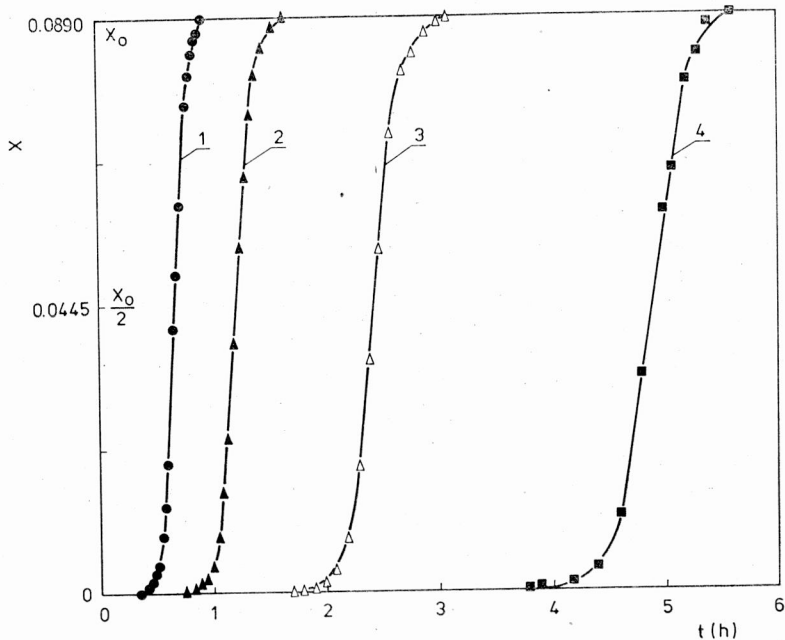


Fig. 1. Experimental sulfate breakthrough curves in sea water desulfation on weak anion resin Kastel A.102

F_1/S : 1 = 0.788 cm/s; 2 = 0.444 cm/s; 3 = 0.222 cm/s; 4 = 0.111 cm/s. (Experimental conditions: $v = 0.41$ l/r; $\bar{C} = 2.7$ eq./l/r; $h = 80$ cm; $S = 2.47$ cm²; $C = 0.59$ eq./l; $X_0 = 0.089$; $n = 3$; $\varepsilon = 0.34$; $d = 0.102$ cm; $\nu = 9.106 \times 10^{-3}$ cm²/s.)

Rys. 1. Doświadczalne krzywe przebiecia siarczanów przy odsiarczaniu wody morskiej na słabej żywicy anionowej Kastel A.102

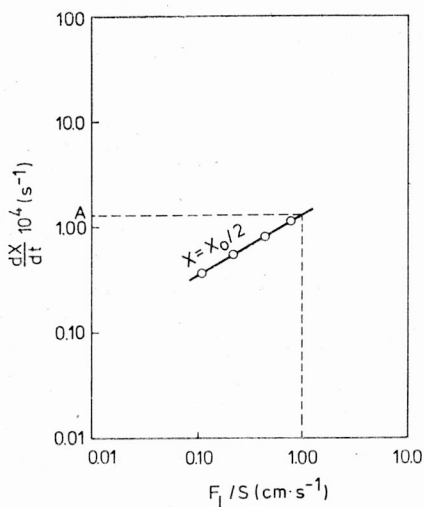


Fig. 2. Midpoint slopes of the sulfate breakthrough curves as a linear function of feed flow rates

Rys. 2. Nachylenia punktu środkowego krzywych przebiecia siarczanów jako funkcja liniowa szybkości przepływu zasilającego

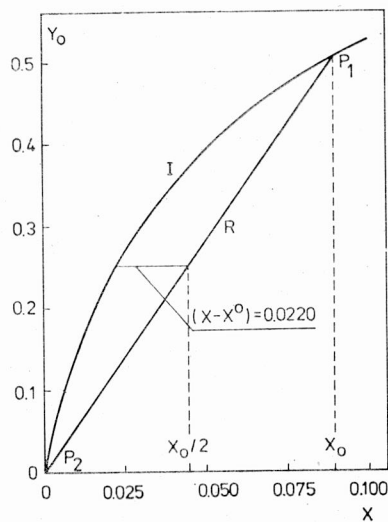


Fig. 3. $\text{SO}_4^{2-}/\text{Cl}^-$ equilibrium isotherm (I) and operating line (R) for sea water desulfation at 25°C

Rys. 3. Izoterma równowagi (I) $\text{SO}_4^{2-}/\text{Cl}^-$ i linia operacyjna (R) dla odsiarczania wody morskiej w 25°C

3. KINETIC PARAMETERS CALCULATION

Mass transfer mechanism in ion exchange and similar processes may be usefully described by the Nernst's diffusion layer theory [5].

According to this theory, the main resistances of the process are due to the ion interdiffusions within two layers, adjacent to the liquid-solid interface, in which the total ion concentration difference between the two phases develops. If one assumes, as usual in ion exchange processes, that the chemical reaction rate is much higher than that of the two diffusional steps, the kinetics of the process may be indifferently described by either one of the following equations:

$$dY/dt = k_l a_l \frac{C}{C} (X - X_i) = k_p a_p (Y_i - Y) = K_l a_l \frac{C}{C} (X - X^*) = K_p a_p (Y^* - Y). \quad (2)$$

In their HTU's calculation for fixed bed gas-solid mass transfer processes, WILKE and HOUGEN [7] found that a dependence of the kinetics on the square root of the flow rate was typical of film diffusion controlled processes under laminar flow conditions ($N_{Re} \leq 350$). The 0.5 exponent value in eq. (1), which we found in our experiments where it was $N_{Re} \leq 2.2$, thus allows to assume that in this process ion interdiffusion within the liquid film is the rate controlling step.

Therefore in our process the exchange rate may be expressed as

$$\frac{dY}{dt} = k_l a \frac{C}{C} (X - X^*), \quad (3)$$

where $k_1 = K_l = K_G$, $X^* = X_i$ and $a = a_p$.

Substituting dX/dt with $X_0 dY/Y_0 dt$ in eq. (1), according to the continuity condition for mixed feed systems, expressed as

$$Y_0 dX = X_0 dY, \quad (4)$$

and combining eqs. (1) and (3), one obtains

$$A = k_l a \frac{X_0 C (X - X^*)}{Y_0 \bar{C} (F_l/S)^{0.5}}. \quad (5)$$

It is then possible to evaluate the liquid mass transfer coefficient, $k_l a$, from the experimental A value corresponding to a selected X , if one may calculate the relative driving force $(X - X^*)$, the other variables of eq. (5) being known.

In continuous processes, the driving force may be evaluated by the equilibrium isotherm and the operating line representing the process in the different experimental conditions. In a previous paper [2], a "fixed bed operating line" concept for the description of the sea water desulfation process on a fixed bed of weak anion resin was illustrated. Such a concept essentially called for an ideal semi-continuous model where the two following assumptions were made for the process during exhaustion or regeneration:

the initial and final bulk average concentrations for the exchanged ions, both in the solid and in the liquid phases, are used for the mass transfer balances;

the stationary solid phase apparently moves through the column, countercurrently to the liquid phase, at a flow rate determined by the ratio between the resin volume and the operation time.

According to this model an integral mass balance may be expressed for the process during exhaustion or regeneration

$$\frac{Y_2 - Y_1}{X_1 - X_2} = \frac{CV}{\bar{C}v} = \frac{CF_l}{\bar{C}F_s}, \quad (6)$$

where $X_{1,2}$ and $Y_{1,2}$ are the final and initial average bulk sulfate equivalent fraction in the liquid and solid phases, respectively.

Equation (6) allows for the operation to be graphically described by the proper operating line on the plane (X, Y) . In our experiments, where resin freshly regenerated with NaCl solution was used and complete equilibration with sea water was achieved in each run, both the exhaustion and regeneration operations may be represented by the same operating line passing through the origin and the point (X_0, Y_0) on the $\text{SO}_4^{=}/\text{Cl}^-$ equilibrium isotherm, as shown in fig. 3.

There results that for $Y_0 = 0.502$ and for $X = X_0/2$, the driving force $(X - X^*)$ reaches its maximum value of 0.022. For this process, eq. (5) gives

$$k_1 a = 0.15 (F_1/S)^{0.5} (s^{-1}). \quad (7)$$

By combining eq. (7) with the well known equations of the height and the number of transfer units, the following expression may be obtained

$$\text{HTU} = \frac{h_z}{\text{NTU}} = \frac{F_1/S}{K_G a} = \frac{(F_1/S)^{0.5}}{0.15}, \quad (8)$$

with HTU values ranging, under the experimental conditions tested, from 2.2 to 5.9 cm.

Finally, by graphical integration of $dX/(X - X^*)$ from $0.05X_0$ to $0.95X_0$ on fig. 3, a value of about 6 is obtained for NTU, so that there results an h_z ranging from 13.5 to 36.0 cm. These values closely conform with the ones that may be obtained by means of empirical correlations [1].

The k_1 coefficient may be generally related to the average $\text{SO}_4^{=}/\text{Cl}^-$ liquid ion interdiffusivity, D_l , by a dimensionless correlation as

$$N_{\text{Sh}} = \frac{1}{a} (N_{\text{Re}})^m (N_{\text{Sc}})^n. \quad (9)$$

Introducing the values $\alpha = 0.28$, $m = 0.5$ and $n = 0.37$ proposed by HIESTER at al. [6] for fixed bed mass transfer processes with laminar flow, and evaluating a according to ERGUN [4] as

$$a = 6(1 - \varepsilon)/d, \quad (10)$$

(in this case $a = 38.82 \text{ cm}^2/\text{cm}^3$), from eq. (8), (9) and (10) one obtains $D_l = 0.36 \times 10^5 \text{ cm}^2/\text{s}$.

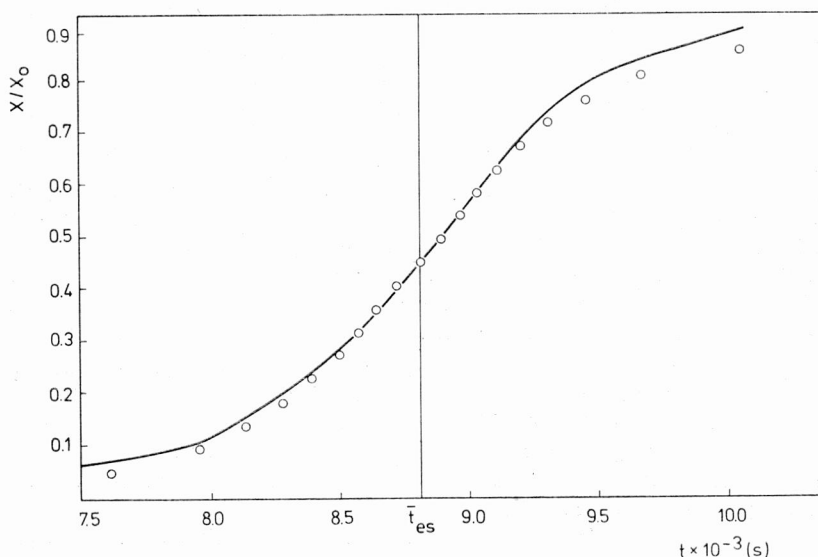


Fig. 4. Calculated $\text{SO}_4^{=}$ breakthrough curve in sea water desulfation on weak anion resin Kastel A.102 for $F_1/S = 0.222 \text{ cm/s}$

Rys. 4. Obliczona krzywa przebiecia $\text{SO}_4^{=}$ przy odsiarczaniu wody morskiej na słabej żywicy anionowej Kastel A.102 dla $F_1/S = 0.222 \text{ cm/s}$

Within the experimental errors and the approximation of calculations made, the value for D_l obtained is also in satisfactory agreement with the value 0.67×10^{-5} cm²/s calculated from the NaCl and Na₂SO₄ diffusion coefficients at infinite dilution [1].

The knowledge of the fundamental kinetic parameters of the investigated process allows for the prediction of the curves for the SO₄²⁻/Cl⁻ exchange under various experimental conditions. According to eqs. (3), (4) and (7), and evaluating the corresponding linear driving force by means of the equilibrium curve and the operating line, the breakthrough curves for the SO₄²⁻/Cl⁻ exchange with the examined resin may be calculated under various experimental conditions. Fig. 4 shows the calculated curve and the experimental points for the SO₄²⁻/Cl⁻ exchange with the resin Kastel A.102 at a liquid flow rate $F_l/S = 0.222$ cm/s. The close agreement with the experimental points confirms the validity of the proposed semi-continuous model

4. CONCLUSIONS

With a simple semi-continuous model, based on the assumption of an apparent flow rate of the stationary solid phase and the use of the initial and final bulk average ion concentrations in mass transfer balances, irrespective of the nature of the involved equilibrium, discontinuous unit operations, such as fixed bed ion exchange, can be treated as continuous ones and the operating line method can be applied. Using linear driving force kinetic equations, if the equilibrium curve for the process is known, the fundamental kinetic parameters involved in process design calculations can be evaluated.

A limited amount of experimental data is needed in order to determine the rate controlling step of the process and the form of the kinetic equation to be used.

Such model has been successfully applied to sea water desulfation on a fixed bed of a weak anion resin.

Resin performances have been predicted that closely conform with the experimental data. The application of such a satisfactory, though approximate procedure allows to overcome the difficulties inherent to mathematical treatment of fixed bed systems and to make a sufficiently rigorous design calculation.

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