

Removal of organic acid salts from 1,3-propanediol fermentation broth by electro dialysis

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ABSTRACT

ED method is employed to effectively remove the organic acid salts in actual PDO fermentation broth. The lower electrical potential is selected to avoid the serious membrane fouling so as to ensure a stable and durative desalination process. Under the selected operation conditions, about 90% of organic acids salts are removed from PDO fermentation broth successfully by ED process. To reduce the loss of PDO product due to the diffusion, the operation time should be considered carefully. And based on mass balance equation and irreversible thermodynamics approach, a mathematical model is developed to describe the desalination process of an aqueous solution containing neutral solute by ED method. While the influence of concentration polarization is reflected by decreasing the conductivity of membrane, the model is verified well to describe the ED processes under varied operation conditions. Through the model, ED process of actual PDO fermentation broth is simulated to get a suitable scope of initial concentration in concentrated compartment.

INTRODUCTION

1, 3-propanediol (PDO) is an important chemical intermediate in the production of polyesters, polyethers and polyurethanes. Microbial fermentation to yield PDO has been paid much attention because of its relatively slight pollution and low cost ^[1]. During fermentation, the accumulation of the byproducts such as acetic acid and lactic acid inhibits the growth of bacillus. Therefore, potassium hydroxide is being added to keep pH value of fermentation broth at 7.0 and thus organic acid salts are formed. While vacuum evaporation is employed to concentrate actual PDO fermentation broth, the existence of salts makes the energy consumption rise, the one-off concentration ratio of PDO less than 30% and about 20% of PDO lose. To realize the industrial production of PDO by fermentation successfully, an effective method is need to be used to remove these organic acid salts from actual PDO fermentation broth. Compared with the processes such as solvent extraction and crystallization, electro dialysis (ED) method has the advantages of low pollution and cost. And it has been widely applied not only in desalination of saline solution, but also in separation of organic acids and their salts in bio-separation processes. So far, several models have been proposed to describe the transports of ions and water under constant current during the desalination and concentration of specific salts and acids by ED process ^[2-4]. However, the contributions of diffusion of ions and osmosis of water on transports of ions and water were usually neglected in these models. And a great amount of ED experiments should be operated to regress the model coefficients. Therefore, it is necessary to develop a more generalized model to understand and describe the ED process better, especially for the desalination process of aqueous solution containing of neutral solute by ED method mentioned above.

In this paper, the possibility of desalination of actual PDO fermentation broth by ED method is discussed. The suitable operation parameters are selected to ensure a stable and durative desalination process, and the loss of PDO product is studied through simulated diffusion experiment.

And a model is attempted to be developed for simulating the desalination process of an aqueous solution containing a neutral solute by ED method. While the model parameters are given, the variations of the concentrations of solutes, the velocity of solution and current density versus the flow length are simulated by the model. And the effects of some variables in the model on desalination process are discussed through simulations to instruct the actual process.

EXPERIMENTAL

Two types of commercial ion-exchange membranes (IEMs) are selected in this work, which are made of Beijing Huan Yu Li Da Equipment Ltd.. ED equipment is designed with dilute compartment (*dc*) and concentrated compartment (*cc*). It is comprised of 10 cell pairs of IEMs with effective area per membrane of 0.0126 m^2 ($0.06 \text{ m} \times 0.21 \text{ m}$) and the thickness of every compartment is 2.7 mm. All ED experiments are operated in a batch mode under constant voltage (see Fig. 1). The actual PDO fermentation broth contains PDO of about 20 g L^{-1} , glycerol of about 12 g L^{-1} , lactate of about 3 g L^{-1} , acetate of about 6 g L^{-1} , which is circulated in dilute compartment. And the CH_3COOK solution with an initial concentration of 0.05 M is circulated in concentrated compartment. The constant voltage across the electrolysers is controlled by the rectifier and ranges from 7 V to 12 V. The flow rates in dilute and concentrated compartments are kept same and range from 40 L h^{-1} to 80 L h^{-1} ($0.7 \text{ cm s}^{-1} \sim 1.4 \text{ cm s}^{-1}$).

In order to study the loss of PDO during desalination, a simulated diffusion experiment is carried out. At zero potential, the high concentration compartment is fed with the PDO solution (20 g L^{-1}), and the low concentration compartment is fed with distilled water. IEM (effective area= 0.001 m^2) is placed between the two compartments.

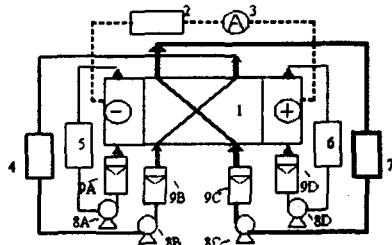


Fig.1 Equipment diagram for desalination of PDO fermentation broth:1.electrolysers cell; 2.DC power;3.amperometer;4.concentrated tank; 5.cathode tank; 6.anode tank; 7.dilute tank; 8A-8D:pump; 9A-9D:flowmeter

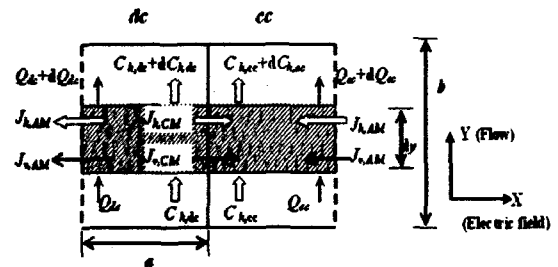


Fig. 2 The analysis diagram of ED process of an aqueous solution containing a neutral solute (dashed line: AM; straight line: CM; $k=s, n$)

THEORETICAL

Analysis of ED process Assumed that it is plug flow in compartments of ED equipment, the ED process of an aqueous solution consisting of a salt (*s*) and a neutral solute (*n*) is analyzed in the two-dimensional directions of electric field (*X*) and flow (*Y*) (see Fig. 2). *a* is the distance between cation-exchange membrane (*CM*) and anion-exchange membrane (*AM*), and *b* is the effective length of a membrane. In the direction of *X*, the salt, neutral solute and water (*w*) transport through the membranes driven by electrical potential and concentration differences. The fluxes of solutes through *CM* and *AM* are presented by $J_{k,CM}$ and $J_{k,AM}$, respectively ($k=s, n$), and the flux of water through *CM* and *AM* are denoted by $J_{v,CM}$ and $J_{v,AM}$, respectively. According to mass balance, the variations of concentrations of solutes and velocity along differential length of flow (*dy*) in dilute and concentrated compartments are expressed as follows, respectively,

$$\frac{dC_{k,k}}{dy} = \frac{1}{u_{k,k} \cdot a} [C_{k,k} (J_{v,CM} + |J_{v,AM}|) - (J_{k,CM} + |J_{k,AM}|)] \quad (1)$$

$$\frac{du_{dc}}{dy} = -\frac{1}{a}(J_{v,CM} + |J_{v,AM}|) \quad (2)$$

$$\frac{dC_{k,cc}}{dy} = \frac{1}{u_{cc} \cdot a} [(J_{k,CM} + |J_{k,AM}|) - C_{k,cc}(J_{v,CM} + |J_{v,AM}|)] \quad (3)$$

$$\frac{du_{cc}}{dy} = \frac{1}{a}(J_{v,CM} + |J_{v,AM}|) \quad (4)$$

Transports of solutes and water through IEM Based on the Kedem-Katchalsky equations, the fluxes of salt, neutral solute and water through IEM and the current density (I) are deduced as follows, respectively,

$$J_s = -RTc_s(1-\sigma_s)L_p(v\Delta C_s + \Delta C_n) + \omega_s RTv\Delta C_s + \frac{\frac{v_1}{2}\tau_1 + \frac{v_2}{2}\tau_2}{Fv} I \quad (5)$$

$$J_n = -RTc_n(1-\sigma_n)L_p(\Delta C_n + v\Delta C_s) + \omega_n RT\Delta C_n \quad (6)$$

$$J_v = -RTL_p(\sigma_n\Delta C_n + \sigma_s v\Delta C_s) + \beta I \quad (7)$$

$$I = -RT\beta\kappa_M(\Delta C_n + v\Delta C_s) + \frac{\frac{v_1}{2}\tau_1 + \frac{v_2}{2}\tau_2}{Fc_s}\kappa_M RT\Delta C_s + \kappa_M \frac{U_M}{d_M} \quad (8)$$

Where, the salt composes of a z_1 -valent cation and a z_2 -valent anion which dissociates into v_1 cations and v_2 anions. $v = v_1 + v_2$, and c_s is defined as the arithmetic mean of the salt concentrations on both sides of a membrane. ω and σ are the permeation and reflection coefficients of solute through membrane, respectively. L_p and β are the hydraulic and electro-osmotic coefficient of water through membrane, respectively. τ is the transport number of ion through membrane. κ_M and d_M are the conductivity and thickness of membrane, respectively. U_M is the potential applied on a membrane.

Process model Introduced the equations (5)-(8) into the equations (1)-(4), a first-order differential equation set (9) is obtained. According to the limited condition of uniform current densities, the current density can be deduced as Equation (10). Where, U_t is the total potential applied on a pair of membranes, κ_{dc} and κ_{cc} are the conductivities of solutions in dilute and concentrated compartments, respectively. And the relationship between conductivity and concentration of salt solution is obtained by regressing the experimental results.

$$\begin{aligned} \frac{dC_{s,dc}}{dy} &= \frac{1}{u_{dc} \cdot a} \{-RTC_{s,dc}[(C_{n,dc} - C_{n,cc})\sum_m(L_{p,m}\sigma_{n,m}) + v(C_{s,dc} - C_{s,cc})\sum_m(L_{p,m}\sigma_{s,m})] + \frac{RT(C_{s,dc} + C_{s,cc})}{2}[(C_{n,dc} - C_{n,cc}) + v(C_{s,dc} - C_{s,cc})] \\ &[(1-\sigma_{s,CM})L_{p,CM} + (1-\sigma_{s,AM})L_{p,AM}] - RTv(C_{s,dc} - C_{s,cc})\sum_m\omega_{s,m} + (C_{s,dc}\sum_m|\beta_m| - \frac{\sum_m[\frac{v_1}{2}\tau_{1,m} + \frac{v_2}{2}\tau_{2,m}]}{Fv})I\} \\ \frac{dC_{s,cc}}{dy} &= \frac{-1}{u_{cc} \cdot a} \{-RTC_{s,cc}[(C_{n,dc} - C_{n,cc})\sum_m(L_{p,m}\sigma_{n,m}) + v(C_{s,dc} - C_{s,cc})\sum_m(L_{p,m}\sigma_{s,m})] + \frac{RT(C_{s,dc} + C_{s,cc})}{2}[(C_{n,dc} - C_{n,cc}) + v(C_{s,dc} - C_{s,cc})] \\ &[(1-\sigma_{s,CM})L_{p,CM} + (1-\sigma_{s,AM})L_{p,AM}] - RTv(C_{s,dc} - C_{s,cc})\sum_m\omega_{s,m} + (C_{s,cc}\sum_m|\beta_m| - \frac{\sum_m[\frac{v_1}{2}\tau_{1,m} + \frac{v_2}{2}\tau_{2,m}]}{Fv})I\} \\ \frac{dC_{n,dc}}{dy} &= \frac{1}{u_{dc} \cdot a} \{-RTC_{n,dc}[(C_{n,dc} - C_{n,cc})\sum_m(L_{p,m}\sigma_{n,m}) + v(C_{s,dc} - C_{s,cc})\sum_m(L_{p,m}\sigma_{s,m})] + \frac{RT(C_{n,dc} + C_{n,cc})}{2}[(C_{n,dc} - C_{n,cc}) + v(C_{s,dc} - C_{s,cc})] \\ &[(1-\sigma_{n,CM})L_{p,CM} + (1-\sigma_{n,AM})L_{p,AM}] - RTv(C_{n,dc} - C_{n,cc})\sum_m\omega_{n,m} + (C_{n,dc}\sum_m|\beta_m|)I\} \\ \frac{dC_{n,cc}}{dy} &= \frac{-1}{u_{cc} \cdot a} \{-RTC_{n,cc}[(C_{n,dc} - C_{n,cc})\sum_m(L_{p,m}\sigma_{n,m}) + v(C_{s,dc} - C_{s,cc})\sum_m(L_{p,m}\sigma_{s,m})] + \frac{RT(C_{n,dc} + C_{n,cc})}{2}[(C_{n,dc} - C_{n,cc}) + v(C_{s,dc} - C_{s,cc})] \\ &[(1-\sigma_{n,CM})L_{p,CM} + (1-\sigma_{n,AM})L_{p,AM}] - RTv(C_{n,dc} - C_{n,cc})\sum_m\omega_{n,m} + (C_{n,cc}\sum_m|\beta_m|)I\} \\ \frac{du_{dc}}{dy} &= -\frac{1}{a} \{-RT[(C_{n,dc} - C_{n,cc})\sum_m(L_{p,m}\sigma_{n,m}) + v(C_{s,dc} - C_{s,cc})\sum_m(L_{p,m}\sigma_{s,m})] + (\sum_m|\beta_m|)I\} \\ \frac{du_{cc}}{dy} &= \frac{1}{a} \{-RT[(C_{n,dc} - C_{n,cc})\sum_m(L_{p,m}\sigma_{n,m}) + v(C_{s,dc} - C_{s,cc})\sum_m(L_{p,m}\sigma_{s,m})] + (\sum_m|\beta_m|)I\} \end{aligned} \quad (9)$$

($m=CM, AM$)

$$I = \frac{U_t - RT[(C_{n,dc} - C_{n,cc}) + \nu(C_{s,dc} - C_{s,cc})] \sum_m (|\beta_m| d_m) + \frac{2RT}{F} \frac{C_{s,dc} - C_{s,cc}}{C_{s,dc} + C_{s,cc}} \sum_m \left(\frac{\nu_1}{z_1} \tau_{1,m} + \frac{\nu_2}{z_2} \tau_{2,m} \right) d_m}{d_{CM} / \kappa_{CM} + d_{AM} / \kappa_{AM} + a / \kappa_{dc} + a / \kappa_{cc}} \quad (10)$$

There are six dependent variables including $C_{s,dc}$, $C_{s,cc}$, $C_{n,dc}$, $C_{n,cc}$, u_{dc} and u_{cc} in equation (9). And the independent variable is the flow length (y). Setting the initial values of variables, the target value of removal ratio of salt (R_s) and the values of other parameters, the equation (9) is solved by the numerical method. While the difference between the calculated and target values of removal ratio of salt ($R_s - R_s^f$) is small enough, the flow length (y^f) for obtaining the target value of desalination ratio is calculated. For continuous operation mode, y^f means the required total length of the membrane. For batch operation mode, the operation time can be calculated by flow length. If there isn't neutral solute in the aqueous solution, the model can be directly used to simulate the desalination process of a salt solution.

RESULTS AND DISCUSSION

Selection of desalination conditions The variations of organic acids salts' molar number in dilute compartment ($n_{s,dc}$) with operation time (t) under different operation conditions are shown in Fig. 3. The total current efficiency (η) and energy consumption (P) for varied potential are given in Fig. 4a at the same desalination ratio of organic acids salts ($R_s=90\%$) and those for varied velocity (u) are shown in Fig. 4b at the same operation time ($t=240$ min). With the increase of potential, the energy consumption increases and the current density decreases gradually. Meanwhile, the loss of PDO increases. And it is shown that the energy consumption has negligible differences with velocity. Since the loss of PDO increases gradually with the velocity, the suitable velocity is selected to be 1.03 cm s^{-1} . Under these conditions, about 90% of organic salts in PDO broth are removed by ED process successfully. Meanwhile, the membrane fouling is alleviated effectively by changing pole and cleaning membranes, so that the further industrial production is possible.



Fig.3 Molar number of organic acids salts in dilute compartment vs. operation time under different potentials (a) and flow rate (b) (a: $u=1.03 \text{ cm s}^{-1}$, $V_{dc}=3 \text{ L}$; b: $U=7 \text{ V}$, $V_{dc}=1 \text{ L}$)

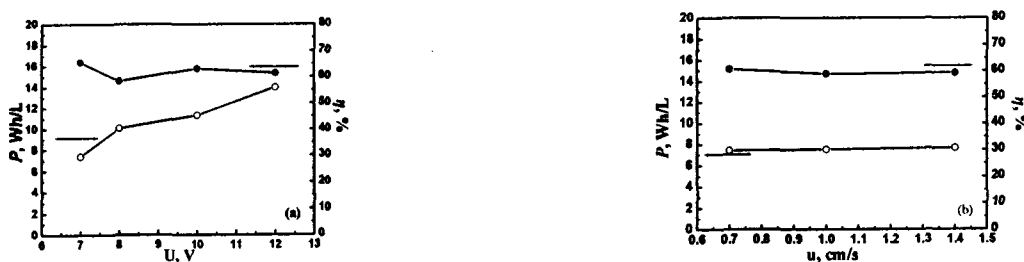


Fig.4 Current efficiency and energy consumption vs. potential (a) and flow rate (b) in ED experiments of PDO fermentation broth

Loss of PDO product through IEMs While the ratio of membrane area to solution volume in simulated diffusion experiment and that in actual ED process are kept equal, the diffusions of PDO are compared and shown in Fig.5. The data in simulated experiment is the sum of the diffusion amount of PDO through AEM and through CEM. It is shown that the diffusion of PDO through IEM is exactly the main reason of its loss. Therefore, the operation time of desalination should not be too long. However, the whole economic estimation is still not considered here.

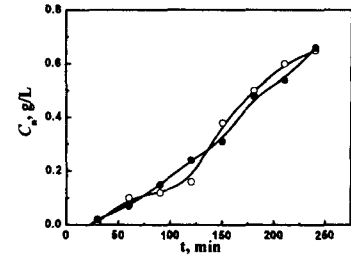


Fig.5 The concentration of PDO in concentrated compartment vs. diffusion time (O: diffusion result in actual ED experiment; ●: diffusion result in simulated diffusion experiment)

Verification of the model For the experiments described in literature [5], the comparisons between simulated and experimental results under different conditions are shown in Fig. 7. During simulation, it is noted that the values of the conductivities of IEMs come from the literature [5], the reflection coefficient of salt through membrane are assumed to be 1.0, and the other transport coefficients come from the literature [6]. As shown in Fig.6a, the simulations from the model are fitted well for the experimental results under high velocity. And for the simulations under varied velocities, the conductivities of membranes in the model are set to be low to reflect the influence of concentration polarization. It is found that the decreasing of conductivity of membrane is effective for verifying the desalination process under low velocity (see Fig.6b).

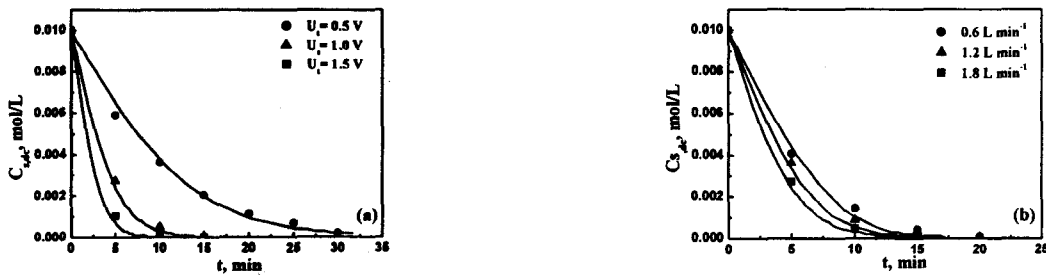


Fig.6 Comparison between simulated results by model and experimental results from literature [4] for desalination of NaCl under varied potentials (a) and flow rates (b) (symbol, experiment results; line, simulated results; a, $u = 1.8 \text{ L min}^{-1}$; b, $U_1 = 1.0 \text{ V}$)

Discussion of the initial values of variables in the model In the following simulations, the desalination of sodium chloride by ED method is regarded as the example. The dimensions of ED equipment are set as same as the values in Section 2, and the number of cell pairs is 2. The potential applied on a pair of membranes is kept at 1.0 V. The reflection coefficients of salt through membranes in the model are assumed to be 1.0, and the other transport coefficients still come from literature [6].

While the initial values of $C_{s,dc}$, u_{dc} and u_{cc} are kept to be 0.05 M, 3.0 cm s^{-1} , 3.0 cm s^{-1} , respectively, the simulated results of the variations of R_s versus y under varied initial values of $C_{s,cc}$ are shown in Fig. 7. As presented in it, the required flow length decreases with the increase of initial concentration in concentrated compartment, which can be explained by the decrease of the electric resistance of solution with the increase of the initial value of $C_{s,cc}$. However, the maximal desalination ratio decreases with the increases of the initial value of $C_{s,cc}$, which isn't be discussed further in this paper. While the initial values of u_{cc} , $C_{s,dc}$ and $C_{s,cc}$ are kept to be 3.0 cm s^{-1} , 0.05 M, 0.05 M, respectively, the simulated results of the variations of R_s with y under varied initial values of u_{dc} are shown in Fig. 8. While the required removal ratios of salt are same, the flow length

increases with the increase of the initial value of u_{dc} . That means, the increase of the volume of desalinated solution needs longer flow length for achieving the same desalination ratio.

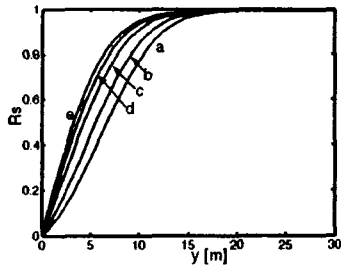


Fig.7 Simulated results of variation of desalination ratio vs. flow length under varied initial values of $C_{s,cc}$ (a, 0.005 M; b, 0.01 M; c, 0.025 M; d, 0.05 M; e, 0.1 M)

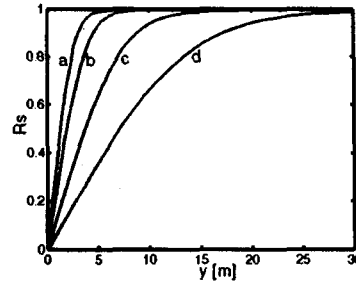


Fig.8 Simulated results of variation of desalination ratio vs. flow length under varied initial values of u_{dc} (a, 1.0 cm s^{-1} ; b, 1.5 cm s^{-1} ; c, 3.0 cm s^{-1} ; d, 6.0 cm s^{-1})

Simulation of desalination process of actual PDO fermentation broth While the acetate is used to substitute all kinds of organic salts in actual PDO fermentation broth, the comparisons between simulated and experimental results under different values of initial concentrations in concentrated compartment are shown in Fig. 9. From it, it is found that the simulations of the model can be used to describe the actual ED process. And for the desalination process of actual PDO fermentation broth, the initial value of $C_{s,cc}$ has a suitable scope, which is accorded with above discussions. Therefore, the model can be further used to instruct this ED process.

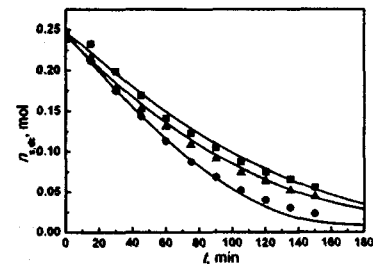


Fig.9 Comparison between simulated results by model and experimental results of desalination of actual PDO fermentation broth under varied initial values of $C_{s,cc}$ (■ 0.01 M; ● 0.05 M; ▲ 0.30 M)

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