SEPARATION OF AQUEOUS MULTI-COMPONENT MIXTURE BY USING HOLLOW FIBER REVERSE OSMOSIS MODULE

by

SENTHILMURUGAN S

Chemical Engineering Department

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Dedicated to my Grandfather and Grandmother

Sri K. Krishna Ramanu Jayam and Smt K. Subbalakshmi

and my parents

Sri S. Subbiah and Smt S Jagajothi

CERTIFICATE

I am satisfied that the thesis presented by ***Senthilmurugan S*** *is worthy of consideration for the award of degree of Doctor of Philosophy and is a record of the original bonafide research work carried out by him under my guidance and supervision and that the results contained in it have not been submitted in part or full to any other university or institute for award of any degree/diploma.*

I certified that he/she has pursued the prescribed course of research.

SHARAD KUMAR GUPTA

Professor

Chemical Engineering Department

Indian Institute of Technology, Delhi

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(SENTHILMURUGAN S)

ABSTRACT

Separation of single and two solutes system from their aqueous solution is carried under a variety of operating conditions by using radial flow hollow fiber reverse osmosis (HFRO) module. The solutes chosen are sodium chloride (NaCl), sodium bromide (NaBr) and potassium bromide (KBr) for inorganic separation and phenol, pentachlorophenol (PCP), and 2,4-dinitrophenol [DNP] for organic separation. For multicomponent separation, experiments are carried for the following ternary systems: (1) NaCl-NaBr-Water, (2) NaCl-KBr-Water, (3) Phenol-PCP-water, (4) Phenol-DNP-water, (5) PCP-DNP-Water. All separation experiments are carried out for a variety of operating conditions such as different feed pressure, feed flow rate, and feed concentration. However literature [76] shows that the rejection of organic compounds change with feed pH. The experiments for organic compounds were performed for different pH

A mathematical model for radial flow HFRO module is developed for both single and two solute systems. Model involves equations of the membrane transport model, concentration polarization model, and local solvent and solute mass balances. The system of coupled partial differential equations is solved numerically using the finite difference method. The three-parameter model has been shown in literature [72,73,70,79] to be more accurate model for describing the mass transport processes in the reverse osmosis membranes. Therefore, the three parameter Spiegler-Kedem (SK) model [14] is used for describing the single solute mass transport across the membrane. The concentration polarization is taken into account by using the film theory [4]. The pressure drop for the permeate and bulk streams are estimated using Hagen-Poiseuille and the Ergun's equation respectively. In case of two solute systems, the mass transport across the membrane and film is described by the extended Spiegler-Kedem (SK) model

[21] and film theory respectively. The mass transfer coefficient used in concentration polarization model is estimated by using the standard correlation available in literature [9,56,59,89].

Two limiting cases of the system of equations above are used to arrive at the analytical solutions and check the validity of the numerical solution. Using simulation studies, the significance of the third membrane parameter, the reflection coefficient is investigated in detail. It is found that when the reflection coefficient is decreased from its maximum value of one, the permeate flow rates are higher and the permeate concentration differs substantially from that reported by the two parameter membrane model of Sekino [56]. The maximum difference in the permeate flow rates between the two cases for sigma $1>\sigma>0.8$ can be as large as 13% while the differences in the permeate concentrations can be as large as 97%.

In the case of multicomponent model, the simulation of the separation of phenol and sodium chloride in an aqueous solution is carried out at different operating conditions and the role of the solute-solute interaction parameter appearing in the extended Spiegler-Kedem model is further investigated. The simulation results indicate that the negative rejection of phenol may be possible if the solute-solute interaction between the phenol and sodium chloride is higher than 8×10^{-11} $m^4/kg/s$.

Optimization of the B9 Permasep hollow fiber reverse osmosis module is studied by changing module physical parameters such as length and diameter of fibers and number of fibers for fixed feed properties, flow parameters such as feed flow rate and pressure. The optimization depends on the objective function. Four objective functions used in the work are derived based on the pressure difference across the membrane, recovery, rejection and volume of the membrane module. Depending on the objective function, the optimum values of physical parameters such as number of fiber, fiber

diameter and length are determined and the present method of optimization is compared with the method of Starov et al. [58,61].

The model for single solute system has five unknown parameters such as three membrane transport parameters (pure water hydrodynamic permeability (A), solute permeability (P_m) and reflection coefficient (σ)) and two constants (a and b) used in the mass transfer coefficient correlation. For two solute system, the extended SK model has one more parameter solute-solute interaction (A[i,j]).

These parameters are estimated by using error minimization simplex search [100]. The pure water hydrodynamic permeability (A) was estimated by using pure water permeability data. The value of A increases linearly as the feed temperature increases. The remaining two parameters of SK model and two parameters of mass transfer coefficient correlation were estimated by using the single solute separation data for constant feed flow rate and feed concentration. The estimated values of constants used in the mass transfer coefficient correlation are found to be in very good agreement with the values available in literature [89]. Further, these constants (a and b) are assumed to be constant. The estimated parameters of SK model are then used for prediction of the remaining data set which has not been used for parameter estimation. The errors between the experimental and theoretical predictions for all the cases are less than 15% for both permeate flow rates as well as permeate concentrations. The model parameters such as the solute permeability and the reflection coefficient are constant for all phenolic compounds and potassium bromide. However, in the case of sodium chloride and sodium bromide, the solute permeability increases as the feed concentration is increased from 500 ppm to 15000 ppm and after this concentration the solute permeabilities become independent of the feed concentration. On the other hand, the reflection coefficient for both sodium chloride and sodium bromide goes through a

minimum and then increases to a maximum before reaching a constant value as the feed concentration is increased. For the organic solutes, the solute permeability (P_m) decreases while reflection coefficient increases as the feed pH is increased.

To understand the importance of the third parameter in Spiegler-Kedem model, the reflection coefficient, the same data is also analyzed by assuming that the mass transport may be described by the solution diffusion (SD) model. It is conclusively shown that for both organic as well as inorganic compounds, the Combined Film Spiegler-Kedem (CFSK) model provides much better theoretical predictions than the Combined Film Solution Diffusion (CFSD) model.

Finally, the solute-solute interaction parameter of extended SK model is estimated for experimentally studied ternary systems data. The estimated parameters of extended SK model are then used for the prediction of remaining data set which is not used for the parameter estimation. The errors between experimental and theoretical predictions are less than 15% for both permeate flow rates as well as permeate concentrations. The value of solute-solute interaction parameter indicates that interaction between the inorganic systems is much stronger than between the organic solutes chosen for the present study. To verify these results, the model predictions are determined by assuming that there is no interaction between the solutes i.e., $A[i,j]=0$. The results show that errors between the experimental and theoretical predictions for this case are very high for the inorganic systems. But for organic systems, the errors of both with interaction and without interaction are negligible.

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