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Ultrafiltration modeling of multiple solutes system for continuous cross-flow process

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Abstract

A mathematical model suitable for the multiple solutes system in continuous cross-flow ultrafiltration is developed. This model is based on mass balance analysis coupled with the filtration theory (osmotic pressure model, Kozeny–Carman equation), resistance-in-series model and gel polarization model. This model is characterized by the parameters R_m, P_m, K_b, K_{bi} and k_i. These parameters are estimated by using the Levenberg–Marquardt method coupled with the Gauss–Newton algorithm based on the experimental data obtained from the treatment of pretreated palm oil mill effluent (POME) as a feed in the pilot plant scale ultrafiltration system. The pretreated POME is composed of a ternary system with the solutes of carbohydrate constituents, crude protein and ammoniacal nitrogen. The simulation results show a good agreement with the experimental data. The proposed model is suitable for predicting the performance of multiple solutes in an ultrafiltration process. The concentration of each solute present is correlated with the COD value of the permeate stream.

Keywords: Membranes; Modeling; Filtration; Mathematical; POME; COD

1. Introduction

Ultrafiltration process uses a porous membrane to separate water and microsolutes from the solution containing macromolecules and colloids. The average pore diameter of the ultrafiltration membrane lies from 10 to 1000 Å (Baker, 2000). Ultrafiltration has become an increasing important separation process for the concentration, purification or dewatering of macromolecules and colloidal species in the solution (Yeh et al., 2004). It is gaining importance for water and industrial wastewater treatment especially in the recovery of chemicals from the industrial wastewater, desalination, drinking water purification, removal of oil from oil–water emulsions (Tansel et al., 2000).

The key factor determining the performance of the ultrafiltration membranes is the gel polarization where the rejected solutes deposited on the membrane surface. The gel polarization causes membrane fouling and leads to the drop in permeate flux. This gel layer of rejected solutes on the membrane surface forms a second barrier to the flow through the membrane.

A number of mathematical models are available in the literature to describe the transport mechanism through the ultrafiltration membranes by considering the gel polarization phenomena. The most common model used in describing the ultrafiltration is the resistance-in-series model (Tansel et al., 2000; Kumar et al., 2004; Gehlert et al., 2005; Bhattacharjee and Datta, 2003). The resistance-in-series model assumes that the flux of permeate is proportional to the transmembrane pressure and inversely proportional to the viscosity of the suspending solution where the parameter of hydraulic resistance is being introduced. The hydraulic resistance is the total resistance exerted by the membrane and solutes.

Damak et al. (2004) developed a fluid dynamic model for the cross-flow filtration tubular membranes. A method of coupling the Navier–Stokes and Darcy equations, using a finite difference technique to simulate laminar fluid flow in the tube and in the porous wall was presented. Djurić et al. (2004) proposed the flux (J_v) models as function of concentration factor (CF), flowrate (Q), temperature (T) and

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transmembrane pressure (ΔP). The one-, two- and three-variable functions are suggested: $J_v^{-1}(\mathrm{CF})$, $J_v^{-1}(\mathrm{CF}, Q)$, $J_v^{-1}(\mathrm{CF}, T)$, $J_v^{-1}(\mathrm{CF}, \Delta P)$, $J_v^{-1}(\mathrm{CF}, Q, T)$ and $J_v^{-1}(\mathrm{CF}, Q, \Delta P)$. These mathematical models predicted the separation time if the initial and final concentrations of permeate are known.

A general membrane fouling model accounting the internal clogging, partial and total clogging, cake deposition and cake deposition with retroflux for ultrafiltration system was developed by Ghaffour (2004). The model predicted the permeate flux and a relationship for the limiting flux against the bulk concentration and it was developed based on the experimental data. Katsikaris et al. (2005) combined the thin film theory and Spiegler–Kedem's model to obtain the mathematical model for the simulation of ultrafiltration system and accounted the concentration polarization phenomena.

Yeh et al. (2004) derived the equations for the prediction of permeate flux in a tubular membrane module from the momentum balance with declining flowrate and transmembrane pressure along the membrane tube. The model predicted the effects of solute concentration, transmembrane pressure, tube radius and tube length on the flux and pressure drop along the membrane tube. Sondhi and Bhave (2001) combined the d'Arcy's permeability model and Kozeny–Carman equation to predict the permeate flux and the cleaning time of ceramic ultrafiltration with back pulsing.

However, the models proposed in the literature are only suitable to predict the performance of ultrafiltration with the single solute system. When multiple solutes system is used, these models can only predict the total permeate concentration of the system. In the industrial application, multiple solutes systems are often encountered and the mass transport of each solute in the multiple solutes system is important. In the present study, the ultrafiltration system is used to separate the organic matters from pretreated palm oil mill effluent (POME). POME is the liquid waste discharged from the palm oil mill with high chemical oxygen demand (COD). The transport of the organic matters (mainly carbohydrate constituents, crude protein and ammoniacal nitrogen) through the ultrafiltration is very important. The transport of these organic matters will finally determine the COD and ammoniacal nitrogen concentration in the permeate. The COD and ammoniacal nitrogen concentration of the final discharge should meet the standard discharge limit of the Environmental Quality Act 1976 set by the Department of Environment (DOE) of Malaysia.

The objective of the present study is to develop a time-dependent mathematical model to predict the performance of an ultrafiltration process in the separation of POME (multiple solutes system). The model is based on the mass balance analysis coupled with the filtration theory (osmotic pressure model, Darcy's law), resistance-in-series and gel polarization models. The measurable objectives in the present study are:

(1) To develop equations (time-dependent) for prediction of the volume flux of permeate and gel layer resistance.
(2) To develop model for the prediction of concentrations of each solute in the permeate of the multiple solutes system.
(3) To estimate the parameters of the model from the experimental data obtained from the ultrafiltration system.
(4) To validate the mathematical model by comparing the simulation results with the experimental data.
(5) To correlate the concentration of each solute with the COD of the permeate obtained from the ultrafiltration system for the treatment of POME.

2. Model development

A mathematical model is developed to provide a conceptual framework for understanding the phenomenon responsible for flux decline for the multiple solutes system in the ultrafiltration process. During filtration process, the solvent is transported by pressure-driven convective flow through the pores. Separation occurs because the solvent is filtered through some of the pores in the membrane. The ultrafiltration membrane rejects the solutes by sieving action.

The membrane rejects the multiple solutes by steric hindrance where the membrane is considered a sieving barrier that retains molecules according to their size. Besides van der Waals, electrostatic or chemical interactions between membrane and solutes or even among solutes themselves play a large part in building of filtration selectivity. The total resulting effects are complex. A typical case is the industrial wastewater containing complex solutions, where all these interactions are involved on numerous and often poorly understood solutes.

The POME, for example, is a complex mixture of organic matters and all specific components of the organic matters could not be determined. The carbohydrate constituents comprise of low molecular weight monosaccharide (180 kg/kmol) to high molecular weight polysaccharide (400,000 kg/kmol). The crude protein comprises from the simplest compounds of amino acids (75 kg/kmol) to the most complex compounds of proteins (450,000 kg/kmol). Nitrogen in POME is originally present in the form of organic (protein) nitrogen, and as time progresses, the organic nitrogen is gradually converted to ammoniacal nitrogen which has the molecular weight of 17–35 kg/kmol.

Darnon et al. (2002) had proposed a model based on the theory of thermodynamic of irreversible process for ultrafiltration system of complex biological solutions. The ultrafiltration of a single protein (β-lactoglobulin) solution was compared with a mixture of yeast extract and β-lactoglobulin. Based on the obtained results, solute–solute interactions in the mixture were negligible especially when the solutes were of biological type and the system was operated at the pH away from their isoelectric point. Therefore, solute–solute interaction can be neglected in the pretreated POME system as the pretreated POME was of biological origin (palm oil fruit) and the system was operated at pH 6 which was away from its isoelectric point.

The membrane continuously rejects the solutes and the rejected solutes are deposited on the membrane surface. At the same time, due to stirring action caused by the superficial velocity, some solutes are removed from the membrane surface and go into the bulk (back transport effect). The deposited layer of rejected solutes on the membrane surface is termed as "gel layer". The rejected solutes are assumed to be deposited on the