

Modeling and Performance Characteristics of Nanofiltration by DSPM and ARX Model

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ABSTRACT

The DSPM (Donnan Steric Pore Model) is integrated with osmotic pressure to develop nanofiltration modeling. The new model establishes the relation between the pressure across the membrane to the concentrations of permeate and retentate at a particular solute concentration in the feed. The model is successfully tested against the experimental data. We also developed the nanofiltration modeling with ARX (Auto Regressive Exogeneous), a type of black box model. The data for modeling is obtained by simulation of the first principle model. With the help of identification toolbox, an ARX model is developed considering pressure across the membrane as input variable (manipulated variable) and percentage rejection as output variable (control variable). The model is validated against a data subset used for estimation of model. However, the models are sustained only at low feed concentrations. The model output data are compared to the actual output data and calculate the mean square errors (MSE). The obtained residuals are well satisfactory in the range of 0.99. Hence, the derived modeling sustains for nanofiltration and its control operations.

Keywords: Nanofiltration, simulation, DSPM, ARX Model

1.0 INTRODUCTION

Nanofiltration membranes provide separation performance between reverse osmosis and ultrafiltration membranes, which makes them useful for separating toxic metals, hardness ions, oil emulsions, and dissolved organics from water. More stringent water quality regulations and decreasing availability of pristine fresh water resources demands improved water purification methods [1, 2]. Nanofiltration has become a popular technology to augment conventional water treatment processes because of its low operating pressure, high retention of multivalent ions and dissolved organic molecules larger than about 300 Da, and relatively low costs. The growing consumption of water in all over the world combined

with the industrial and agricultural activities is increasing salinity and pollutant (e.g. nitrates) levels in water. Nanofiltration membrane processes are better suited for the removals of ions from aqueous solutions with higher permeate fluxes than those obtained by reverse osmosis at the same applied pressure. Therefore, NF can be a good option either to reuse brackish water in many industrial applications or to obtain drinking-water (Van der Bruggen and Vandecasteele, 2003). The NF modelling is very useful to evaluate the most suitable membrane configurations for a particular water composition. Several models have been developed to model the transport of the different feed components inside the membrane in order to obtain their concentration in the permeate. The phenomenological approaches are not

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useful for complex ionic mixtures because NF performance is strongly dependent on feed composition [3].

Design and operation of NF plants or NF-assisted treatment has been and continues to be the subject of numerous R&D endeavors. However, no generalized procedure is concluded to enable prediction of a NF system performance under variable source conditions. The performance, in terms of flux decline, depends on numerous variables, including, but not limited to, membrane characteristics and module geometry, raw water characteristics, concentrations and type of pollutants and operating conditions. In order to develop a performance prediction methodology, the data available from numerous published endeavors should be reduced and managed to enable development of empirical formulae correlating flux decline with principal operating parameters and water characteristics [4]. There is a pressing need for simulation tools in NF because the complexity of the transport mechanisms, coupled with the wide range of different nanofilters and plant designs available, makes it extremely difficult to choose the right membrane and plant design for a given application in a reliable and cost effective way [5].

A new, semi-empirical model for solvent transport through nanofiltration membranes, based on Hagen–Poiseuille and other derived models is discussed by Geens *et al.* [6]. Al Zoubi *et al.* [7] did experiments and modeling for three commercial nanofiltration membranes (NF90, NF270, N30F) used to treat highly concentrated different salts solutions (KCl, Na₂SO₄, and MgSO₄) in a cross-flow filtration set-up. Chakraborty *et al.* [8] studied the effect of different process parameters on separation of dye conducting experiments using a 400 molecular weight cut-off membrane

and develops a mass transfer model to predict permeate flux and concentrations in a batch cell.

2.0 METHODS

2.1 Modeling the Nanofiltration Process

A semi empirical model is developed from the mass balance equations starting from the extended Nernst-Planck equation. [9]

$$j_i = -D_i \frac{dC_i}{dx} - z_i D_i C_i \frac{F}{RT} \frac{d\phi}{dx} + K_i C_i V \quad (1)$$

After applying the electrical neutrality conditions, the above equation can be written as

$$J_i = M_i' \frac{dC_i}{dx} + M_i C_i J_v \quad (2)$$

The diffusion effects can be neglected when we deal with liquids, so the term including $\frac{dC_i}{dx}$ can be eliminated. So flux is a function of J_v , which depends upon the pressure applied or the trans-membrane pressure. The concentration of the retentate is rising continuously during the concentration process, which means the increase of the osmotic pressure as well. The higher and higher osmotic pressure reduces the driving force during the constant trans-membrane pressure tests. The permeate flux is reduced by the increasing osmotic pressure and the fouling resistance. The flux can be expressed as the function of the driving force and the resistances as

$$J = \frac{(\Delta P - \Delta \pi)}{\mu R_{tot}} \quad (3)$$

The osmotic pressure-concentration relationship has been established by [9],

$$\Delta\pi = \beta C_r RT \quad (4)$$

The equation (3) represents a straight line, intercept $\frac{\Delta P}{\mu R_{tot}}$, slope $\frac{\beta RT}{\mu R_{tot}}$. Experiments are done at varying pressures to calculate the parameters membrane resistance and concentration polarization index β .

To calculate the membrane fouling, tests are run with pure water, before and after the experimental runs. When no solutes are present, $C_r=0$, hence

$$J_w = \frac{\Delta P}{\mu R_M} \quad (5)$$

After the experiment, pure water can be loaded and test is run for different pressures, which gives us an increased resistance, R_{tot} .

$$J_w = \frac{\Delta P}{\mu R_{tot}} \quad (6)$$

The model derived from ENP and osmotic pressure equations are combined together, for the semi empirical model, and Hagen-Poiseulli's equation is used to substitute for flux and bringing in the pressure term,

$$MC_p \frac{r_p^2}{8\mu\lambda} \Delta P = J_w - \frac{\beta RT C_r}{\mu R_{tot}} \quad (7)$$

Combining equations 3, 4 and 7, we have

$$\frac{r_p^2}{8\mu\lambda} n \Delta P [1 - MC_p] = \frac{\beta RT C_r}{\mu R_{tot}} \quad (8)$$

or

$$J_v [1 - MC_p] = \frac{\beta RT C_r}{\mu R_{tot}} \quad (9)$$

The above model gives the relation between permeate retentate concentrations and the effective pressure/flux. From the equation it is clear that the concentrations depend

upon the nature of solute ions and the total membrane resistance.

2.2 ARX Model

$$A(q^{-1}) y(t) = q^{-d} B(q^{-1}) u(t) + e(t) \quad (10)$$

The coefficient of polynomials A and B are estimated by minimizing the sum of the squared equation error $\varepsilon(t)$ defined as the difference between the actual and estimated outputs.

$$\begin{aligned} \Phi(t) &= [y(t-1) \dots y(t-n_a) \ u(t-1) \dots u(t-d-n_b)]^T \\ \theta &= [-a_1 \dots -a_{n_a} \ b_0 \dots b_{n_b}]^T \end{aligned} \quad (11)$$

where ϕ is the regression vector, which contains all the past inputs and past outputs.

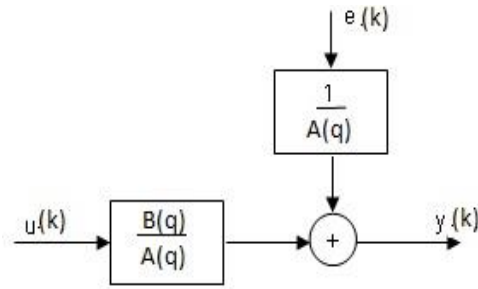


Figure 1 ARX Structure

Using the data, identification toolbox in MATLAB is made to good use in formulation of the following models.

To estimate the parameters a_i and b_i of the ARX model shown in Figure 1, the arx function is used.

$$m = \text{arx}(z, [na \ nb \ nk]);$$

where z is a data object, defining the inputs and outputs, $[na \ nb \ nk]$ are the corresponding orders and delays that define the exact structure of the model. The function implements least squares estimation method, using the MATLAB “/” operator for over determined linear equations.

2.3 Estimated Models

For feed concentration of 10mg/L MgSO₄ the ARX model of 3rd order evaluated is:

$$A(q) = 1 - 1.333 q^{-1} - 0.3333 q^{-2} + 0.6667 q^{-3}$$

$$B(q) = -3.094e-005 q^{-1} + 6.189e-005 q^{-2} - 3.094e-005 q^{-3}$$

For feed concentration of 5 mg/L MgSO₄ model obtained is:

$$A(q) = 1 - 1.333 q^{-1} - 0.3333 q^{-2} + 0.6667 q^{-3}$$

$$B(q) = 0.000272 q^{-1} - 0.000544 q^{-2} + 0.000272 q^{-3}$$

A data subset is of the data used for estimation of the models is considered for model validation. The pressure values are gives as the input and a plot is made between the obtained rejections output and the pressure input. In this way the model is validated.

3.0 RESULT AND DISCUSSION

3.1 Effect of Pressure on Rejection at Different Feed Compositions

Model validation is the final stage in system modeling. Here, the estimated model will be concluded whether it can represent the system or not. To validate the model, the estimated model will be used to generate the prediction output based on a given input. Then the generated output will be compared with the measured output. The errors between the measured and the predicted output are called the prediction error or residual. It can be realized by

$$\epsilon(x) = y(x) - y'(x) \quad (12)$$

Rejections calculated are tabulated in Table 1 for 5mg/L feed solution. The rejections are calculated at 1, 2, 2.5, 3, 4, 5, 6 kg/cm² pressures using the formula

$$\%R = 100 \left[1 - \frac{c_p}{c_b} \right] \quad (13)$$

3.2 Simulated v/s Experimental Rejections, at Various Feed Concentrations

The experimental observations are plotted in Figure 2 and the results obtained from the simulation of model are compared with the experimental data and plotted in Figure 3. The maximum rejection observed is 57%, which implies that, with increase in feed concentration, rejection reduces keeping the pressure constant. So higher rejections are possible only at higher pressures, and depends on the feed concentration. The higher the feed concentration, the higher pressure should be. This is evident from Figure 2, 3 and 4.

Table 1 Pressure v/s rejections for 5mg/L feed solution

Pressure (kg/cm ²)	% Rejection simulated	% Rejection experimental
1	22.41	29.01
2	23.38	30.69
2.5	23.91	31.45
3	24.45	32.38
4	25.29	33.68
5	26.16	34.76

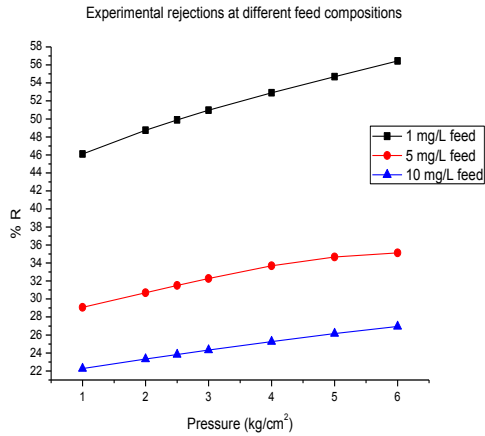


Figure 2 Comparison of % rejection at different feed compositions

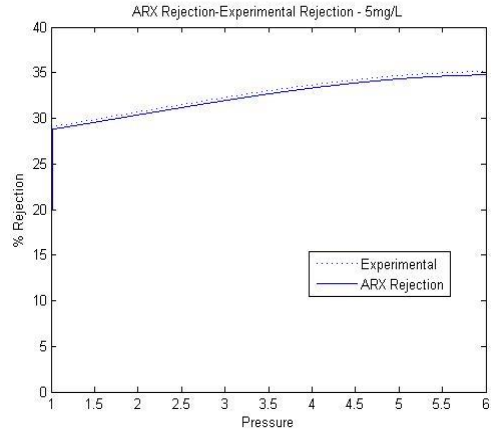


Figure 4 Experimental and ARX Rejections for 5mg/L solution

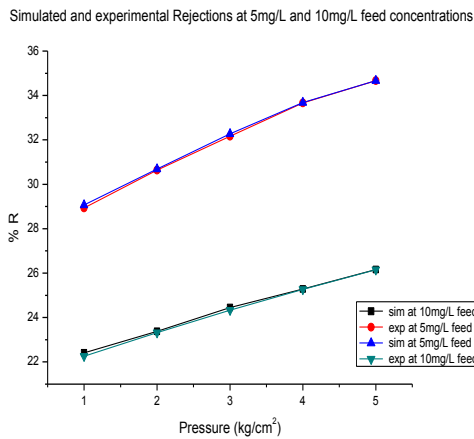


Figure 3 Simulated v/s experimental rejections for feed concentrations

In Figures 4 and 5, the formulated ARX models are simulated, and are compared to the experimental observations. It should be noted that the models will vary with the operating conditions. The given models in this paper are valid only on room temperature and given range of pressures. The simulated and experimental results are observed to be well in agreement with each other.

The order of the ARX model is taken as 2 by trial and error. Higher orders were seen to be giving considerable errors, order 2 gave the best fit. The residuals calculated for 5mg/L feed were 0.005 on an average, which proves the model is acceptable for prediction purposes.

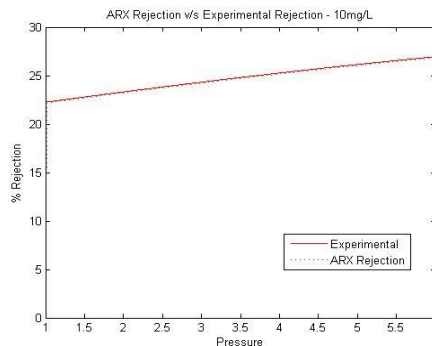


Figure 5 Experimental Rejection and ARX rejection for 10mg/L solution

The rejections calculated from the model equation and the rejections simulated using ARX model is compared in the following plot. It can be seen that the ARX model is able to predict the rejections obtained experimentally with negligible error of less than 0.5%.

3.3 Comparison of ARX with Models

Both the ARX and first principle models outputs are presented in Figure 6, for comparison purposes.

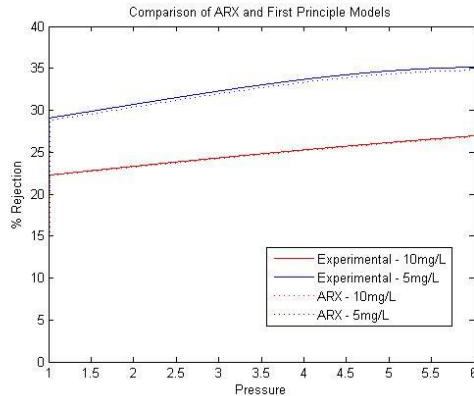


Figure 6 Comparison of ARX and first principle models

4.0 CONCLUSIONS

It is verified that the first principle model and ARX model is in good agreement with the experimental results. The proposed ARX model can be used to proceed further for control design of the nanofiltration process. The R^2 value of the ARX models were found out to be 0.9986 and 0.9991 for 5mg/L feed solution model and 10mg/L feed solution model respectively which makes them an ideal starting point for development of control strategies.

NOMENCLATURE

P	Applied Pressure
R_{tot}	Total Membrane Resistance
M	Fitting Parameter
R_M	Membrane Resistance
C_R	Retentate Concentration
C_P	Permeate Concentration
R	Rejection of solute
D	Diffusion coefficient
z_i	Valency of the ion i
J	Flux

R	Universal Gas Constant
C_i	Concentration of ion i in the solution
r_p	Pore radius of membrane
σ_i	Reflection coefficient of ion i
μ	Absolute viscosity of the solution
β	Ratio of concentration on membrane layer to concentration on retentate
π	Osmotic Pressure
λ	Thickness of the membrane

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