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# Modeling the permeate transient response to perturbations from steady state in a nanofiltration process

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#### ABSTRACT

Knowledge of the transient response to perturbations from steady state is of importance in treatment processes in order to predict the time required to achieve the maximum effect of any feed water concentration change. Experimentation was conducted to evaluate the membrane permeate transient response for single-stage and three-stage nanofiltration membrane systems when each system's feed water experienced a perturbation in water quality with a sudden increase in chloride. The transient response of a single nanofiltration membrane was described by a first order system with a time constant of 3.8 min. The transient response to a permeate concentration change in a nanofiltration membrane process was 99% realized in 7 min. Mathematical models were developed that accurately described permeate chloride concentrations as a function of time after a step-change occurred in feed water chloride concentration levels feeding the systems. Results indicate that first order modeling is satisfactory for the description of the transient response of staged nanofiltration systems.

Keywords: Membrane; Transient response; Modeling; Permeate water quality

### 1. Introduction

Pressure-driven membrane processes can be described by mathematical models. The basic models for reverse osmosis consist of extensions of the Nernst-Planck equation such as the homogeneous solution diffusion (HSD) and Donnan–Steric–Pore (DSP) models, the film theory model, coupling, and various empirical models for salt flux [1–9]. These models can be used to predict the resulting permeate water quality based upon feed water quality membrane properties, salt diffusion coefficients, water recovery, and feed pressure. Diffusion, sieving, convection, and other mechanisms can affect mass transport in membrane processes. The work described herein applies to diffusion-controlled mass transport.

It is generally accepted that the homogeneous solution diffusion (HSD) theory accurately described mass transfer through polymeric membranes [10,11]. According to this theory, the active layer of the membrane acts as a homogeneous phase in which water and solute pass

through a tortuous path. The solvent component passes through the membrane at the high pressure side driven by pressure, and the solute molecules diffuse through the membrane driven by a concentration gradient. Consequently, a definite equilibrium distribution of all solutes exists at the membrane/solution interface. Water and solute in the membrane are transported across the film, and driven in response to the pressure and concentration gradients, respectively, and their separate fluxes are influenced by their mobility's in the membrane.

At present many models are available to designers to capture steady-state behavior by estimating the equilibrium concentrations for HSD-derived models for a particular set of operating conditions; however, models capable of describing transient phenomena are few. One such model for a two-stage system has been presented [12]. Dynamic models for predicting transient phenomena in process systems have been developed for fuel cells but few if any exist for membrane processes [13,14].

Dynamic models would be useful for predicting changes in permeate conditions in a membrane system, and offer additional insights into how quickly the process can respond to a feed water concentration change. Such information could be useful to those water systems that vary their water supply sources having different qualities. Operators could predict changes expected in permeate quality on a daily basis based on changes in source water qualities. This paper presents the results of experimentation conducted to verify transient models for singlestage and three-stage nanofiltration processes.

#### 2. Mathematical fundamentals

The equations for the water mass transfer flux are proportional to the pressure differential across the membrane. The flux of water passing through the membrane can be predicted by the solvent mass transfer coefficient (MTC), the differential pressure and the osmotic pressure, as shown in Eq. (1):

$$F_{W} = K_{W} \left( \Delta P - \Delta \pi \right) = \frac{Q_{p}}{A} \tag{1}$$

where  $F_W$  is the water flux  $(L^3/L^{2*}t)$ ,  $K_W$  is the water mass transfer coefficient  $(t^{-1})$ ,  $\Delta P$  is the transmembrane pressure gradient  $(M/L^2)$ ,  $\Delta \pi$  the transmembrane osmotic pressure gradient  $(M/L^2)$ ,  $Q_p$  the permeate flow  $(L^3/t)$ , and A is the membrane area  $(L^2)$ .

Note that the osmotic pressure gradient through the membrane can be estimated from the total dissolved solids (TDS) concentration gradient, which assumes the ratio of 1 psi per 100 mg/L TDS [15]. This ratio is commonly used as a reliable rule-of-thumb to estimate osmotic pressure of aqueous solutions within the water industry.

The movement of solute through the membrane can be predicted by the solute concentration differential between the membrane surface and the permeate stream as shown in Eq. (2):

$$F_{S} = K_{S}\left(C_{m} - C_{p}\right) = K_{S}\left[\left(\frac{C_{f} - C_{c}}{2}\right) - C_{p}\right] = \frac{Q_{p}C_{p}}{A}$$
(2)

where  $F_s$  is the solute flux (M/L<sup>2</sup>\*t),  $K_s$  the solute mass transfer coefficient (L/t),  $C_m$  the concentration at the membrane surface (M/L<sup>3</sup>),  $C_f$  the concentration of the feed (M/L<sup>3</sup>),  $C_p$  the concentration of the permeate (M/L<sup>3</sup>) and  $C_c$  is the concentration of the concentrate (M/L<sup>3</sup>).

Eqs. (3) and (4) describe the water and solute mass balance around a membrane with both permeate and

concentrate stream outputs as follows:

$$Q_f = Q_p + Q_c \tag{3}$$

$$Q_f C_f = Q_p C_p + Q_c C_c \tag{4}$$

where  $Q_f$  is the feed hydraulic flow (L<sup>3</sup>/t),  $Q_p$  the permeate hydraulic flow (L<sup>3</sup>/t) and  $Q_c$  the concentrate hydraulic flow (L<sup>3</sup>/t).

Eq. (5) describes the fraction water recovery for a membrane system as follows:

$$R = \frac{Q_p}{Q_f} \tag{5}$$

where *R* is the fraction water recovery

Eqa. (1)–(5) can be solved for the steady-state permeate concentration given in Eq. (6). The homogeneous solution diffusion (HSD) model can be utilized to predict permeate concentrations, given the solvent and solute MTC, water recovery, transmembrane pressure, and feed concentration [16].

$$C_{p} = \frac{K_{s}C_{f}}{\left[K_{W}\left(\Delta P - \Delta\pi\right)\left(\frac{2-2R}{2-R}\right) + K_{s}\right]}$$
(6)

Eq. (6) is predicated on a linear change in concentration from the feed to the concentrate, and shows that permeate concentration decreases with increasing pressure, decreasing recovery, or feed stream concentration. The concentration of inorganic solutes in permeate from a nanofiltration (NF) membrane increases as recovery increases and pressure decreases [16]. The linear HSD model does not take into account the effect of concentration polarization on mass transport at the membrane surface.

The basic assumptions in Eqs. (1) and (2) that the solvent and solute MTCs are constant allow some inferences to be made concerning permeate water quality and pressure. The permeate solute is predicted to pass through the membrane at a rate controlled by the concentration gradient. In addition, Eq. (1) indicates that passage of permeate solvent (water) through the membrane will vary directly with pressure differential. Consequently, since the solvent flux increases with pressure and because solute flux through the membrane is independent of pressure, it is possible to lower the permeate concentration by increasing the operating pressure.

#### 3. Materials and methods

#### 3.1. Single-stage NF system

In order to measure the transient response of a concentration change in a single NF membrane system a study was done to determine the response time to steady state following a change in chloride concentration. Initially, the transient experiments were performed to determine how long it would take the single-stage system to come to steady state after a step concentration increase. However, this initial experiment was repeated on a larger three-state pilot plant on a different well supply so that a detailed analysis of a membrane system could be made.

A schematic of the single-stage NF system is shown in Fig. 1. In the single-stage evaluation, the permeate flow from the nanofiltration membrane (Dow Filmtec NF-70) was adjusted to 0.5 gpm, which corresponded to a 4.1 gpm feed flow, 12% water recovery (no recycle of concentrate was used in the transient response investigations), and a flux of approximately 12.1 gal/ft<sup>2</sup>/d (gal/sfd). A central Florida groundwater well located on the campus of the University of Central Florida (Orlando, Florida) was used as a source of water supply (feedwater) to the pilot systems. The well supply contained a background chloride concentration of less than 2 mg/L.

A schematic of the three-stage NF system is shown in Fig. 2. The pilot plant operating characteristics for the three-stage pilot plant are given in Table 1. A second experiment was conducted using TDS to measure the input change to a feed stream chloride increase in the feed water, but instead of being monitored by grab water samples for chloride, a conductivity meter was used to monitor concentration changes in the permeate stream. The water source for the three-stage NF system was a different ground water supply in central Florida, having average background chloride concentration of approximately 30 mg/L.

4. Mathematical model development

When a feed water quality change occurs in an ideal membrane process where there exists complete rejection,

Since the groundwater source had only trace levels of chloride present ( $<2.0 \text{ mg/L Cl}^-$ , or less than the detection limit), sodium chloride was used as the chemical tracer. A stock solution of NaCl (108 g/L) was fed to the system via a chemical feed pump at a rate of 9.7 mL/min. After the NaCl feed was initiated, samples of feed permeate and concentrate were taken every 2 min for the first 10 min. Chloride mass balances accounted for 94% chloride recovery in the membrane output of all chloride input to the membrane.

#### 3.2. Three-stage NF system

In order to evaluate the transient response of a concentration change in a multi-stage membrane system, the feed flow into the three-stage pilot plant was spiked with 80 mg/L of chloride in the form of sodium chloride, and the permeate chloride concentration was monitored over time. The water source for the single-stage was a 200-foot-deep well in central Florida having a background chloride concentration of approximately 2 mg/L. The chloride spike was determined by observing the steady-state feed water input following the increased chloride feed.

the initial and final steady-state-permeate concentrations will be the same and there will be no transient path taken between the two states. However, this will not be the case when only partial solute rejection occurs and a rapid water quality change is experienced in a membrane system.

When a NF system at steady state experiences a change in the concentration for the feed stream, the permeate concentration of any solute that is controlled by diffusion will undergo a transient concentration change. The equations describing the dynamic behavior of the permeate concentration were developed for a complete mix, one-stage system (first order), responding to a step disturbance in the feed concentration.

The first-order transient response of any solute concentration in the permeate stream (state 1) of a membrane system using a complete mix model is shown as differential [Eq. (7)] and integrated (for time  $t>\Delta$  only) [Eq. (8)]with system time constant ( $\Theta_i$ ) and time delay ( $\Delta_i$ ):



Fig. 1. Illustration of a single-stage NF pilot system with recycle.



Fig. 2. Illustration of the three-stage NF pilot system.

#### Table 1

Operating characteristics for a chloride tracer evaluation of the three-stage NF plant

Stage	Q <sub>f</sub> (gpm)	Q <sub>p</sub> (gpm)	C <sub>f</sub> (mg/L)	$C_p$ (mg/L)	Feed pressure (psi)	Recovery (%)	Flux (gal/sfd)	$K_W$ (d <sup>-1</sup> )	<i>K</i> <sub><i>s</i></sub> (ft/d)
1	27.2	11.7	110	14.1	92.0	43.0	15.3	0.00968	0.218
2	15.5	4.8	182	22.9	77.0	31.0	12.5	0.00943	0.196
3	10.7	2.5	254	64.6	63.3	23.4	13.0	0.01171	0.505

$$\left(\theta_{i} \cdot \frac{\partial C_{p_{i}}}{\partial t}\right) + C_{p_{i}} = Z_{i}C_{f_{i}}$$

$$\tag{7}$$

$$C_{p_i} = Z_i C_{f_i} \left( 1 - e^{\left\{ \left[ -(t_i \Delta_i) \right] / \theta_i \right\}} \right)$$
(8)

where  $C_{p_i}$  is the permeate stream concentration deviation (mg/L),  $C_{f_i}$  the feed stream concentration deviation (mg/L),  $Z_i$  the dimensionless gain term, *i* the stage number, *t* the time (min),  $\Delta_i$  the delay time and  $\Theta_i$  is the stage time constant (min).

The gain term can be viewed as a ratio of the ultimate change in the permeate output stream divided by the ultimate change in the step feed concentration input. Since the response is assumed to be first-order, the time constant ( $\Theta_i$ ) represents the time, *t*, when 63.2% of the ultimate change occurs (accounting for delay time,  $\Delta$ ).

The homogeneous solution diffusion model presented earlier can now be modified to reflect a transient response to steady state by using the first-order differential equation representing complete mix given by Eq. (7). Recall that the homogeneous solution diffusion model describes mass transport in the permeate stream from a membrane system, and the permeate solute concentration has been shown to be dependent upon several operational variables. In its simplicity, this model allows the effect of five independent variables on permeate water quality to be considered in predicting the permeate concentration if several operating parameters are known. For example, if pressure is increased and all other variables are held constant, then the permeate concentration will decrease. On the other hand, the permeate concentration will increase if recovery is increased and all other variables are held constant as seen in Eq. (6).

The gain term given in Eq. (8) can be incorporated into Eq. (6) for the transient response description from the membrane system, such that:

$$C_{p_i} = Z_i C_{f_i} \tag{9}$$

where

$$Z_{i} = \frac{K_{S_{i}}}{K_{W_{i}} = (\Delta P - \Delta \pi) \left(\frac{2 - 2R}{2 - R}\right) + K_{S_{i}}}$$
(10)

Although the concentrate stream appears not to be fundamentally involved in an unsteady-state membrane stage analysis, it can be shown that the concentrate stream proves to be an integral parameter when considering an unsteady state membrane system analysis. Note that the solute mass balance at a specific water recovery around a single membrane stage can be given by Eq. (11). The concentrate concentration can then be predicted by combining the stage gain, recovery, and feed concentration as shown in Eq. (12):

$$C_{c_i} = \frac{Q_{f_i}C_f - Q_{p_i}C_{p_i}}{Q_{c_i}} = \left(\frac{C_{f_i}}{1 - R_i} - \frac{R_iC_{p_i}}{1 - R_i}\right)$$
(11)

$$C_{c_i} = C_{f_{i+1}} = \frac{C_{f_i} - R_i Z_i C_{f_i}}{1 - R_i} = C_{f_i} \left(\frac{1 - Z_i R_i}{1 - R_i}\right)$$
(12)

Therefore, for any arrayed membrane system, the concentrate stream of stage i becomes the feed stream to the next state i+1. Eq. (12) can be simplified by defining an

additional term which relates the recovery and gain term for each stage, such that:

$$C_{c_i} = X_i C_{f_i} \tag{13}$$

where

$$X_i = \left(\frac{1 - Z_i R_i}{1 - R_i}\right) \tag{14}$$

Incorporation of Eq. (13) into Eq. (8) allows for the development of Eq. (15), which predicts the transient response for any stage permeate stream for any  $t > \Delta$ .

$$C_{p_{\text{stage }i}} = Z_i \prod_{j=2}^{i} X_{j-1} \prod_{k=1}^{i} 1 - e^{\left[-(t-\Delta_k)/\theta_k\right]}$$
(15)

The concentration of the system permeate stream can be predicted by flow weighting the solute concentration from each stage, and is shown in Eq. (16). The stage permeate flow is given as  $A_i K_w \Delta P_i$  (gal/min).

$$C_{p \text{ system}} = \frac{C_{f_i} \sum_{i=1}^{n} A_i K_{w_i} \Delta P_i Z_i \prod_{j=2}^{i} X_{j-1} \prod_{k=1}^{i} 1 - e^{\left[-(t-\Delta_k)/\theta_k\right]}}{\sum_{i=1}^{n} A_i K_{w_i} \Delta P_i}$$
(16)

Note that the model given in Eq. (16) is developed only for membrane systems that used the concentrate stream from the proceeding stage as the feed stream in the succeeding stage, excluding the stage 1 feed. Development of models describing permeate concentration in a membrane system where succeeding stage permeate is used as proceeding stage feed could be done using the previous technique; however, the developed model in Eq. (16) described high recovery membrane systems that are more common to potable water treatment.

The model shown as Eq. (16) equated permeate concentration ( $C_p$ ) for a membrane system as a function of: each individual stage (*i*), the membrane surface area ( $A_i$ ), water mass transfer coefficient ( $K_{w_i}$ ), transmembrane pressure ( $\Delta P_i$ ), combined solute and solvent mass transfer coefficients for the concentrate stream ( $Z_i$ ), a factor relating stage feed stream concentration to initial feed stream concentration ( $X_{j-1}$ ), in addition to cumulative time following transient initiation (*t*), stage delay or lag time ( $\Delta$ ), and a first-order time constant ( $\Theta_i$ ) in the unsteady state. It should be noted that at time infinity a steady-state model develops from Eq. (16), and the steady-state model is given in Eq. (17):

$$C_{p \text{ system}} = \frac{C_{f_i} \sum_{i=1}^{n} A_i K_{w_i} \Delta P_i Z_i \prod_{j=2}^{i} X_{j-1}}{\sum_{i=1}^{n} A_i K_{w_i} \Delta P_i}$$
(17)

# 5. Permeate transient response in a single-stage NF system

The actual data and the theoretical response resulting in the steady-state values of 41.2, 38.0 and 16.2 mg/L chloride in the concentrate, feed and permeate streams are shown in Fig. 3. Using statistical software (SAS<sup>®</sup>), nonlinear regression was used in order to determine the single-stage NF membrane time constant and single-stage delay time. It was determined that the first-order time constant was 3.8 min (assuming an instantaneous response for the feed stream). The single-stage NF plant had a 2-min delay time for the permeate stream response, specific to the system configuration. The nonlinear total sum of squares (SST) was 1044, and the regression sum of squares of the error (SSE) was 5.55, having an asymptotic standard error of 0.025 representing an acceptable measure of the time constant.

The transient response to a permeate concentration change in the single-stage NF membrane would be 95.5% complete after 13.8 min from the time of initiation.

# 6. Permeate transient response in a three-stage NF system

The models given by Eqs. (15) and (16) allow permeate concentrations to be evaluated for varying system and stage feed concentrations, solute and solvent mass transfer coefficients (MTCs), transmembrane pressures, water recoveries, and transient response. Consequently, an investigation was initiated in order to examine the threestage nanofiltration system.

Nonlinear regression statistical software (SAS<sup>®</sup>) was used to analyze the delay time,  $\Delta$ , and the time constant,  $\theta$ , which could be estimated for each stage from the transient chloride response over time. This method of regression analysis reports the SSE for statistical representation. The delay times and time constants were selected for each stage that minimized the sum of squares of the error in the nonlinear first order regression model. These values were incorporated into Eqs. (15) and (16) in order to estimate the resulting permeate concentration of the three-stage membrane system.

The delay times and time constants determined by nonlinear regression analysis for model development are shown in Table 2. In addition the SST, the SSE and the asymptotic standard error value are given for each stage

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Fig. 3. Simulated first-order transient response to step chloride concentration increase through a single NF membrane showing actual and theoretical feed, permeate, and concentrate chloride concentrations.



Fig. 4. Stage 1 simulated first-order transient response plus delay time to step chloride increase.



Fig. 5. Stage 2 simulated second-order transient response plus delay time to step chloride increase.

Table 2				
Summary of nonlinear regression	parameter estimation for ste	p chloride input to	three-stage membran	e plant

Stage	No. obs.	$\Delta$ (min)	θ (min)	Asymptotic standard error	SST	SSE
1	12	1.0	0.57	0.197	999	1.4
2	12	1.2	1.28	0.074	2681	10.9
3	12	1.9	1.30	0.136	23282	161.8

Table 3

Operating characteristics for the TDS tracer evaluation of the three-stage NF plant

Stage	Q <sub>f</sub> (gpm)	Q <sub>p</sub> (gpm)	C <sub>f</sub> (mg/L)	$C_p$ (mg/L)	Feed pressure (psi)	Recovery (%)	Water flux (gal/sfd)	$K_W(d^{-1})$	$K_{S}(\mathrm{ft/d})$
1	27.5	12.1	693	69.2	99.5	44.0	15.7	0.00919	0.168
2	15.4	5.1	1183	103.4	85.1	33.1	13.3	0.00905	0.137
3	10.3	2.8	1718	257.2	72.8	27.2	14.6	0.01042	0.290

#### Table 4

Summary of nonlinear regression parameter estimation for step TDS input to the three-stage membrane plant

Stage	No. obs.	$\Delta$ (min)	θ (min)	Asymptotic standard error	SST	SSE
1	22	0.8	0.56	0.003	217	2.6
2	22	1.3	0.87	0.001	319	2.0
3	22	2.0	1.19	0.136	2591	56.0



Fig. 6. Stage 3 simulated third-order transient response plus delay time to step chloride increase.



Fig. 7. System transient response plus delay time to step chloride increase.

analyzed. The values listed in Table 2 were deemed to be found acceptable measures of the time constant parameter. The delay times given in Table 2 increase with stage number or position as would be expected because of the increasing time required to reach each succeeding stage. The stage 1, 2 and 3 water fluxes for this investigation were 15.3, 12.5 and 12.8 gal/sfd. The time constants are small and bear no obvious relationships to any of the other system or stage parameters shown in Table 1.

The calculated (predicted) transient response of the first, second and third stage permeate concentration based on Eq. (15) are shown in Figs. 4–6, respectively. The reader should note that the stage 2 results include the dynamics of stage 1 and stage 2, and the stage 3 results include the dynamics of stages 1, 2, and 3.

The calculated transient response of the system permeate concentration is shown in Fig. 7. The actual chloride response for stage and system are shown in Figs. 4–7 as specific data entries. The actual and predicted chloride response presented in Figs. 4–7 shows that the response for each membrane stage as well as the system can be accurately modeled by combining the HSD with a first-order complete mix model with delay for the tran-



Fig. 8. First-order, second-order and third-order transient response excluding delay time to step TDS increase for Stages 1, 2 and r, Respectively.

sient response. Consequently, the data and model indicate that the membrane response is rapid, and the transient response for the NF system was realized in less than 10 min. From the experimental data, 99% of the system transient response was estimated to be realized in 7 min.

Table 5 Time and chloride concentration change for a single-stage NF process

Time interval (min)	Feed conc.	Chloride conc.		
intervar (inint)	(1116/ 2)	Permeate (mg/L)	Conc. (mg/L)	
0	2.0			
2	24.0			
4	34.2	8.9	23.8	
6	34.2	10.8	38.7	
8	35.5	11.8	40.9	
10	37.1	13.8	41.6	
15	35.2	16.0	40.4	
30	38.0	16.2	41.4	

System settings = background feed stream chloride levels: 2 mg/L

Flows (gpm):	
Feed	4.10
Permeate	0.53
Concentrate	3.57
Pressures (psi):	
Feed	50
Permeate	0
Concentrate	46
pH:	
Feed	6.03
Permeate	6.09
Concentrate	6.18
Concentrate	0.10

## Table 6

Time internal

Time and chloride concentration for the three-stage NF membrane process

Chloride concentration

TDS Tracer Evaluation. Using grab sampling as the method for assessing chloride changes provided limited data within the actual transient region, as sampling constraints limited the number of data points that could be taken with the first several minutes of the step chloride input. In order to verify the response of a chloride increase in the three stage system, a second experiment was performed using a TDS (conductivity) meter in order to better elucidate the unsteady-state region of the permeate stream transient response.

As in the case of the chloride study, a step input of chloride in the form of NaCl was initiated to the threestage membrane system. However, no samples of the stage and system permeate streams were required; rather, the change in the TDS concentration of the permeate concentration of the permeate streams was monitored using a calibrated digital conductivity meter. This method would allow permeate TDS concentration to be monitored every 10 s and hence would provide more information as to the general form or shape of the unsteady-state region of the transient response.

Table 3 lists the TDS transient evaluation operating conditions. The conditions listed in Table 3 are very close to the conditions experienced during the chloride tracer evaluation (Table 1). Fig .8 depicts stages 1, 2 and 3 TDS permeate concentrations versus time, excluding delay time, for all TDS observations taken every 10 s.

(mmi)					
_	System feed (mg/L)	Stage 1 permeate (mg/L)	Stage 2 permeate (mg/L)	Stage 3 permeate (mg/L)	System permeate (mg/L)
0	30.2	4.2	5.1	13.1	7.1
1	_	4.2	5.4	13.3	6.9
2	111.0	12.7	10.7	14.3	13.9
3	_	13.2	19.9	33.7	20.3
4	112.0	13.2	19.4	58.7	21.3
5	_	13.9	21.4	61.4	21.3
6	110.0	13.9	20.4	64.0	21.8
7	_	14.0	21.4	60.6	21.8
8	111.0	13.9	22.5	63.2	21.8
9	_	13.9	22.5	62.2	21.3
10	111.0	14.1	22.5	64.8	21.8
15	110.0	14.1	23.0	64.6	21.8
30	110.0	14.1	23.1	64.8	21.8
45	112.0	14.2	22.9	64.4	21.2
60	119.0	14.6	22.6	64.6	21.5
75	107.0	14.3	22.7	64.8	21.7
90	112.0	14.1	22.7	64.8	21.8

Background chloride =30.2 mg/L.

Table 7	
Time and TDS concentration for the three-stage NF system	

Time internal (min)	TDS concentration						
	System feed (mg/L)	Stage 1 permeate (mg/L)	Stage 2 permeate (mg/L)	Stage 3 permeate (mg/L)	System permeate (mg/L)		
0	380	32.9	53.7	132.0	50.1		
10	399	32.8	53.7	129.9	50.1		
20	461	32.7	53.5	132.0	49.8		
30	556	32.9	53.7	130.9	50.0		
40	632	32.9	53.6	131.7	50.1		
50	701	32.9	53.3	132.0	50.1		
60	722	35.4	53.6	131.9	50.6		
70	723	43.1	53.7	131.4	52.3		
80	722	48.5	53.7	132.0	54.9		
90	721	55.2	54.1	132.0	57.3		
100	722	60.7	57.5	131.8	60.4		
110	720	64.0	63.8	132.0	62.8		
120	722	66.1	69.6	132.0	65.1		
130	719	67.2	76.5	132.2	68.0		
140	720	68.8	83.5	134.3	69.6		
150	722	69.0	90.2	140.9	72.4		
160	722	69.2	95.2	166.0	76.0		
170	722	69.3	97.3	191.2	78.9		
180	721	69.3	99.0	215.2	81.0		
190	722	69.3	101.4	231.9	82.7		
200	722	69.4	102.1	242.8	84.4		
210	_	69.3	102.9	248.7	85.3		
220	_	69.3	103.3	252.3	85.8		
230	_	69.3	103.4	254.7	86.1		
240	_	69.3	103.9	256.0	86.3		
250	_	69.3	103.4	256.9	85.8		
260	_	_	103.4	257.2	86.1		
270	_	_	103.4	257.1	86.3		
280	_	_	103.4	257.0	86.3		
290	_	—	103.4	257.2	86.3		
300	_	_	103.4	257.3	86.3		
310	_	_	_	257.1	86.3		
320	_	—	—	257.3	86.2		
330	_	_	_	257.2	86.3		
340	_	_	_	257.2	86.3		
350	_	—	—	257.2	86.3		

Nonlinear regression (SAS®) was used to determine stage delay times and time constants in the same manner as the chloride study, and Table 4 lists the results. A comparison of the delay times in Tables 3 and 4 shows that delay times increase with stage number, which would be expected with an arrayed membrane system. Stages 1, 2 and 3 water fluxes were 15.8, 13.3 and 13.0 gal/sfd, respectively.

The time constants given in Table 4 may be more representative of each stage since there is a distinct difference in the time constant between stages 2 and 3 not realized by the chloride study (Table 2). This would be expected since the unsteady-state region of the transient response had been fully established by the TDS measurements taken in 10 s intervals (Fig. 8). Table 5 provides the summary chloride data for the single-stage steady-state transition study as a reference, whereas Table 6 provides the summary chloride data for the three-stage system. TDS data for the three-stage system is provided in Table 7.

Consequently, based on the TDS regression results and the characteristic forms of stages 1, 2 and 3 in Fig. 8, there exists strong evidence that would indicate that first order modeling with delay is satisfactory for the description of the transient response of staged nanofiltration systems.

#### 7. Conclusions

A model was derived by combining the HSD model with a complete-mix first order model with delay that accurately described the response from a single-stage and three-stage nanofiltration membrane (pilot) plant. The transient response of a nanofiltration membrane was described by a first order system with a delay time of 2.0 min and a time constant of 3.8 min. The transient response of a three-stage system was rapid with delay times in the system less than 2 min. The average delay time and time constant for each membrane stage were: 0.9 and 0.6 min for stage 1; 1.2 and 1.0 min for stage 2; and 2.0 and 1.3 min for stage 3, respectively. This work provides membrane practitioners a tool for predicting permeate water quality following a change in feed water quality using Eqs. (15) and (16).

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