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# Fractional modelling of the reverse osmosis process used for dam water desalination

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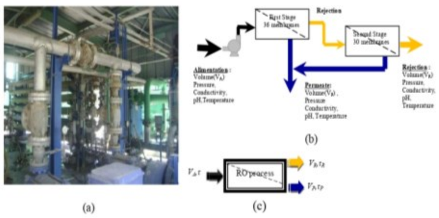
**Graphical abstract**




The RO desalination process (a): Picture; (b): block flow diagram (c): Fractional modelling inputs and outputs to monitor the performance of the RO process.

## Abstract

This paper deals with new fractional models to follow the performance of a dam water reverse osmosis (DWRO) desalination system using the dimensionless cumulative volume of alimentation, permeate and rejection. The experimental data consist of 2561 points collected over 4 years period from 66 organics reverse osmosis (RO) membranes. The accuracy of the established fractional models was verified using statistical criteria and a comparison with ordinary models. The fractional dimensionless models (FDM) with optimal kinetic constants provided an accurate result and perfect consistency with the experimental data. As such, the coefficient of determination ($R^2$) values were 0.9975, 0.9750 and 0.9801, with lower average absolute relative deviation (AARD) around 8.03, 0.53 and 0.45, through lower root mean squared error (RMSE) about 1.452, 0.976 and 0.880 for alimentation, permeate and rejection, respectively.

**Keywords:** Fractional modelling, dimensionless parameters, kinetic separation, desalination, reverse osmosis

## 1. Introduction

The reverse osmosis (RO) process is considered one of the most important desalination technologies due to its advantages, including flexibility, high efficiency and ease of operation (Feria-Díaz *et al*., 2021). It can be used to produce drinking water and process water for various industrial applications, such as food and pharmaceutical. Since its invention in the 1950s (Glater, 1998), the RO process has been extensively studied to enhance its development (Abid *et al*., 2012; Dimitriou *et al*., 2017; Alsarayreh *et al*., 2020). Monitoring the performance of RO process is necessary to identify early symptoms of failure in order to improve maintenance and extend the process lifetime. However, one of the major limitations to adequately ensure its performance monitoring is the matter accumulation on the membrane, such as concentration polarization and fouling. This limitation gets hard the supervision of the RO membrane's performances and the involvement of multiple parameters in the separation process. This deficiency can be attributed to its enormous complexity leading to the uncertainties of the operating parameters (flow rate, pressure ...etc.).

Mathematical modelling has been widely employed to accurately describe the performance of the RO process. Developing an appropriate mathematical model that accounts the fouling is essential for optimizing design and improving efficiency, thus reducing the overall costs. However, the majority of previous modelling studies (Ruth *et al*., 1933; Hermans and Bredée, 1935; Ho and Zydney, 2000; Jamal *et al*., 2004 ; Fouladitajar *et al*., 2013; Tien *et al*., 2014; Heidari *et al*., 2017; Goldrick *et al*., 2017; Debnath *et al*., 2019; Tong *et al*., 2020; Xu *et al*., 2020; Heidari *et al*., 2021; Azizi *et al*., 2022; Bchiti *et al*., 2022) have relied on a limited range of experimental data, thus limiting their range of validity. On the other hand, the classical models cannot best represent all the phenomena that occur during the membrane separation process, unlike fractional models that have proven their performance for other processes (Kashchenko and Nikitin, 2014; Zhai *et al*., 2015; Padrino, 2017; Obembe *et al*., 2018; Kumar *et al*., 2019; Ramírez *et al*., 2017; De Souza Matias *et al*., 2019; Lemus-Mondaca *et al*., 2021; Mahdad *et al*., 2021a; Mahdad *et al*., 2021b; Friesen *et al*., 2015;

Nikan *et al*., 2020; Mirza *et al*., 2021; El-Gazar *et al*., 2021).

In this paper, new fractional dimensionless models (FDM) have been proposed to follow the performance of the DWRO desalination process using the dimensionless cumulative volumes of alimentation, permeate, and rejection. The proposed models were mathematically developed from the pseudo nth order (PNO) equation and resolved by the establishment of a software program. The FDMs were thoroughly tested using statistical criteria to assess their accuracy in representing the 2561 cumulative volumes of experimental data collected over the 4-year lifetime of the RO membranes.

## 2. Materials and methods

### *2.1. Description of water treatment by the ro process*

The DWRO process was carried out at the antibiotic complex of Medea (North Algeria) for the production of ultra-pure water. The water stream, coming from the pre-treatment unit, is processed in the RO plant operating according to the scheme illustrated in Figure 1. The RO plant comprises eleven modules, each containing six membranes. They are arranged in two consecutive stages, where the first one includes six modules and the second consists of five modules. Each pressure vessel of the DWRO plant contains a spiral wound polyamide membrane. The technical specifications of the studied RO unit are summarized in Table 1.

The experimental data were collected at the alimentation, permeate and rejection of the RO unit every 2 hours over a span of 4 years covering the lifespan of the RO membranes. Throughout the monitoring period, the RO membranes were not replaced but underwent 22 chemical cleaning operations, whose cleaning periods are presented in Table 2.

**Figure 1.** The RO desalination process (a) Picture; (b) block flow diagram (c) Fractional modeling inputs and outputs to follow the performance of the RO process

**Table 1.** Technical specifications of the RO desalination process

| Specification | Parameter | Value |
|---|---|---|
| **Membrane** | Membrane type | ROGA® - HR 8.5” “spirale“ |
| | Number of modules (-) | 11 |
| | Number of membranes (-) | 66 |
| | Total surface area ($m^2$) | 38.6 |
| | Efficiency (%) | 75 |
| | Total treated water flow ($m^3.h^{-1}$) | 92 |
| | Permeate flow ($m^3$ $h^{-1}$) | 69 |
| **Alimentation** | TDS ($mg.L^{-1}$) | 1960 –30120 |
| | Salinity (%) | ≤1.3 |
| | Turbidity (JTU) | ≤0.19 |
| | Total hardness (mg. $L^{-1}$) | ≤1100 |
| **Operating conditions** | Operating pressure (Bars) | 35– 41 |
| | Operating temperature (°C) | 20 – 40 |
| | Operating pH (-) | 4 – 6 |

**Table 2.** Chemical cleaning cycles of the RO membranes

| **Cleaning cycle** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ***t* (h)** | 3126 | 3414 | 3798 | 3942 | 4086 | 4566 | 5262 | 5766 | 6438 | 6606 | 6966 |
| ***τ* (-)** | 0.09 | 0.10 | 0.11 | 0.11 | 0.11 | 0.13 | 0.15 | 0.16 | 0.18 | 0.18 | 0.19 |
| **Cleaning cycle** | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
| ***t* (h)** | 11142 | 11382 | 11526 | 11838 | 11886 | 11982 | 12462 | 12822 | 13182 | 13734 | 15534 |
| ***τ* (-)** | 0.31 | 0.32 | 0.32 | 0.33 | 0.33 | 0.33 | 0.35 | 0.36 | 0.37 | 0.38 | 0.43 |

### *2.2. Fractional modelling*

#### *2.2.1. Model approach*

The fractional models, established in this study for the RO process, were developed from the PNO equation that was originally proposed for expressing solid-liquid adsorption (Lagergren, 1898; Blanchard *et al*., 1984; Morais *et al*., 2007; Özer, 2007; Morais *et al*., 2008; Leyva-Ramos *et al*., 2010; Tseng *et al*., 2014). This adsorption mechanism is considered one of the mechanisms leading to RO membranes fouling and, consequently, to the reduction of permeate flow (Lee and Elimelech, 2006; Fritzmann *et al*., 2007; Qrenawi and Abuhabib, 2020; Ahmed *et al*., 2023). It is assumed that, during the flow of solute-rich water through an RO membrane, a portion of this solute will be adsorbed on the membrane, while the remaining portion will be removed. The adsorption kinetics of the solute can be expressed by equation (1):

$$\frac{dq(t)}{dt} = k_n^{'}\left(q_{\max} - q_t\right)^n \quad (1)$$

Where q(t) is the adsorbed amount of solute per unit mass of the membrane (mg g-1); qmax is the maximum adsorption capacity of the membrane per unit mass of the membrane (mg g-1); t is the filtration time (h); k'n is the rate constant of adsorption reaction of the PNO equation ((mg g-1)1-nh-1); n is the order of adsorption reaction (-).

On the other hand, membrane fouling can be characterized by the retention rate (γ) which represents the ratio between the adsorbed mass (mad) and the initial mass (min) of solute. It can be expressed according to equation (2):

$$\gamma = \frac{m_{ad}}{m_{in}} \quad (2)$$

The $m_{ad}$ and $m_{in}$ can be expressed by equation (3) and equation (4), respectively:

$$m_{ad} = q(t).M \quad (3)$$

$$m_{in} = v(t).C_{in} \quad (4)$$

Where $C_{in}$ is the initial mass concentration of solute in the feed suspension (mg $L^{-1}$); $M$ is the mass of RO membrane (g); $v(t)$ is the cumulative volume of the filtrate ($m^3$).

By replacing equation (3) and equation (4) in equation (2), the adsorbed amount of solute can be expressed according to the equation (5):

$$q(t). = \frac{\gamma.v(t).C_{in}}{M} \quad (5)$$

By replacing equation (5) in equation (1) and simplification, we obtain the equation (6):

$$\frac{dv(t)}{dt} = k_n^{'}.\left(\frac{\gamma.C_{in}}{M}\right)^{n-1}\left(v_m - v(t)\right)^n \quad (6)$$

Assuming that $K_n = k_n.\left(\frac{\gamma.C_{in}}{M}\right)^{n-1}$, the equation (6) can be written as the equation (7) (Adda *et al*., 2020; Mesli *et al*., 2022):

$$\left.\begin{aligned}\frac{dv(t)}{dt} &= K_n.\left(v_m - v(t)\right)^n\\ v_{t=0} &= v(0) = 0\end{aligned}\right\} \quad (7)$$

Where $K_n$ is the rate constant of filtration of the O-PNO equation ($L^{1-n}$ $h^{-1}$), $v_m$ is the maximum cumulative volume of the filtrate ($m^3$);

*2.2.2. Solution of the differential equation*

The differential equation (7), which expresses the variation of cumulative volume, has been resolved using ordinary and fractional methods (Caputo derivative, Laplace Transform) for the different order of *n* (0, 1, 2 and *n*). An example is presented below for the pseudo-zero order kinetics (n=0), which the equation (7) can be expressed by the equation (8):

$$\left.\begin{aligned}\frac{dv(t)}{dt} &= K_0\\ v(0) &= 0\end{aligned}\right\} \quad (8)$$

Where $K_0$ is the rate constant of filtration of the O-PZO equation (L $h^{-1}$).

Adopting the ordinary solution, the equation (8) can be expressed as the equation (9):

$$\int_0^{v_t} dv(t) = K_0 d(t) \quad (9)$$

By integration of equation (9) we get the equation (10):

$$v(t) = K_0.t \quad (10)$$

Adopting the fractional solution, the equation (8) can be expressed as the equation (11):

$$\left.\begin{aligned}{}_oD_t^{\alpha}v(t) &= K_{0f}\\ v(0) &= 0\end{aligned}\right\} \quad (11)$$

Using Laplace's direct and reverse transformation, equation (11) can be expressed as equation (12):

$$v(t) = \frac{K_{0f}.t^{\alpha}}{\Gamma(\alpha+1)} \quad (12)$$

Where $K_{0f}$ is the rate constant of filtration of the F-PZO equation (L $h^{-\alpha}$); $\alpha$ is the fractional order of time (-); $\Gamma$ is the Gamma function.

The same procedure is applied to resolve the deferential equation (7) for the others pseudo-orders kinetic (1, 2 and *n*). The ordinary and fractional dimensional models are presented in the Table 3.

**Table 3.** The Ordinary and fractional dimensional models developed in this work

| Solution type | Pseudo Order | Formula | Equation |
|---|---|---|---|
| ODE | 0 | $v(t) = K_0.t$ | (13) |
| | 1 | $v(t) = v_m\left(1 - e^{-K_1.t}\right)$ | (14) |
| | 2 | $v(t) = \frac{t}{1 + v_m.K_2.t}$ | (15) |

| | | | |
|---|---|---|---|
| | n | $v(t)=v_m\left[1-\frac{1}{\left[\left((n-1).v_m^{\ n-1}.K_n.t\right)\right]^{\frac{1}{n-1}}}\right]$ | (16) |
| **FDE** | 0 | $v(t)=\frac{K_{0f}.t^{\alpha}}{\Gamma(\alpha+1)}$ | (17) |
| | 1 | $v(t)=v_m\left[1-\sum_{n=0}^{\infty}\frac{(-1)^n.K_{1f}^{\ n}.t^{\alpha.n}}{\Gamma(\alpha.n+1)}\right]$ | (18) |
| | 2 | $v(t)=v_m\left[1-\frac{\Gamma(\alpha+1)}{\Gamma(\alpha+1)+v_m.K_{2f}.t^{\alpha}}\right]$ | (19) |
| | n | $v(t)=v_m\left[1-\left[\frac{\Gamma(\alpha+1)}{\Gamma(\alpha+1)+(n-1).v_m^{\ n-1}.K_{nf}.t^{\alpha}}\right]^{\frac{1}{n-1}}\right]$ | (20) |

Where $K_1$ is the rate constant of filtration of the O-PFO equation ($h^{-1}$); $K_{1f}$ is the rate constant of filtration of the F-PFO equation ($h^{-\alpha}$); $K_2$ is the rate constant of filtration of the O-PSO equation ($L^{-1}\ h^{-1}$); $K_{2f}$ is the rate constant of filtration of the F-PSO equation ($L^{-1}\ h^{-\alpha}$); $K_{nf}$ is the rate constant of filtration of the F-PNO equation ($L^{1-n}\ h^{-\alpha}$).

*2.2.3. Transformation to dimensionless models*

There are several significant advantages to describe the RO process using dimensionless models, including: simplify the parametric representation, reducing the number of variables and enabling cross-scales experiments. The dimensional models, presented in Table 3, were transformed to dimensionless models according to the equations (21) and (22), respectively:

$$V=\frac{v(t)}{v_m} \tag{21}$$

$$\tau=\frac{t}{t_m} \tag{22}$$

*Where* $V$ is the dimensionless cumulative volume of the filtrate (-); $\tau$ is the dimensionless filtration time (-); $t_m$ is the maximum filtration time (h).

An example of the transformation to a dimensionless model is presented below for the pseudo-zero order kinetics (n=0). By replacing the equations (21) and (22) in the equation (13), we obtain the equation (23):

$$V.v_m=K_0.t_m.\tau \tag{23}$$

Assuming that $K_0.\frac{t_m}{v_m}=k_0$, the equation (23) can be written as the equation (24):

$$V=k_0.\tau \tag{24}$$

The same steps are followed to make the transformation to dimensionless models for the others pseudo-orders kinetic (1, 2 and *n*). The ordinary dimensionless models (ODM) and the fractional dimensionless models (FDM) are presented in Table 4.

Where $k_n$, $k_0$, $k_1$, $k_2$ are the constants of ordinary dimensionless models for *n*, 0, 1 and 2 order, respectively (-); $k_{nf}$, $k_{0f}$, $k_{1f}$, $k_{2f}$ are the constant of fractional dimensionless models for *n*, 0, 1 and 2 order, respectively (-).

The transformation of experimental values of *v(t)* and *t* to dimensionless values were achieved by relating them to the maximum experimental value $v_m$ and $t_m$, respectively. The maximum experimental values are presented by Table 5.

**Table 4.** The ordinary and fractional dimensionless models developed in this work.

| Classification | | Model code | Formula | Equation |
|---|---|---|---|---|
| **ODM** | 0 | O-PZO | $V=k_0.\tau$ | (24) |
| | 1 | O-PFO | $V=1-Exp(-k_1.\tau)$ | (25) |
| | 2 | O-PSO | $V=\frac{1+(k_2-1).\tau}{1+k_2.\tau}$ | (26) |
| | n | O-PNO | $V=1-\left[\frac{1}{1+(n-1).k_n.\tau}\right]^{\frac{1}{n-1}}$ | (27) |
| **FDM** | 0 | F-PZO | $V=\frac{k_{0.f}}{\Gamma(\alpha+1)}.\tau^{\alpha}$ | (28) |
| | 1 | F-PFO | $V=1-Exp(-k_{1.f}.\tau^{\alpha})$ | (29) |

| | | | |
|---|---|---|---|
| 2 | F-PSO | $V=\dfrac{k_{2.f}.\tau^{\alpha}}{\Gamma(\alpha+1)+k_{2.f}.\tau^{\alpha}}$ | (30) |
| n | F-PNO | $V=1-\left[\dfrac{\Gamma(\alpha+1)}{\Gamma(\alpha+1)+(n-1).k_{n.f}.\tau^{\alpha}}\right]^{\frac{1}{n-1}}$ | (31) |

**Table 5.** Maximum experimental values of cumulative volume and filtration time

| Parameter | Alimentation | Permeate | Rejection |
|---|---|---|---|
| $v_m$ ($10^{+3}$.m$^3$) | 3603.78 | 2144.07 | 1496.72 |
| $t_m$ ($10^{+3}$.m$^3$) | 36.37 | 36.37 | 36.37 |

### *2.3. Solving of the dimensionless models*

The resolution of the developed ODM (equation (24) to (27)) and FDM ((equation (28) to (31)), presented in Table 4, and the determination of its optimal kinetic constants (*n*, *α*, $k_n$ and $k_{nf}$) have been conducted by setting up an establishment a MATLAB software program.

### *2.4. Evaluation of the models accuracy by statistical criteria*

The applied models accuracy was assessed by the statistical criteria which quantify the error between the model results and the experimental values. The statistical criteria, used in this work, include the root mean squared error (RMSE) (Adda *et al*., 2020), the average absolute relative deviation (AARD) (Jouyban *et al*., 2002), the coefficient of determination ($R^2$) (Soleimani *et al*., 2018), the mean absolute error (MAE) (Soleimani *et al*., 2018), the sum of squares regression (SSR) (Coker, 1995) and the sum of squares error (SSE) (Coker, 1995), as follows:

$$RMSE=\sqrt{\frac{\sum_{i=1}^{N}\left(y_{i,\exp}-y_{i,cal}\right)^{2}}{N}} \qquad (32)$$

$$AARD=\frac{1}{N-Z}\sum_{i=1}^{n}\left(\left|\frac{y_{i,cal}-y_{i,\exp}}{y_{i,\exp}}\right|\right)\times 100\% \qquad (33)$$

$$R^{2}=1-\frac{\sum_{i=1}^{N}\left(y_{i,\exp}-y_{i,cal}\right)^{2}}{\sum_{i=1}^{N}\left(y_{i,\exp}-\bar{y}\right)^{2}} \qquad (34)$$

$$MAE=\frac{1}{n}\sum_{i=1}^{n}\left|y_{i,\exp}-y_{i,cal}\right| \qquad (35)$$

$$SSR=\sum_{i=1}^{N}\left(y_{i,cal}-\bar{y}\right)^{2} \qquad (36)$$

$$SSE=\sum_{i=1}^{N}\left(y_{i,\exp}-y_{i,cal}\right)^{2} \qquad (37)$$

## 3. Results and discussion

### *3.1. Models' reliability and accuracy*

The model's reliability and accuracy present the deadliest step in this study using the statistical criteria and the ability of the model's regression. In order, the statistical criteria and the kinetic constants of the developed ODM and FDM are shown in Tables 6, 7 and Figure 2.

Based on the results presented in Table 6, it is evident that the fractional dimensionless models (F-PNO) gave the best values of statistical criteria, compared to the other tested models. This accuracy can be reflected with perfect $R^2$ (0.9975, 0.9750, 0.9801) and with lowers AARD (8.03, 0.53, 0.45), RMSE (1.452, 0.976, 0.880) and MAE (50.0109, 0.0032, 0.0026) for the alimentation, permeate and rejection, respectively.

The kinetic constants (Table 7) of fractional models (F-PNO) gave the following values of *n* (0.15, 1.59, 1.50), *α* (2.1693, 1.0425, 0.9206) and $k_{nf}$ (2.74, 92.28, 50.94) for alimentation, permeate and rejection, respectively.

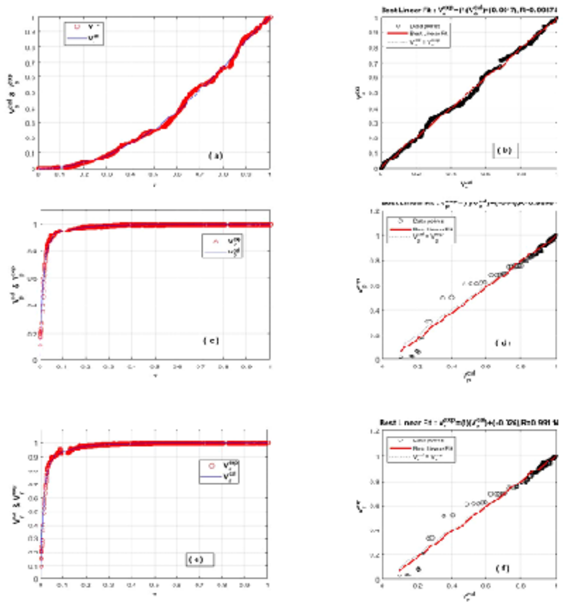


**Figure 2.** Scatter plot of the calculated values, by the F-PNO, versus the experimental values of dimensionless cumulative volume: for alimentation (a, b), permeate (c, d) and rejection (e, f)

Figure 2 argue the previous results, such as the scatter plot of the calculated values, by the fractional models (F-PNO), versus the experimental values of the dimensionless cumulative volume for alimentation (a, b), permeate (c, d) and rejection (e, f) were established the best regression.

**Table 6.** The statistical criteria of ODM and FDM for the dimensionless cumulative volume of alimentation, permeate and rejection

| Classification | | Statistical criteria | | | | | |
|---|---|---|---|---|---|---|---|
| | | $R^2$ | RMSE | AARD | MAE | SSR | SSE |
| Alimentation | O-PZO | 0.8305 | 11.907 | 418.57 | 0.1062 | 218.961 | 36.297 |
| | O-PFO | 0.7074 | 15.646 | 527.31 | 0.1364 | 216.336 | 62.670 |
| | O-PSO | -5.4171 | 73.269 | 2.9E5 | 0.6728 | 1371.128 | 1374.289 |
| | O-PNO | 0.8284 | 11.978 | 413.73 | 0.1064 | 217.853 | 36.729 |
| | F-PZO | 0.9968 | 1.619 | 13.96 | 0.0121 | 214.165 | 0.671 |
| | F-PFO | 0.9894 | 2.976 | 19.21 | 0.0242 | 214.310 | 2.267 |
| | F-PSO | 0.9739 | 4.668 | 30.56 | 0.0385 | 214.741 | 5.578 |
| | **F-PNO** | **0.9975** | **1.452** | **8.03** | **0.0109** | **214.158** | **0.540** |
| Permeate | O-PZO | -45.914 | 42.341 | 36.78 | 0.3551 | 99.730 | 458.939 |
| | O-PFO | 0.9395 | 1.520 | 1.20 | 0.0096 | 9.945 | 0.591 |
| | O-PSO | -0.0456 | 6.321 | 2.94 | 0.0131 | 10.140 | 10.229 |
| | O-PNO | 0.9309 | 1.624 | 0.62 | 0.0035 | 9.783 | 0.676 |
| | F-PZO | 0.48929 | 4.418 | 3.35 | 0.0232 | 9.782 | 4.996 |
| | F-PFO | 0.96447 | 1.16 | 0.88 | 0.0072 | 9.850 | 0.348 |
| | F-PSO | 0.9698 | 1.07 | 0.58 | 0.0035 | 9.799 | 0.295 |
| | **F-PNO** | **0.9750** | **0.976** | **0.53** | **0.0032** | **9.786** | **0.244** |
| Rejection | O-PZO | -44.520 | 42.139 | 36.75 | 0.3538 | 99.072 | 454.584 |
| | O-PFO | 0.9280 | 1.675 | 1.28 | 0.0103 | 10.174 | 0.719 |
| | O-PSO | -0.0524 | 6.408 | 3.13 | 0.0144 | 10.425 | 10.510 |
| | O-PNO | 0.9671 | 1.133 | 0.62 | 0.0040 | 9.997 | 0.328 |
| | F-PZO | 0.5212 | 4.322 | 3.34 | 0.0230 | 9.986 | 4.781 |
| | F-PFO | 0.9705 | 1.072 | 0.78 | 0.0064 | 10.034 | 0.294 |
| | F-PSO | 0.9718 | 1.047 | 0.73 | 0.0049 | 10.026 | 0.281 |
| | **F-PNO** | **0.9801** | **0.880** | **0.45** | **0.0026** | **9.998** | **0.198** |

*3.2. Comparison between the fractional dimensionless models and others models*

A comparison was established between the proposed fractional models (F-PNO) and other models in the literature (Table 8) according to the statistical criteria, the number of data points and the number of compartments of the studied process.

Such as, the proposed fractional models (F-PNO) provide an accurate result and a perfect consistency to the experimental data, against the literature models, with an excellent $R^2$ values (0.9975, 0.9750, and 0.9801) and with lowers AARD, RMSE, SSR and SSE for the three compartments of DWRO process: alimentation, permeate and rejection, respectively.

**Table 7.** The kinetic constants of ODM and FDM for the dimensionless cumulative volume of alimentation, permeate and rejection

| Classification | | Kinetic constants | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *n(-)* | *α (-)* | $k_0$*(-)* | $k_1$*(-)* | $k_2$*(-)* | $k_n$*(-)* | $k_{0f}$*(-)* | $k_{1f}$ *(-)* | $k_{2f}$ *(-)* | $k_{nf}$ *(-)* |
| Alimentation | O-PZO | 0 | --- | 0.75 | --- | --- | --- | --- | --- | --- | --- |
| | O-PFO | 1 | --- | --- | 0.96 | --- | --- | --- | --- | --- | --- |
| | O-PSO | 2 | --- | --- | --- | -43.001 | --- | --- | --- | --- | --- |
| | O-PNO | 0.18 | --- | --- | --- | --- | 0.78 | --- | --- | --- | --- |
| | F-PZO | 0 | 2.0132 | --- | --- | --- | --- | 2.10 | --- | --- | --- |
| | F-PFO | 1 | 3.0352 | --- | --- | --- | --- | --- | 2.31 | --- | --- |
| | F-PSO | 2 | 4.1253 | --- | --- | --- | --- | --- | --- | 1.62E2 | --- |
| | **F-PNO** | **0.15** | **2.1693** | **---** | **---** | **---** | **---** | **---** | **---** | **---** | **2.74** |
| Permeate | O-PZO | 0 | --- | 1.53 | --- | --- | --- | --- | --- | --- | --- |
| | O-PFO | 1 | --- | --- | 46.90 | --- | --- | --- | --- | --- | --- |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | O-PSO | 2 | --- | --- | --- | 181.69 | --- | --- | --- | --- | --- |
| | O-PNO | 1.84 | --- | --- | --- | --- | 148.24 | --- | --- | --- | --- |
| | F-PZO | 0 | 0.0551 | --- | --- | --- | | 0.9998 | --- | --- | --- |
| | F-PFO | 1 | 0.6443 | --- | --- | --- | --- | --- | 13.52 | --- | --- |
| | F-PSO | 2 | 1.2883 | --- | --- | --- | | --- | | 3.74E2 | --- |
| | **F-PNO** | **1.59** | **1.0425** | **---** | **---** | **---** | **---** | **---** | **---** | **---** | **92.28** |
| **Rejection** | O-PZO | 0 | --- | 1.54 | --- | --- | --- | --- | --- | --- | --- |
| | O-PFO | 1 | --- | --- | 44.92 | --- | --- | --- | --- | --- | --- |
| | O-PSO | 2 | --- | --- | | 190.74 | | --- | --- | --- | --- |
| | O-PNO | 1.79 | --- | --- | --- | --- | 107.15 | --- | --- | --- | --- |
| | F-PZO | 0 | 0.0577 | --- | --- | --- | --- | 0.9996 | --- | --- | --- |
| | F-PFO | 1 | 0.5987 | --- | --- | --- | --- | --- | 11.24 | --- | --- |
| | F-PSO | 2 | 1.2166 | --- | --- | --- | --- | --- | --- | 270.09 | --- |
| | **F-PNO** | **1.50** | **0.9206** | **---** | **---** | **---** | **---** | **---** | **---** | **---** | **50.94** |

***Table* 8.** Comparison between the proposed fractional dimensionless models and others models in the literature

| **Process** | **Application** | **Compartiment** | **Type of membrane** | **Number of data points** | **Type of model** | **Formula of model** | **R²** | **RMSE** | **AARD** | **MAE** | **SSR** | **SSE** | **Reference** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RO | Treatment of Ground water | Alimentation | Polyamide (ROGA® - HR 8.5”) | 2561 | F-PNO | $V=1-\left[\frac{\Gamma(\alpha+1)}{\Gamma(\alpha+1)+(n-1).k_{n.f}.\tau^{\alpha}}\right]^{\frac{1}{n-1}}$ | 0.9975 | 1.452 | 8.03 | 0.0109 | 214.158 | 0.540 | This work |
| | | Permeate | Polyamide (ROGA® - HR 8.5”) | 2561 | F-PNO | $V=1-\left[\frac{\Gamma(\alpha+1)}{\Gamma(\alpha+1)+(n-1).k_{n.f}.\tau^{\alpha}}\right]^{\frac{1}{n-1}}$ | 0.9750 | 0.976 | 0.53 | 0.0032 | 9.786 | 0.244 | |
| | | Rejection | Polyamide (ROGA® - HR 8.5”) | 2561 | F-PNO | $V=1-\left[\frac{\Gamma(\alpha+1)}{\Gamma(\alpha+1)+(n-1).k_{n.f}.\tau^{\alpha}}\right]^{\frac{1}{n-1}}$ | 0.9801 | 0.880 | 0.45 | 0.0026 | 9.998 | 0.198 | |
| MF | Retention of organic compound | Retentate | Polycarbonate track-etched (PCTE) | < 15 | Fractional pseudo $n^{th}$ order | $V(t)=V_{\max}\left[1-\frac{\Gamma(\alpha+1)}{\left[\Gamma(\alpha+1)+(n-1).K_{n.f}.V_{\max}^{n-1}.t^{\alpha}\right]}\right]^{\frac{1}{n-1}}$ | 0.9989 | 0.0091 | ----- | 0.0064 | ----- | ----- | (Mesli *et al.*, 2022) |
| NF/RO | Removal of NaCl from water | Permeate | PolyamideBW 30LE400 | <07 | Complete pore blocking | $J=J_0.Exp(-K_b.t)$ | 0 ,9500 | 0,0270 | ----- | ----- | ----- | ----- | (Bchiti *et al.*, 2022) |
| | | | Polyamide (NF270) | <07 | Complete pore blocking | $J=J_0.Exp(-K_b.t)$ | 0,9500 | 0,0250 | ----- | ----- | ----- | ----- | |
| | | | Polyamide (NF90) | <07 | Complete pore blocking | $J=J_0.Exp(-K_b.t)$ | 0,9600 | 0,0290 | ----- | ----- | ----- | ----- | |
| MF | Retention of collagen protein | Retentate | High-density polyethylene | <20 | Cake filtration intermediate blockage | $V=\frac{1}{K_i}Ln\left(1+\frac{K_i}{K_c.J_0}\left(\sqrt{1+2.K_c.J_0^2.t}-1\right)\right)$ | 0,9900 | ----- | ----- | ----- | 1.913E-4 | 6.525E-4 | (Heidari *et al.*, 2021) |
| MF | Retention of organic molecules | Retentate | Polycarbonate track-etched | <15 | Ordinary pseudo $n^{th}$ order | $V(t)=V_m-\left[\frac{V_m^{n-1}}{1+\left((n-1).K_n.V_m^{n-1}.t\right)}\right]^{\frac{1}{n-1}}$ | 0,9970 | 0.0171 | ----- | 0.2141 | ----- | ----- | (Adda *et al.*, 2020) |
| NF/RO | Treatment of waste | Permeate | Aromatic polyamide composite | <60 | Normalized interme | $J=\frac{J_{pss}.Exp(k.J_{pss}.t)}{J_{pss}+Exp(k.J_{pss}.t)-1}$ | 0,9910 | ----- | ----- | ----- | ----- | ----- | (Tong *et al.*, 2020) |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | water | | | | diate blocking | | | | | | | | |
| MF | Retention of colloidal and organic compounds | Retentate | Micro-fluidic Mimic | <600 | Complete pore blocking | $J = J_0.Exp(-K_b.t)$ | 0,9768 | ----- | ----- | ----- | ----- | ----- | (Debnath *et al*., 2019) |
| DF | Purification of several monoclonal antibodies compounds | Rejection | Cellulose(XOHC) | <500 | Cake-adsorption fouling | $CF_{cap,i} = \alpha_0 + \alpha_1.K_{C,i} + \alpha_2.K_{A,i} + \alpha_3.K_{C,i}^2$ | 0,8600 | ----- | ----- | ----- | ----- | ----- | (Goldrick *et al*., 2017) |
| MF | Separation of bovine serum albumin protein solution | Permeate | Polyethylene | <31 | Cake filtration intermediate blocking | $V = \frac{1}{K_i} Ln\left(1 + \frac{K_i}{K_c.J_0}\left(\sqrt{1 + 2.K_c.J_0^2.t} - 1\right)\right)$ | ----- | ----- | ----- | ----- | ----- | 1.9982 | (Heidari *et al*., 2017) |
| MF | Separation of mixture Oil/Water | Permeate and Rejection | Polyvinylidene fluoride | <60 | Intermediate blocking | $V = \frac{1}{K_i} Ln(1 + K_i.J_0.t)$ | 0,9896 | ----- | ----- | ----- | ----- | ----- | (Fouladitajar *et al*., 2013) |
| | | | | <60 | Genetic programming | $Y = \cos\sin\cos(\log(\sin x_1 + \sin\sin\sin x_1) - ((\sin x_2.\cos x_2.\cos\cos x_1) + \cos\cos\cos(\sin\sin(((\log x_2.\log x_1.x_1.x_1).(-\sin\log x_2 - (\cos\cos\cos(x_1.x_2).\log(x_2.\sin x_1).\cos\log\cos x_2.\cos x_2) + \sin\sin\sin x_1)) - x_1).(\cos(\log x_2 - (x_1 + x_2)) - (x_2.(\cos\cos((\log(\cos x_1 + \log x_1.\cos x_1)).\cos((x_2 - 2.\cos x_2.x_2))) + x_1).(\cos((\cos\log\cos x_2).(x_2.\log(x_2.\sin x_1)))).x_2)) - \cos x_1)))$ | 0,9999 | ----- | ----- | ----- | ----- | ----- | |

*$CF_{cap}$ is the filter capacity at pressure i (L $m^{-2}$). J is the filtrate flux (L $m^{-2}$ $h^{-1}$). P is the pressure (Pa).*

## 4. Conclusion

In this study, improved fractional dimensionless models have been developed from the pseudo nth order equation and validated by statistical criteria to comprehensively follow the DWRO desalination process using the dimensionless cumulative volume of alimentation, permeate and rejection. The validation of developed models was conducted using 2561 experimental data points collected over a span of 4 years from 66 organics RO membranes.

Such as, the fractional dimensionless models with the optimal kinetic constant (n, α, kn and knf) demonstrated an accurate result and a perfect consistency to the experimental data of DWRO desalination process. The statistical criteria were perfect with high values of R2 (0.9975, 0.9750 and 0.980) and with lower values of AARD, RMSE, SSR and SSE for alimentation, permeate and rejection, respectively. As though, the optimal order of the fractional model has the advantage of using for universal separating kinetic via RO process.

### Abbreviation

| | |
|---|---|
| AARD | Average Absolute Relative Deviation |
| DF | Depth Filtration |
| DWRO | Dam Water Reverse Osmosis |
| FDE | Fractional Differential Equation |
| FDM | Fractional Dimensionless Models |
| F-PFO | Fractional Pseudo-First-Order |
| F-PNO | Fractional Pseudo-nth-Order |
| F-PSO | Fractional Pseudo-Second-Order |
| F-PZO | Fractional Pseudo-Zero-Order |

| | |
|---|---|
| MAE | Mean Absolute Error |
| MF | Microfiltration |
| NF | Nanofiltration |
| ODE | Ordinary Differential Equation |
| ODM | Ordinary Dimensionless Models |
| O-PFO | Ordinary Pseudo-First-Order |
| O-PNO | Ordinary Pseudo-nth -Order |
| O-PSO | Ordinary Pseudo-Second-Order |
| O-PZO | Ordinary Pseudo-Zero-Order |
| PNO | Pseudo nth Order |
| $R^2$ | Coefficient of Determination |
| RMSE | Root Mean Squared Error |
| RO | Reverse osmosis |
| SSE | Sum of Squares Error |
| SSR | Sum of Squares Regression |
| TDS | Total Dissolved Salt |

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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