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Research Article

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Improving Membrane Filtration Performance through Time Series Analysis

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Abstract:
For ultrafiltration, and membrane filtration more generally, the quantitative determination of the modes of fouling remains a subject of great interest. Herein a clear method for determining the modes from a time series of volumetric flux $J(t)$ is given and illustrated with previously published filtration data of bergamot juice (Journal of Membrane Science 524 (2017) 108-116). The emphasis is upon the robust methodology which is of general applicability and offers a straightforward approach to the modelling of flux decline. The method is best viewed as being an empirical method that determines the point at which there is a switch from one mode to another is determined in a clear-cut manner and it yields excellent equations for $J(t)$. For the example chosen, the initial 4 L/m$^2$ generates some pore blocking after which the main mode of fouling is cake build-up. The variation of overall resistance with time is also informative and analysis of this series was used to check the result for the initial phase of fouling as determined from the time series of volumetric flux. A strength of the integral approach is that it enables one to establish whether the initial fouling is different in character from the subsequent fouling. Having this information can improve membrane selection and overall membrane filtration performance.

Keywords: ultrafiltration; fouling analysis; modes of fouling; fruit juice; membrane filtration performance; time series analysis
1. Introduction

Over the past four decades numerous sets of membrane filtration data have been assessed to determine the modes of fouling. These data, often presented graphically, are a time series of fluxes which are often determined from having measured the mass of permeate collected as a function of time. Since ultrafiltration membranes in industry are operated in a cross-flow mode, it is essential that allowance is made in the governing equations for the removal of foulants from the membrane surface. In a previous contribution to the literature [1] three inter-linked areas were advanced. One concerned a re-evaluation of the derivation of the flux decline relationships given in the seminal paper outlining the concept of critical flux [2]. Linked to this an alternative hydrodynamic dependency for the removal term was suggested. Instead of the removal term being simply proportional to shear stress (and independent of flux) it was suggested that the removal term could be a function of both factors by being proportional to shear stress and inversely proportional to flux (this being consistent with a model for micro-sieves [3]). Whilst the hydrodynamic dependency of the removal term is still worth of further investigation, it is important to be able to differentiate between the various phases of fouling and this differentiation might be considered a prerequisite. Thus this contribution is focussed almost exclusively upon the third area, namely use of the integral method of fouling analysis to make this differentiation. This method enables one to determine (a) the modes of fouling; (b) the switch point from one mode of fouling to another and (c) the characteristic equation for each mode. The implicit restriction inherent in the integral method is that the different membrane fouling modes are sequential and not simultaneous. For example, it is useful when fouling might initially be dominated by a phase of pore blocking and then by a phase in which cake formation is predominant.

The previous work mentioned above [1] dissipated its efforts across the aforementioned three areas which is probably why the authors of a recent paper [4] did not compare their approach
with the integral method of analysis. They used fruit juice ultrafiltration to explore the applicability of using ARIMA models. The nature of ARIMA – auto regressive (AR), integrated (I), moving average (MA) models will be outlined later. At this point it is simply noted that later a few points of commonality between the integral analysis approach and the ARIMA models will be mentioned in Section 2.6. Before reaching this point, the reader is reminded about the four fouling mechanisms for porous membranes (namely (i) complete pore blocking; (ii) internal pore blocking; (iii) partial pore blocking; and (iv) cake filtration), then some analytical approaches from the 1990’s are summarised. Section 2.4 provides a detailed derivation of the integral method of fouling analysis and thereby answer the question “What is the integral method”. Subsequently in Section 3, the filtration data for bergamot juice [4] is used to detail how the application of the integral approach can readily be made in practice. Demonstrating how the integral method of fouling analysis can be applied readily and accurately is the principal aim of this paper. A strength of this integral approach is that it enables one to establish whether the initial fouling is different in character from the subsequent fouling. Such information can improve membrane selection.

2. Theory
2.1 Early work on fouling in dead-end filtration
With regard to dead-end filtration, Hermia was the first person to provide a single equation linking the four blocking filtration laws for porous media, and the first to give a physical derivation of the so-called intermediate blocking law [5]. In his seminal paper on constant pressure filtration he references the development of these laws over the period from the 1930’s to the 1960’s and showed that the expressions for (i) complete pore blocking; (ii) internal pore blocking; (iii) partial pore blocking; and (iv) cake filtration can be linked, for constant pressure filtration, by a single equation:

\[
\frac{d^2t}{dV^2} = k_n \left( \frac{dt}{dV} \right)^n
\]  

(1)
where \( t \) is time, \( V \) is filtrate volume, \( n \) is an index characteristic of a particular mode of blocking and \( k_n \) is a constant that is dependent upon the mode of blockage and is tabulated in Table 1. A schematic of the modes of blockage is given in Figure 1.

**Figure 1** Illustration of the principal mechanisms for the fouling of porous membranes. Adsorption is not included. Source is [1].

In earlier work (e.g. [5]) the expression relating to internal pore blocking was referred to as the Standard Blocking Filtration Law. When this relationship is applicable in dead-end mode, \( t/V \) is linearly related to \( t \). The other classic relationship for dead-end filtration is the so-called Cake Filtration Law. Here \( t/V \) is linearly related to \( V \).

Writing \( dV/dt \) for convenience as \( y \), equation (1) can be re-written to introduce flux due to \( y = AJ \). Developing the left-hand side of (1)

\[
\frac{d(1/y)}{dV} = \frac{-1}{y^2} \frac{dy}{dV} = \frac{-A}{(AJ)^2} \frac{dJ}{dV} = \frac{-A}{(AJ)^2} \frac{dt}{dV} = \frac{-A}{(AJ)^3} \frac{dJ}{dt} = k_n \left( \frac{1}{y} \right)^n
\]

Substituting \( y = AJ \) on the right-hand side:

\[
\frac{-dJ}{dt} = \frac{k_n}{A} (AJ)^{3-n}
\]

For dead-end filtration, equation (3) relates flux decline to flux and the mode of fouling. Unlike equation (1), there is a physical significance to this equation. Furthermore, anticipating the developments in section 2.4, flux can be related to volume of filtrate:

\[
- \int_{J_0}^J J^{n-2} dJ = k_n A^{2-n} \int_0^t J \, dt = k_n A^{1-n} V
\]
In writing the above note was taken of the fact that \( V = A \int_0^t J \, dt \). Later use is made of the term specific volume, \( v = V / A \).

### 2.2 Early work on fouling in cross-flow membrane filtration

The remainder of this paper will use the term ‘fouling’ instead of ‘blockage’ and refer to ‘permeate volume’ rather than ‘filtrate volume’ because the focus is upon flux decline in membrane application. By including a removal term into the basic differential equations which represent three of the four fouling mechanisms Field et al [6] extended Hermia’s analysis to cross-flow filtration. The fourth fouling mechanism is the so-called standard blocking mechanism which involves intra-pore fouling. As this mechanism by definition cannot be mediated by solute/particle back diffusion from the membrane surface Hermia’s expression for the \( n = 1.5 \) mode does not need to be modified for cross-flow. Overall the equations can be elegantly unified into the following generic equation:

\[
-\frac{dJ}{dt} = K_n J^{2-n} (J - J_R)
\]

for \( J > J_R \)

where \( J \) is volumetric flux, \( n \) is an index characteristic of a particular mode of blocking and \( K_n \) is a constant that is dependent upon the mode of blockage and \( J_R \) is related to the cross-flow removal from the surface of the membrane as discussed elsewhere [6]. Herein flux decline is modelled empirically and this term is taken to be a modelling constant. Also, and the importance will become apparent in section 2.4, equation (5) can be developed in a manner akin to equation (4):

\[
- \int_{J_0}^J J^{n-2} \, dJ = K_n \int_0^t (J - J_R) \, dt = K_n (v - J_R t)
\]

where \( v \) is a specific volume; the volume of permeate per unit area of membrane.

Arnot et al [7] used equation (5) to determine the dominant fouling mechanism in a system treating an oily-water emulsion. They found that fouling was either by incomplete pore blocking (\( n = 1 \)) or ‘cake’ filtration (\( n = 0 \)) and depended on the membrane used and the
operating conditions. In order not to give undue emphasis to early or late times, the data were fitted in both flux and resistance form simultaneously. It will be immediately apparent from the following equation that as the flux declines the fouling resistance will increase so that if one is minimising the sum of the square of errors more weight will be given to fluxes at early times (because these fluxes are larger) and to resistances at later times because resistances increase with time. In the absence of an osmotic pressure difference across the membrane, the classic expression for volumetric flux is:

\[ J = \frac{\Delta P}{\mu(R_m + R_f)} \]  

(7)

where \( \Delta P \) is the pressure difference across the membrane, \( \mu \) is the viscosity of the permeate, \( R_m \) is the hydraulic resistance of the clean membrane, and \( R_f \) is the resistance due to fouling.

For use in section 2.3, it is noted that from equation (7) it follows that:

\[ \frac{dR_f}{dt} = \frac{\Delta P}{\mu J^2} \left( -\frac{dJ}{dt} \right) \]  

(8)

**2.3 Evaluation of the rate of change of resistance**

For a positive flux the value of \( \frac{dJ}{dt} \) will always be negative or zero; this is both intuitively obvious and a clear consequence of equation (5). Furthermore \( \frac{d^2J}{dt^2} \) is always negative or zero thus \( \frac{dJ}{dt} \) always decreases with respect to time until it is zero. However, the behaviour of, \( \frac{dR_f}{dt} \), is not necessarily a mirror image of \( \frac{dJ}{dt} \) [8]. Combining equations (5) and (8) it is found that:

\[ \frac{dR_f}{dt} = \frac{\Delta P K_n (J - J_R)}{\mu J^n} \]  

(9)
The term $dR_f/dt$ is always positive or zero, but the change in it with respect to flux (or time) can be positive as well as negative. Further differentiation yields:

$$\frac{d^2 R_f}{dt^2} = \frac{\Delta P K_n}{\mu J^{n+1}} [(1 - n)J + nJ_R] \frac{dJ}{dt}$$

(10)

For cake and intermediate cases (or more generally for $0 \leq n \leq 1$), $d^2 R_f/dt^2$ will, for all time values, be negative because the right-hand side of equation (10) reduces to a positive term multiplied by $\frac{dJ}{dt}$, which is negative. However for ‘complete’ pore blocking one obtains from equation (10) that:

$$\frac{d^2 R_f}{dt^2} = \frac{\Delta P K_n}{\mu J^3} [2J_R - J] \frac{dJ}{dt}$$

(11)

Thus when $J$ is more than $2J_R$ the value given for equation (11) is positive and $dR_f/dt$ initially increases with time. As discussed elsewhere [8], if the fouling mechanism is characterised by ‘complete’ pore blocking (and $J > J_R$) there should be a maximum in a plot of $dR_f/dt$ versus time plot. This method for determining the modes of fouling is not the focus of this paper; here it is used as a secondary check.

2.4 Integral method of fouling analysis

The principal advantage of this method over that in section 2.3 or say the one used by others e.g. [9] is the avoidance of the need to numerically differentiate data and thereby introduce uncertainties. The integral method is a practical method for identifying whether the initial fouling of a membrane is by the same mode as the subsequent fouling. The left-hand side of equation (6) takes four forms depending upon the value of $n$. The generic form is written as $f_n(J, n)$ and the specific forms are given in Table 1.

<table>
<thead>
<tr>
<th>Value of $n$</th>
<th>0</th>
<th>1</th>
<th>1.5</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_n(J, n)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In summary the method consists of five stages.

1. The time evolution of volumetric flux \( J \) is plotted so as to capture the trend in the data, and to establish a suitable first estimate of the cross-flow removal term, \( J_R \) from the flux asymptote. Label this estimate \( J_{Re} \).

2. Using the data from stage 1, a time series of \( \nu - J_{Re}t \) values are created and these become the abscissa values on the x-axis. The ordinate values are the four \( f_n(J, n) \) functions as given in Table 1.

3. If one \( f_n(J, n) \) function fits the data well, one can explore the possibility that there is just one mode of fouling, but the four curves are likely to indicate points of inflection at a common value of \( \nu - J_{Re}t \) [1].

4. Using data up to the point of inflection candidate values of \( n \) for the first phase of fouling are obtained.

5. Next data beyond the inflection point is used to establish the possible modes of fouling in the second phase.

6. Assuming that there is just one change in mode, the final stage is optimisation of the parameter values so as to have expressions for flux as a function of time.

Returning to equation (6), and dividing through by \( t \) it readily seen that it can be written as:

\[
\frac{f_n(J,n)}{t} = \frac{K_n\nu}{t} - K_nJ_R
\]  

(12)
For each putative value of $n$, the left-hand side can be established from the data, likewise $\frac{v}{t}$.

Hence equation (12) can be used to form four equations of the form $y = mx + c$ and one can readily establish the form that gives the best fit to the data and hence the appropriate value of $n$ (establishing the mode) and the corresponding values of $K_n$ and $J_R$. Therefore the integral method enables one to determine (a) the modes of fouling; (b) the switch point from one mode of fouling to another and (c) the characteristic equation for each mode.

2.5 Application of ARIMA models to ultrafiltration

The Box-Jenkins ARIMA approach is named after the two statisticians, George Box and Gwilym Jenkins, and is well established in the statistical literature. It is “essentially an exploratory data-oriented approach that has the flexibility of fitting an appropriate model, which is adapted from the structure of the data itself” [4]. Typically, four ARIMA models (211, 112, 212 and 111) are built to find which gives the best fit to the experimental data. The main differences between them is the order of the autoregression and the order of the moving average. This is reflected in the first and last digits of the labelling. Hence the ARIMA 111 model is first order autoregressive and has a first order moving average whereas the ARIMA 212 model is second order with respect to both the autoregression and the moving average. The ARIMA 211 model includes is second order for autoregression but the moving average is first order while the ARIMA 112 model includes a first order autoregressive element and a second order moving average. For membrane models concerned with fruit juice filtration one only need to mention non-seasonal ARIMA models. The ARIMA (p,d,q) categorisation refers, in sequence to the order of the autoregressive model (p), the degree of differencing (d), and the order of the moving-average (q). The application of this approach to ultrafiltration has until recently been limited.
2.6 Comparison of modelling approaches

Whilst a detailed comparison of the integral method of flux analysis with other methods is not the main focus of this paper, a few remarks will be made. Unlike Hermia’s approach there is due allowance for cross-flow through the inclusion of a removal term in the underlying mass balance. As with the method evaluating the rate of change of resistance (section 2.3) there is an endeavour to establish whether there is an initial mode of fouling distinct from a later mode, but they differ in that one involves numerical differentiation and the other numerical integration. The ARIMA model, is not a black-box in the same sense as artificial neural networks (ANNs) but any link to physical phenomena is missing. Interesting the main study on the use of ARIMA models for ultrafiltration of fruit juices found that the data for three different fruit juices were fitted by three different ARIMA models, the 111, 211 and 212 models [4]. Although the integral method was formulated from the physical models of Hermia, the four forms of equation (6) like the four principal ARIMA models can be viewed just in empirical terms, i.e. as expressions verifiable by observation or experience rather than theory or mechanistic modelling. Certainly, the output from the integral analysis is not restricted to a particular type of feed suspension and/or a single back-transport mechanism. This is a key point of commonality between the integral method of fouling analysis and the ARIMA modelling of others [4].

3. Practical implementation of Integral method of fouling analysis

Demonstrating that the integral method of fouling analysis can be applied readily and accurately to give a high quality representation of flux decline is the principal aim of this paper. The filtration data for bergamot juice [4] has been chosen so as to have a comparison with the ARIMA output. The source paper also contained data on pomegranate juice but “the UF of
pomegranate juice presented a not stationary behaviour” [4] and so this data was not considered further. The first stage as mentioned in section 2.4 is to plot volumetric flux ($J$) against filtration time. The flux data is available in terms of mass collected per unit area per unit time and the density of the permeate was assumed to be that of water. The data are used to generate Figure 2. From this, a value of the flux asymptote, $J_{Re}$, is found for use in stage 2.

![Figure 2](image.png)

**Figure 2** UF permeation data for bergamot juice taken from [4]. Polysulphone 100 kDa membrane of 0.16 m$^2$ operated with a TMP of 1 bar at 20 °C.

With a $J_{Re}$ value of 3 LMH, the four $f_n(J, n)$ functions given in Table 1 are plotted as functions of $v - J_{Re}t$; the creation of this plot is Stage 2. To make the plots a value of the initial flux, $J_0$, is required and an appropriate estimate can be obtained from the flux-time plot. A value of 20 LMH was used and the output is shown in Figure 3.

Stage 3 is an evaluation of the plot shown in Figure 3. If a single mode of fouling were to describe the whole data set, then one of the curves in Figure 3 would be a straight line. This is not so. The inflection in the curves around the 5th data point in Figure 2 indicates the need to examine the early data separately from the later data.
Stage 4 is concerned with an analysis of the data before the point of inflection. These are used to establish the most appropriate value of $n$ for the first stage of fouling. As indicated in Figure 4 and discussed in section 4 the appropriate value is $n=2$.

![Figure 3](image.png)

**Figure 3** Initial evaluation of the permeation data. Note the inflection in the curves around the 5th datum point.

Due to stage 3 having suggested two consecutive phases of fouling, stage 5 concerns the evaluation of the rest of the data. As indicated in Figure 5 the fit for both $n=1$ and $n=0$ are good. The $R^2$ value for $n=1$ is marginally better but the curvature in the line for $n=1$ is greater so both $n=1$ and $n=0$ are candidate values. Once optimal values of the parameter are established for each candidate mode, overall goodness of fit values can be used to determine the modes that best represents the data for each phase of fouling. This almost completes the description of how the integral method of fouling analysis can be readily implemented. The final stage is the conclusive finalisation of the modes of fouling and the determination of flux as a function of time. This is covered at the beginning of the next section.
4. Results and Discussion

When as indicated in Figure 4 the appropriate value of the fouling mode for the first phase of fouling is \( n=2 \), then the relevant equation that requires fitting is:

\[
J = J_0 - K_1(v - J_{R1}t) \tag{13}
\]
where $K_1$ and $J_{R_1}$ have subscript ‘1’ to indicate the first phase of fouling. In addition to fitting these two parameters $J_0$ is also unknown because the first data point is for $t = 5$ min. As there are three adjustable parameters and only five data points for this initial phase the fit for $n=2$ is excellent and therefore it prudent to check, if possible, whether $d^2R_f/dt^2$ is positive during this phase. As indicated in the Appendix there is a change in gradient in the resistance-time plot, but the 5 minute time interval between data points did not give unambiguous confirmation that $n>1$ because numerical differentiation was ‘noisy’.

Having determined the mode of fouling for the first phase, the remaining data point (>65) were analysed to decide between $n=1$ and $n=0$. The $R^2$ value was superior for the latter mode and the overall result is shown in Figure 6 and parameter values are given in the appendix.

![Figure 6](image)

**Figure 6** UF permeation of bergamot juice: comparison of flux data with modelling output from the integral method. The initial curve (green) reflects a $n=2$ mode of fouling and the subsequent curve (red) reflects fouling due to cake formation.

As shown in Figure 6, the overall fit is excellent and $R^2$ value is 0.995 which is superior to the value of 0.968 obtained using the ARIMA method [4]. It is said that the ARIMA method is a means by which a “time series can be approximately modelled” [4]. The method here can be considered a means by which a “time series of permeate flux can be appropriately modelled”.
‘Appropriate’ rather than ‘approximate’ because it gives insight into the mode of fouling albeit not into precise mechanisms. Indeed, to evaluate fully the membrane performance at laboratory and industrial scale it is necessary to distinguish between any initial pore blocking (which may indicate that the membrane pores are too large) and the development of cake layers which will generally build up on the membrane surface. A strength of the integral approach is that it enables one to establish whether the initial fouling phase has a fundamentally different origin from the subsequent fouling. Often there is a paucity of data points in this region which is why a cross-checking method involving $dR_f/dt$ was introduced.

Although the classical analysis of dead-end filtration used plots of $t/V$ vs $V$ to test for cake formation ($n=0$) and $t/V$ vs $t$ to test for standard blocking i.e. intra pore fouling, cross-flow analysis generally converts its data straight to flux-time data even though it is collected generally as mass-time data. For the optimal use of the method elucidated here, the retention of mass-time data is to be encouraged together with a bias towards have more data at early times. In the chosen example the initial 4 L/m$^2$ generates some pore blocking after which the main mode of fouling is cake build-up. This value equates to a liquid layer with a depth of 4mm, and it is the foulant in this layer which roughly doubles the overall resistance because of its interaction with the membrane.
5. Conclusion

The variation of overall resistance with time is informative as a check but the integral method of fouling analysis is key to having a robust empirical process which determines the switch point from one mode of fouling to another and the characteristic equation for each mode. Herein the stages of this straightforward process have been set out and illustrated with respect to the ultrafiltration of bergamot juice. For some feed-membrane pairs (such as the one examined here) the initial phase of fouling has a relatively short duration but during this period the flux is roughly halved. An undoubted strength of the integral approach is that it enables one to decide whether there is, or is not, the initial fouling is of a different character from the rest of the fouling.

References
APPENDIX

Evaluation of the rate of change of resistance

In section 2.3 it was noted that if \( n > 1 \), then the term \( \frac{d^2 R_f}{dt^2} \) can be positive. It was shown that for ‘complete’ pore blocking (\( n = 2 \)) the rate of change of \( dR_f/dt \) with respect to time is given by:

\[
\frac{d^2 R_f}{dt^2} = \frac{\Delta PK_n}{\mu j^3} [2J_0 R - J] \frac{dJ}{dt}
\]

(11)

However full use of this expression is not required; one simply evaluates \( dR_f/dt \) and plots this data versus time. Resistance-time data for the bergamot juice is given in Figure A1 and derived from this the \( dR_f/dt \) vs time plot for bergamot is given in Figure A2.

**Figure A1** Evolution of the overall resistance \((10^{12} \text{ m}^{-1})\) during the UF of bergamot juice

**Figure A2** Evolution of \( dR_f/dt \) during the UF of bergamot juice

As noted in section 4 this data is ‘noisy’. The cause is the 5 minute interval between data points. Even with a 2 minute interval (Figure A3) the data is still noisy but the positive initial gradient was clear [8].
Figure A2 Evolution of $dR_f/dt$ during microfiltration of 2% dry weight yeast suspension using a nominal 0.2 µm Ceramesh membrane unit operated at 0.5 bar with Re = 470 [8]

Details for first phase of fouling
The expression with $n=2$ was found to be superior and the relevant values of the parameters in equation (12) are:

<table>
<thead>
<tr>
<th>$J_0$ (LMH)</th>
<th>$J_{R1}$ (LMH)</th>
<th>$K_1$ (h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.13</td>
<td>7.02</td>
<td>4.59</td>
</tr>
</tbody>
</table>

Equation (12) can be converted to an equation giving flux as a function of time:

$$J = (J_0 - J_{R1})\exp(-K_1 t)$$

Details for second phase of fouling
The expression with $n=0$ was superior and the relevant values of the parameters are:

<table>
<thead>
<tr>
<th>$J_0$ (LMH)</th>
<th>$J_{R2}$ (LMH)</th>
<th>$K_2$ (h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.23</td>
<td>1.18</td>
<td>0.0101</td>
</tr>
</tbody>
</table>

From Table 1, the flux equation is: $1/J = 1/J_0 + K_2(v - J_{R2}t)$