The Modified Fouling Index Revisited: Proposal of A Novel Dimensionless Fouling Index for Membranes

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***Abstrac*-Fouling represents one of the major problems confronting the use of membranes in reverse osmosis processes. Direct and indirect consequences of fouling are decline of the permeation flux over time, reduced lifetime of membranes, more frequent washings (periodic stopping of operations), and thus greater consumption of chemicals and additional energy expenses to compensate for the decrease in membrane permeability. A brief review of studies performed on fouling indicators and experimental tests developed is presented. The goal of the present study is to present a dimensionless grouping of a limited number of parameters that could eventually serve as a fouling index under a large range of operating conditions. This is performed by an appropriate nondimensionalization of the equation of Ruth. The dimensionless number which is obtained is termed dimensionless fouling index (DFI) and can be interpreted as the ratio of the membrane resistance to that of the cake due to the concentration of the raw water.**

Keywords— fouling index, fouling, membrane, reverse osmosis, nondimensionalization

I. INTRODUCTION

One of the major problems confronting the use of membranes in reverse osmosis processes is fouling that could be termed the "Achilles heel" of this very promising technology. Fouling is defined as the process resulting in the loss of membrane performance [1]. It is caused by the accumulation of material at the membrane surface. When a membrane system operates at constant trans-membrane pressure, the most problematic consequence of fouling is the decline, sometimes very pronounced, of the permeation flux over time. Fouling can be viewed as an equivalent additional resistance to flow through the membrane. It can also influence the separation ability of a membrane acting as a second barrier which is superimposed on the membrane. Matter accumulation may occur at the surface of a membrane. Particles can block the pores and, in the case of a membrane with pores large enough relative to the substances in the water to be treated, there may be an adsorption and / or deposition of fouling substances on the inner wall of pores. In the fouling models proposed by several authors and presented later, it will be seen that, in general, researchers consider that there is first a blockage/obstruction of pores, followed by the growth of a cake at the surface of the membrane. This cake is characterized by a porosity of its own, a specific resistance opposite to flow through the membrane, a cohesion, a specific density, and a more or less homogenous granulometry [2].

Thus, it can be asserted that fouling is the main limitation for membrane separation. It is therefore necessary to know the various phenomena involved as well as the relationships and models that allow describing them. It is also important to review the state of the art regarding the solutions proposed so far to anticipate, limit or remedy fouling if possible.

This topic has been the subject of numerous research studies on modeling of fouling [3], fouling indicators) [4, 5, 6, 7, 8] or fouling mechanisms [9].

Effective control of fouling requires a proper diagnosis the fouling species that are present in a specific process. Natural waters contain a variety of components. The size, nature and physico-chemical characteristics of these components determine the fouling potential of given water. The role of a fouling indicator is to integrate all these factors into a single parameter.

Fouling indicators developed so far are based on tests with MF or UF membranes. However, several questions arise regarding the effectiveness of these indicators to predict fouling:

- Can the same fouling indicator cover a wide range of water quality?
- Is the fouling potential of water an intrinsic characteristic of that water or is it dependent on the membrane used?
- In the same vein, if the test for determining the fouling indicator uses filtration on a given membrane, to what extent is it possible to predict the performance of another membrane?

- If the test is used to determine the fouling indicator uses a dead-end cell, to what extent is it possible to predict the performance in tangential flow filtration?

Although it is not easy to provide a comprehensive response to these questions, an attempt is made to present an inventory of tests developed and used so far to see their benefits but also their limitations.

II. REVIEW ON FOULING INDEX WORK

In order to better predict fouling, Boerlage S. et al. [10] have worked extensively on the development of the MFI-UF. This method, using ultrafiltration membranes, takes account of fouling due to particles whose size is less than 0.05 microns. Membranes of two materials (polysulfone (PS) and polyacrylonitrile (PAN)) with cutoff ranging from 1 to 100 kDa are tested. The filtration is carried out at constant trans-membrane pressure (1 bar) with an acquisition of filtered volume every minute. They have emphasized the influence of the test temperature, which affects the viscosity and can significantly alter the experimental results. With the operating protocol described, the value of the MFI-UF is determined for the acrylonitrile (PAN) membranes after 20 to 50 hours of testing. The MFI-UF is not obtained in these times for the polysulfone (PS) membranes though.

The values obtained by this protocol vary between 2,000 and 13,300 s/l² while the MFI0, 45 ranges from 1 to 5 s/l² for the tap water used. The very large values of the MFI-UF show the inefficiency of traditional microfiltration membranes for determining the proper fouling potential. These high values of the MFI-UF are explained by the retention of particles of very small diameter. As a matter of fact, the MFI value is inversely proportional to the square of the diameter of the particles forming the cake. The MFI-UF turns out to be weakly dependent on the cutoff of membranes used. Values of 2000 and 4500 s/l² respectively were obtained for the PAN and PS membranes with cutoff ranging between 3 to 100kDa. This conclusion is valid within the range of cutoffs tested and for the type of water used in the tests. Following these tests, a PAN membrane of 13kDa cut off is proposed as a reference membrane for determining the MFI-UF. The limiting parameter is the duration of the test (over 20 hours).

Another method of determining the MFI-UF at constant filtration flux is also developed. This method is used to determine the MFI-UF in a shorter period (1-5h) [11]. The results also highlight the fact that the value of the MFI-UF at constant flux is stable over a short period of time relative to the MFI-UF at constant pressure.

Using the same assumptions as Boerlage S. et al. [10] and J.H. Roorda et al. [12] define the MFI-UFn (normalized MFI-UF), which is calculated with the same experimental formula as that used by Boerlage S. et al. [10]. The only difference is that they normalize the MFI values with respect to a membrane area of 1m ² and a TMP of 1 bar. Instead of following the evolution of the filtrate volume at constant pressure, it is the evolution of the trans-membrane pressure (TMP) at a constant flow rate which is monitored. The MFI-UF values obtained at constant TMP are higher than those obtained at constant flow rate; this can be explained by the compressibility of the cake.

Khirani S. et al. [13] have used NF membranes at constant TMP in order to improve the representativeness of MFI in NF/RO. This study showed that dissolved organic matter is responsible for fouling in NF/RO and must be taken into account when measuring the fouling potential. Thus, the NF-MFI allows better reflecting fouling by organic matter and the effectiveness of pretreatment. Determining the fouling index is performed within even shorter time in this case (about 1h).

June-Seok Choi et al. [14] have developed a more complex fouling index called CFI (combined fouling index). This index is based on the implementation a model in the form of as a linear relationship involving different MFI expressions. This is intended to represent various types of membranes (ultrafiltration and microfiltration) for selective separations of different types of fouling materials. This fouling index is used to measure the impact of each type of fouling material on the FDR (flux decline rate) in RO/NF as contributing factors to overall fouling involved in the model describing the CFI.

Youngbeom Yu et al. [15] have developed a new approach to evaluate the fouling potential of water supply in RO and NF. Multi membranes MMAS (multiple membrane array system) in which MF, UF and NF membranes are connected in series (the selection of membranes is based on the theory of cake filtration) is designed for separating and targeting the different types of fouling matters in waters and assessing their fouling potential. Thus, particulate, colloidal and organic matters are separated sequentially by MF, UF and NF membranes respectively. The MFI is determined for each separation resulting in three measurements: particle-MFI, colloid-MFI and organic-MFI. After an optimization of the series of MF, UF and NF membranes configurations, the results show that the evaluation of fouling potential of different types of water (raw seawater, pre-treated seawater) by the MMAS method is more precise. This method gives more information compared to conventional methods (SDI, MFI). Fouling potential indexes determined by the MMAS method accurately reflect changes in terms of water quality by the various pretreatments (sand filtration, microfiltration and ultrafiltration). Traditional measures, on the other hand, are not sensitive enough to detect these changes. It is also shown that fouling potentials evaluated by MMAS are better correlated with the rate of flow decrease determined by RO pilots. This allows stating that the MMAS provides a better prediction of fouling and a better indication for the selection of the appropriate pre-treatment.

A fouling index called Cross Flow Sampler Modified Fouling Index in Ultrafiltration (CFS-MFIUF), measured at constant flow, is developed by Lee Nuang Sim et al. [16]. This method is capable of capturing particles while simulating the hydrodynamic conditions of tangential flow in RO. Traditional fouling indices such as the MFI are measured during filtration and hydrodynamic conditions of RO are not taken into account. The results of humic acids and silica have shown that the CFS-MFIUF is not only sensitive to the presence of colloids in solution but also to organic matter. Indeed, a linear relationship between this indicator and the concentration of humic acids added to the silica is obtained. On the other hand, the comparison between measurements of the CFS-MFIUF and the MFI-UFconst.flux (Modified Fouling Index in Ultrafiltration at constant flow) shows that the conventional MFI-UFconst.flux tends to predict a larger fouling compared to the CFS-MFIUF. The CFS-MFIUF allows a better detection of the improvement in water quality after pre-treatment compared to the MFI.

The CFS-MFIUF predicts a PTM profile in agreement with the actual behavior in RO with only 11% deviation in the absence of dissolved salts. This allows saying that the CFS-MFIUF is a more realistic approach to the determination of fouling potential in RO. By cons, in the presence of dissolved salts, the PTM profile predicted by the CFS-MFIUF corresponds to the formation of a cake added to the osmotic pressure generated by the amount of salts in solution. This is not consistent with the actual behavior in RO and indicates the importance of the effect of the presence of osmotic pressure on the cake formation in RO fouling. This contribution must therefore be taken into account in the measurement of CFS-MFIUF.

A recent study [17] based on a comparison of different MFI: MFI-UF at constant pressure, MFI-UF at constant flux and CFS-MFIUF (Crossflow Sampler-Modified Fouling index-Ultrafiltration) as well as the determination of factors influencing the performance of these indicators has been performed. This study highlights the conditions to be considered during the measurement of the CFS-MFIUF to allow a more realistic assessment of fouling in RO.

III. CONTEXT OF THE PROPOSAL OF A NEW FOULING INDEX

Through the foregoing presentation, we have tried to summarize the work done so far in order to improve the prediction of fouling. It turns out; however, that the representativeness of these methods in real conditions is questionable due to:

- Difference in filtration mode,
- Cutoff of membranes unrepresentative of the molecular weight distribution of the various compounds present in water.

It is therefore necessary to try to develop other methods of measurement that would better predict the potential of membrane fouling in reverse osmosis and nanofiltration. Such methods would serve on the other hand to test the effectiveness of different pretreatment methods by assessing the fouling potential of the pretreated water.

The MFI-UF has been the object of much criticism as for its effectiveness in predicting fouling in membrane filtration plants. It is in this direction that many research studies have been conducted in order to address weaknesses in the MFI, introducing correction factors (deposition factor, compressibility factor, etc...) to improve its extrapolation and representativeness in real conditions. In the same way, fouling indicators derived from the original MFI were also implemented such as the MFI-UF at constant flow, the CFS-MFIUF, the NF-MFI, etc. in order to improve the predictive power of this index.

In the literature, we encounter a wide range of experimental values of MFI-UF dependent on operating conditions, the membranes used and the quality of the filtered water. The interpretation of these results and their impact on fouling in RO or NF is difficult because fouling mechanisms depend on the filtering technique used. It is for this reason that guiding values of the MFI-UF can be recommended for determining an acceptable level in terms of fouling prior to the RO/NF operation. Our approach is to propose a fouling indicator resulting from the nondimensionalization of the Schippers and Verdouw equation (model of cake type fouling).

The arguments for this approach are related to the recognized benefits of dimensionless equations.

The description of the system by an equation regrouping many dimensional parameters and variables is reduced through nondimensionalization to an equation containing a single dimensionless number. The advantage of a dimensionless equation is that it describes all similar physical systems, allowing moving from one scale to another (scale up-down). A dimensionless number can generally provide valuable estimates of magnitude; the value of these estimates is related to the choice of the scale. In general, a dimensionless number has a physical interpretation that contributes to the physical understanding of the phenomenon. Thus, in our case, the use of a dimensionless fouling index is justified by the difficulty in the interpretation and exploitation of the values of the dimensional MFI-UF.

The goal of the present study is to reduce the number of parameters needed to interpret the values of the original MFI-UF obtaining estimates for a single index based on certain parameters independently. Two parameters are particularly sought: the membrane type and the concentration of raw water.

Ultimately, analysis of the results obtained by experiments under different conditions of membrane type and concentration of water and their compliance with the objectives will enable us to draw conclusions about the validation of this approach. Unfortunately, the lack of adequate equipment and the lack of all needed data to make the necessary transformations using experimental results found in the literature make this step unattainable at this stage. The authors are perfectly aware of this limitation. Nevertheless, the findings of the present study are presented to the scientific community with the deliberate intent of sharing the dimensionless index which is obtained in the hope of seeing it validated by available or future experimental work.

IV. DERIVATION OF THE NEW DIMENSIONLESS FOULING INDEX

The cake filtration model is widely used. It describes the process of filtration when a cake is gradually and regularly formed on the surface of the membrane. The basic assumption of this model is that the quantity of matter deposited on the surface of the filter is proportional to the filtered volume of water. The model leads to a simple equation derived from the linearization of Ruth's equation and is particularly interesting for the development of fouling indicators. Based on this approach [4] proposed a fouling indicator called "Modified Fouling Index" (MFI) that holds account of the mechanisms which control fouling.

Based on the fundamental equations of filtration and taking into account the linearization of Ruth's equation, the cake filtration model leads to a dimensional equation involving the variables (*t*, *V*) and the parameters (μ, *r*, *C*, ΔP, *S*, R_m):

$$\frac{t}{V} = \frac{\mu r C}{2\Delta P S^2} V + \frac{\mu R_m}{S \Delta P} \tag{1}$$

With

$$\frac{\mu r C}{2\Delta P S^2} = \text{MFI} \tag{2}$$

The MFI expression is in the form of a group of dimensional parameters, the dimension of the MFI is (time/length^6) or in (s/l^2) if liter is used as the volume unit.

Where *V* is the filtrate volume and *t* is the filtration time. ΔP is the applied transmembrane pressure, μ the water viscosity, R_m the membrane resistance, A the membrane surface area, *r* the cake specific resistance and *C* is the concentration of the bulk.

In order to nondimensionalize (1), reference parameters (scales) need to be introduced. These parameters should be representative of characteristic values of the variables (*V*, *t*) in Ruth's equation. To do this, the best choice of reference scales is described by the following values:

- Volume scale (V_f)

$$V_f = \frac{R_m S}{rC} \tag{3}$$

This volume is introduced by Ruth, it is used to incorporate the contribution of the membrane resistance by equating it to a fictional cake layer with equivalent resistance. This fictitious layer is supposed to have formed before the actual start of the filtration process and corresponds to the passage of a fictitious volume (V_f) of filtrate.

$$t_{ref} = \frac{1}{R_m J_0} \tag{4}$$

With

$$J_0 = \frac{\Delta P}{\mu R_m} \tag{5}$$

J_0 being the clean water flux of the new membrane at the pressure of the experiment (CWF). Thus, the reference time t_{ref} depends only on the initial characteristics of the membrane.

The choice of these parameters is not arbitrary; their values depend on the initial characteristics of the membrane and the water to be filtered. Taking into account all these considerations, the following dimensionless variables are introduced:

$$V^* = \frac{V}{V_f} \quad \rightarrow V = V^* V_f \tag{6}$$

$$t^* = \frac{t}{t_{ref}} \quad \rightarrow t = t^* t_{ref} \tag{7}$$

From (1):

$$\begin{gathered} \frac{\mu r C}{2\Delta P S^2} V^2 + \frac{\mu R_m}{S \Delta P} V = t \\ \rightarrow V^2 + \frac{2 R_m S}{rc} V = \frac{2\Delta P S^2}{\mu r C} t \end{gathered} \tag{8}$$

Combining (8) and (3), the following expression is obtained:

$$\begin{gathered} V^2 + 2V_f V = \frac{2\Delta P S^2}{\mu r C} t \\ \rightarrow V + 2V_f = \frac{2\Delta P S^2}{\mu r C}\left(\frac{t}{V}\right) \end{gathered} \tag{9}$$

The nondimensionalization process is then performed as follows based on (9):

$$V^* V_f + 2V_f = \frac{2\Delta P S^2}{\mu r C}\left(\frac{t}{V^* V_f}\right)$$

Dividing by V_f:

$$V^* + 2 = \frac{2\Delta P S^2}{\mu r C}\left(\frac{t}{V^* V_f^2}\right) \Rightarrow V^* + 2 = \frac{2\Delta P S^2}{\mu r C V_f^2}\left(\frac{t}{V^*}\right) \tag{10}$$

Then, introducing t_{ref} in (10):

$$\begin{gathered} V^* + 2 = \frac{2\Delta P S^2}{\mu r C V_f^2}\left(\frac{t^* t_{ref}}{V^*}\right) \\ \rightarrow V^* + 2 = \frac{2\Delta P S^2 t_{ref}}{\mu r C V_f^2}\left(\frac{t^*}{V^*}\right) \end{gathered} \tag{11}$$

Replacing V_f and t_{ref} by their expressions of (3) and (4) in (11), the following expression is obtained :

$$V^* + 2 = \frac{2 r C \Delta P}{\mu R_m^3 J_0}\left(\frac{t^*}{V^*}\right) \tag{12}$$

Combining (12) and (5), the following expression is obtained:

$$V^* + 2 = \left(\frac{2rC}{R_m^2}\right)\left(\frac{t^*}{V^*}\right)$$

This dimensionless equation can then be written in a form which is similar to Ruth's linearization as follows:

$$\frac{t^*}{V^*} = \frac{R_m^2}{2rC} V^* + \frac{R_m^2}{rC} \tag{13}$$

Where $\frac{R_m^2}{2rC}$ is a dimensionless number that can be termed "dimensionless fouling index" (DFI) by analogy to (1), where:

$$\mathrm{DFI} = \frac{R_m^2}{2rC} \quad (14)$$

So that (13) can finally be written in the following form:

$$\frac{t^*}{V^*} = \mathrm{DFI}(V^* + 2) \quad (15)$$

Making a comparison between the two forms (dimensional and dimensionless) of the equation, it appears that the dimensionless form reduces to a simple linear equation that depends on a single parameter which is the dimensionless fouling index (DFI) as defined in (14) . It appears that DFI depends only on R_m, r and C. Nevertheless, one should bear in mind that it is no longer t/V which is written as a function of V but their dimensionless counterparts. Consequently, the effect of the other parameters (μ, ΔP, S) is implicitly taken into account.

The dimensionless fouling index is a group of dimensional parameters that can be interpreted as the ratio of the membrane resistance to that of the cake due to the concentration of raw water. So the larger it is, the larger is the potential of the membrane to fouling when treating the given water.

V. CONCLUSION

Fouling represents one of the major problems confronting the use of membranes in reverse osmosis processes. In the present study, a brief review of studies performed on fouling indicators. Fouling indicators developed so far are based on tests of frontal filtration with MF or UF membranes and take the form of dimensional coefficients dependant on a multitude of operating parameters. Furthermore, their values take cover extremely large intervals, which does not allow giving clear indications regarding guideline values signaling the onset of fouling or strong fouling potential.

The goal of the present study is to present a dimensionless grouping of a limited number of parameters that could eventually serve as a fouling index under a large range of operating conditions. This is performed by an appropriate nondimensionalization of the equation of Ruth's equation and the following conclusions are made:

- The dimensionless number which is obtained is termed dimensionless fouling index (DFI) and can be interpreted as the ratio of the membrane resistance to that of the cake due to the concentration of raw water.
- It is hoped that the proposed number will allow formulating appropriate fouling potential indicators falling in relatively moderate ranges under different operating conditions. This would confer a more "universal" character to the guideline values inferred and would certainly be of great convenience for industrial applications.
- It is perfectly clear that the validation of the present approach requires performing experiments under different conditions of membrane type and a range of particulate and/or dissolved material. Unfortunately, the lack of adequate equipment and the lack of all needed data to make the necessary transformations using experimental results found in the literature make this step unattainable at this stage.

The authors are perfectly aware of this limitation. Nevertheless, the findings of the present study are presented to the scientific community with the deliberate intent of sharing the dimensionless index which is obtained in the hope of seeing it validated by available or future experimental work.

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