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The Boundary Flux: New Perspectives for Membrane Process Design

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In the last decades much effort was put in understanding fouling phenomena on membranes. Many new concepts have been introduced in time, and parallel to this many parameters capable to quantify fouling issues and fouling evolution.
One successful approach was the introduction of the critical flux theory. At first validated for microfiltration, the theory applied to ultrafiltration and nanofiltration, too. The possibility to measure a maximum value of the permeate flux for a given system without incurring in fouling issues was a breakthrough in membrane process design. Nevertheless, the application to the concept remains very limited: in many cases, in particular on systems where fouling is a main issue, critical fluxes were found to be very low, lower than economical feasibility permits to make membrane technology advantageous. Despite these arguments, the knowledge of the critical flux value still remains and must be considered as a good starting point for process design concerning productivity and longevity.
In 2011, a new concept was introduced, that is the threshold flux. In this case, the concept evaluates the maximum permeate flow rate characterized by a low constant rate fouling regime, due to formation of a secondary, selective layer of foulant on the membrane surface. This concept, more than the critical flux, may be a new practical tool for membrane process designers.
In this paper a brief review on critical and threshold flux will be reported and analyzed. In fact, critical and threshold flux concepts share many common aspects which merge perfectly into a new concept that is the boundary flux. The validation will occur mainly by the analysis of previous collected data by the authors, during the treatment of olive mill wastewater. A novel membrane process design method based on the boundary flux will then be presented.

1. Introduction

In the last decade membrane technologies gain market and are used as stand-alone, integrated or substitutive processes. The technology is very appealing, both from technical and economic point of view, and has many advantages if compared to conventional technologies. On the other side, one main drawback is membrane fouling, which represents a main constraint holding membrane technologies away from a definitive maturation.
Many concepts to explain the fouling phenomena in membrane processes have been proposed during the last decades in order to overcome the knowledge gap. The need to describe fouling issues and evolution as a function of time may represent the difference for membrane technologies to become the reference technology in many industrial applications.
Nowadays, proper membrane process design can be a difficult task to accomplish when fouling is present and must be considered. The designer normally should consider the project variables concerning productivity and selectivity and follow these targets; in the presence of fouling, additional parameters, in particular the longevity

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of the membrane modules and the constancy of the permeate fluxes as a function of time must be considered. Fouling leads to a reduction of the permeate flux rate and parallel to this, may lead to sensibly shorten the life time of membrane modules. The presence of fouling, and the consequent reduction of permeate fluxes as a function of time, forces the designer to over-design the membrane plant in order to guarantee sufficient operating autonomy to conduct the process for a certain period of time at or above the permeate project values (Saad, 2005). In most cases the over-design is performed a forfeit or by past experience of the designer, starting only from the knowledge of the permeate project value, without considering in detail the entity and nature of fouling. Some examples of existing overdesigned membrane plants are reported in bibliography, when membranes are used as stand-alone technology (Hassan et al., 2010) or in combined processes such as membrane bio-reactors (Pirokova, 2006). In other cases, even worse, engineers underdesign the membrane plant, depending on higher operating conditions, which are not sustainable for long period of time. In both cases the designer partially failed in engineering the process, which becomes at the end too costly or not reliable, therefore reducing the overall confidence towards membrane technology if compared to existing conventional one.

For liquid-liquid separation processes, Field et al. introduced the concept of critical flux for microfiltration, stating that there is a permeate flux below which fouling is not promptly observed (Field et al., 1995). Afterwards, it was possible to identify critical flux values on ultrafiltration (”UF”) and nanofiltration (“NF”) membranes systems, too (Mänttäri and Nystörm, 2000). Nowadays, the critical flux concept is well accepted by both scientists and engineers as a powerful membrane process optimization tool as long critical fluxes apply. In case of most real waste water streams Le Clech et al. noticed that operations below the critical flux may not be sufficient in order to have zero fouling rates (Le Clech et al., 2006). Moreover, the measurement of critical fluxes was often not possible, and in order to overcome this problem, the identification of "apparent" critical points were used. Therefore it appears that membrane systems treating real waste water streams do not exhibit a critical flux in strict way. To overcome this limitation in the definition of critical flux, in a recent paper, Field and Pearce introduced for the first time the concept of the threshold flux (Field and Pierce, 2011). Summarizing briefly the concept, the threshold flux is the flux that divides a low fouling region, characterized by a nearly constant rate of fouling, from a high fouling region, where flux dependant high fouling rates can be observed. Finally, Stoller and Ochando-Pulido performed some research on this topic by using olive mill wastewater streams, both exiting the 2-phase with (Ochando-Pulido et al., 2014) and without (Ochando-Pulido and Stoller, 2014) and the 3-phase olive oil production processes, again with (Stoller et al., 2014) and without (Stoller and Ochando-Pulido, 2012) pretreatment processes. As a research output, the Authors merged the two separate concept together, pointing out their mathematical and qualitative similarity, into the concept of the boundary flux (Stoller and Ochando-Pulido, 2014). Moreover, the relationship between a proper pretreatment tailoring and boundary fluxes was further investigated by using coagulation and photocatalysis as a pretreatment step, by adopting magnetic core (Ruzmanova et al., 2013a) or doped titania nanoparticles (Ruzmanova et al., 2013b)

In this paper, a very brief review on the boundary flux will be reported. The concept will then be used to propose a membrane process design method which aims to define a suitable membrane area value to operate the plant always below boundary flux conditions that is without triggering irreversible membrane fouling. The use of this simple, yet reliable method may be of great benefit to membrane practitioners.

Moreover, a practical example performed on the design of batch membrane plants for the treatment of olive mill wastewater streams (3-phase) by means of ultrafiltration and nanofiltration will here be presented.

2. The boundary flux equations

The boundary flux divides the operation of membranes in two different regions: a lower one, where no or a small, constant amount of fouling triggers, and a higher one, where fouling builds up very quickly. The relevant equations may be written as:

$$dm/dt = - \alpha;\ J_p(t) \leq J_b \quad (1)$$

$$dm/dt = - \alpha + \beta\ (J_p(t) - J_b);\ J_p(t) > J_b \quad (2)$$

where:

- α, expressed in [L h^{-2} m^{-2} bar^{-1}], represents the constant permeability reduction rate suffered by the system and will be hereafter called the sub-boundary fouling rate index. α is a constant, valid for all flux values.
- β, expressed in [h^{-1} m^{-2} bar^{-1}], represents the fouling behavior in the exponential fouling regime of the system, and will be hereafter called super-boundary fouling rate index. β appears to not be a constant, and changes with the transmembrane pressure TMP.

In case the value of α is equal to zero, critical flux conditions are met; in the opposite case, the threshold flux concept applies.
The boundary flux value itself is a function of many parameters, mainly affected by hydrodynamics (Re number), temperature (T) and the solute concentration (KP). In this work the key parameter KP will be the COD value of the feedstock. If the other parameters remain constant, the relationships can be summarized separately in the following set of equations:

$$J_b\,(Re) = J_b\,(Re\rightarrow\infty)\ (\ 1 - e^{\ A\ Re})\tag{3}$$
$$J_b\,(T) = A_T\ T^2 + B_T\ T + C_T\tag{4}$$
$$J_b(KP,t) = w\ P_b(0) - \alpha\ t\ P_b(0) - [\ w\ p_1 - \alpha\ p_1\ t + m_1\ P_b(0)\ ]\ KP + m_1\ p_1\ KP^2\tag{5}$$

with A, A_T, B_T and C_T fitting parameters. It is interesting to notice that only the last one is a function of time as well, even if KP remain constant during operation. On contrary, by proper control systems, both Re and T can be maintained constant by fixing their set-point. In eq.(5) w, m_1 and p_1 are fitting parameters of the respective equations fitting the membrane permeability m and the osmotic pressure π to KP, respectively:

$$m(KP,t) = w - m_1\ KP\tag{6}$$
$$\pi(KP) = p_1\ KP\tag{7}$$

and where $P_b(0)$ is the applied operating pressure at the boundary flux conditions at the start of operation, in detail:

$$P_b(0) = TMP_b + \pi(KP)|_{t=0}\tag{8}$$

The pure water permeability, that is w, may be a function of time depending from the amount of irreversible fouling formed over on the membrane.
The definition of a value for J_b permits to determine the range of validity of eq.(1), here of interest for membrane process design purposes.
The model is completed by two equations concerning permeate fluxes and selectivity, that is:

$$J_p(t) = J_p(0) - \alpha\ TMP(t)\ t;\ J_p(0\div t) \le J_b\tag{9}$$
$$R(KP) = \sigma\ TMP\ (\ TMP + \gamma\ )^{-1}\tag{10}$$

where σ is the reflection coefficient and γ a fitting parameter.

3. The membrane process design method

The proposed equations are suitable for batch membrane processes and are used to determine the membrane area required to permit operation below boundary flux conditions. The membrane area A depends on the adopted control strategy. Mainly two main membrane processes control strategies are adopted, that is controlling the permeate flow rate by changing the applied pressure value by a regulation valve on the retentate line (FC), or controlling directly the constancy of the applied pressure (PC).
Without going into much detail about the mathematical elaboration of the relevant expressions, in case of FC, the membrane area is evaluated by:

$$A = F_p\ (\ 1 - 0{,}01\ \delta\ )^{-1}\ J_b(\tau)^{-1}\ (\ 1 + 0{,}01\ (\ N - 1\ )\ \tau\ \ \Delta w\%\ )\tag{11}$$

where F_p is the desired permeate flow rate, δ a safety margin in design (in the order of 5-10%), N the number of batches before the substitution of the membrane modules, τ the operating time, and Δw% the recovery percentage compared to the previous pure water permeability value at start of operation.
In case of PC, the expression becomes:

$$A = F_p\ (\ J_b(0) - 0{,}5\ \alpha\ TMP_b\ (1 - 0{,}01\ \delta\ )\ \tau\ )^{-1}\ (\ 1 + 0{,}01\ (\ N - 1\ )\ \tau\ \ \Delta w\%\ )\tag{12}$$

It is interesting to notice that $A_F \ge A_P$, thus in most cases the PC strategy appears to be the best choice concerning costs. On the other hand, this strategy does not permit to achieve the constancy of the permeate flow rate exiting the membrane process. In case this stream is further used by down-stream processes, a FC strategy suits probably better.

Moreover, the use of a PC strategy does not require the knowledge of a value of J_b at the end of operation, and such as does not require the use of a simulation software as the one developed by Stoller [xx].

4. Results and discussion

Chapter 2 For the boundary flux measurements, the pressure cycling method was used. Details of this method are reported elsewhere (Stoller, 2013). Moreover, by using a proper experimental device, reported elsewhere (Stoller et al., 2013), the values of the input parameters to the set of equations were determined (Stoller et al., 2013). The obtained data is reported in Table 1. In the same Table, the simulation software was used to estimate the operating time and compared to experiments. The error on the estimated operating time to reach the target recovery Y* was equal to 6% and 2% for UF and NF, respectively.

Table 1: Results of the validation procedure of the simulation software (SIM) compared to experimental measurements (EXP)

Membrane type	UF		NF	
Operation mode	Batch at constant TMP sub boundary		Batch at constant TMP sub boundary	
A [m^2]	2.51		2.51	
δ [%]	5.0		5.0	
P [bar]	9.5		8.5	
σ [-]	0.15		0.65	
γ [-]	1.5		0.6	
p_1 [bar^{-1} KP^{-1}]	0		$1.0\ 10^{-4}$	
m_1 [L h^{-1} m^{-2} bar^{-1} KP^{-1}]	$2.3\ 10^{-5}$		$5.0\ 10^{-5}$	
J_b [l h^{-2} m^{-2}]	5.9		6.9	
P_b [bar]	10.0		9.0	
α [L h^{-2} m^{-2} bar^{-1}]	$27.0\ 10^{-3}$		$19.1\ 10^{-3}$	
w [L h^{-1} m^{-2} bar^{-1}]	1.05		1.11	
KP(0) [mg/L]	COD: 20000		COD: 6800	
V(0) [L]	34		25	
	EXP	SIM	EXP	SIM
Y* [%]	73.5	73.5	84.0	84.0
τ [min]	343	365	179	183
Error	6.4 %		2.2 %	

At the boundary flux conditions, the COD rejection values of the UF and NF feedstock are 0.13 and 0.61, respectively.

The developed model provided by reliable input data was then used to estimate the required membrane area of a batch membrane process plant capable to treat 1 m^3 of OVW for three years before a membrane module substitution. These results, labeled SIM, are shown in Table 2 and compared with those obtained by the use of eq. (11) and eq. (12), labeled CALC.

In case of FC strategy, a value of $J_b(\tau)$ must be known, and the relevant KP(τ) value was roughly estimated by:

$$KP(\tau) = KP(0)\ (1 - Y^* + Y^* R(TMP_b))\ (1 - Y^*)^{-1} \quad (14)$$

Table 2: Membrane process design for the treatment of 1 m^3 of OVW with (SIM) and without (CALC) the aid of the simulation software, respectively

	UF		NF	
Y* [%]	95.0		80.0	
δ [%]	5.0		5.0	
τ [h]	10		10	
N [-]	270		270	
Δw% [% h^{-1}]	16.0 10^{-3}		9.0 10^{-3}	
V(0) [L]	855		812	
	SIM	CALC	SIM	CALC
PC STRATEGY				
P [bar]	9.5	9.5	8.5	8.5
Ymax [%]	95.0	95.0	75.0	75.0
A [m^2]	22.6	21.2	15.2	16.5
Difference [%]	6.1		8.5	
FC STRATEGY				
KP(τ)		COD: 69400		COD: 23392
F_P [L h^{-1}]	85.5		81.2	
Ymax [%]	95.0	95.0	80.9	75.0
A [m^2]	29.1	27.8	18.9	17.2
Difference [%]	4.5		9.0	

By using the proposed method the miss design is less than 10 % in all cases if compared to the results obtained by using a much more precise simulation software.

5. Conclusions

A method to calculate the required membrane area on the basis of the boundary flux theory was here developed and reported. A simulation software was used to compare results. Experimental work was required in order to determine the input parameters for both the model and the method.
The comparison of the obtained results shows that the proposed method is capable to evaluate the correct membrane area required to operate batch membrane processes in sub boundary flux conditions with an error within 10%.

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