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Study On Fouling Behaviour Of Ultrafiltration And Nanofiltration During Purification Of Different Organic Matter Polluted Wastewaters

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The boundary flux concept is a profitable tool to analyse fouling issues in membrane processes. The boundary flux value separates an operating region characterized by reversible fouling formation from irreversible one. Boundary flux values are not constant, but function of time, as calculated by the sub-boundary fouling rate value. The knowledge of both parameters may fully describe the membrane performances in sub-boundary operating regimes.

Many times, for wastewater purification purposes, ultrafiltration and nanofiltration membranes are employed to treat different wastewater streams. This appears to be feasible from both technical and economical point of view many times. Whereas initial productivity and selectivity to reach the desired purification targets are generally guaranteed, key to reach process feasibility is that the membrane must resist to fouling issues, with a limited reduction of the performances as a function of time. In other words, longevity of the membranes must be that high to minimise their substitution and, consequently, operating (consumable) costs for the replacement.

In this work, after a brief introduction to the boundary flux concept, for many different wastewater, the boundary flux and sub-boundary fouling rate values of different microfiltration and ultrafiltration membranes will be discussed and compared. By this approach, it will be possible to separate those systems where the use membranes for their treatment results successfully from those that represent a challenge (from a technical and/or economic point of view). This will depend sensibly of the feedstock characteristics and, in detail, on the particle size of the suspended matter and guidelines for process designers will be discussed.

In most cases, it will be shown that membranes appear to perform very well, making this technology very interesting for many case studies.

1. Introduction

Ultrafiltration (UF) and nanofiltration (NF) are widely used for wastewater stream treatment purposes. Typical pore sizes of UF and NF ranges from about 1 to 10 nm and 0.1 to 1 nm, respectively. In this range, multiple large and small molecules are retained. On the other hand, ions (monovalent) and smallest molecules passes through the membrane.

The liquid phase of the feed flow passed though the membrane at moderate pressure values and relative high fluxes. The technology exhibits many advantages such as to perform the separation of pollutants without addition of further chemicals, to permit operation at ambient temperature, produces constant product quality regardless of feed quality, is capable of exceeding regulatory standards of water quality and plant dimensions are limited.

Industries such as chemical and pharmaceutical manufacturing, food and beverage processing, and waste water treatment, employ ultrafiltration in order to recycle flow or add value to later products. Blood dialysis also utilizes ultrafiltration. UF can be used for the removal of particulates and macromolecules from raw water to produce potable water. It has been used to either replace existing secondary and tertiary filtration systems

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employed in water treatment plants or as standalone systems. UF is also used extensively in the dairy industry; particularly in the processing of cheese whey to obtain whey protein concentrate (WPC) and lactose-rich permeate. In a single stage, a UF process is able to concentrate the whey 10–30 times the feed.

NF is the follow-up membrane to UF if higher purification is required. This membrane is used in the Pharmaceutical industry, Oil and Petroleum chemistry, for the purification of gas condensates, production of Natural Essential Oils and similar products as well as in wastewater treatment plants.

A major phenomenon that limits the performances of the membranes is fouling. The initial performances of UF and NF, exhibited by the new membranes, may be quickly lost due to fouling. Moreover, the membrane will suffer from irreversible pore occlusion: therefore, the longevity will result sensibly decreased.

Membrane fouling, expressed as a permeate flux reduction as a function of time given by some phenomena different than polarization and/or aging of the membrane, can be subdivided in three main typologies:

1. A reversible fouling; this kind of fouling strictly follows the driving force amplitude, e.g. operating pressure values. As soon as the pressure over the membrane is reduced, this fouling is eliminated after a certain (short) period of time by the same quota.

2. A semi-reversible fouling; this kind of fouling accumulates over the membrane surface and cannot be easily eliminated. The only way to eliminate this kind of fouling is to stop the separation process and clean or wash the membranes, with water or aqueous solution of chemicals, respectively. Although this kind of fouling is after the cleaning/washing procedure almost eliminated, it represents a problem in the continuous process operation since it forces to process shut-down at timed intervals.

3. An irreversible fouling; once formed, this kind of fouling cannot be eliminated by any procedure. It is the main cause of membrane failure concerning productivity.

In all cases, during operation of tangential cross flow separation by membranes, all three fouling types will unavoidably appear and form. The existence of different fouling typologies affecting membranes were previously explained by Bacchin et al. and Oringer et al., and are based on the assumption of possible local conditions triggering different liquid/gel phases over the membrane and in the membrane pores due to the concentration profiles by polarization [33,34].

Field et al. introduced the critical and boundary flux concepts. Summarizing, both critical and threshold fluxes divide the operation of membranes in two regions: a lower one, where no or a small, constant amount of fouling (mostly reversible and/or semi-reversible) triggers, and a higher one, where (irreversible) fouling builds up very quickly.

By using a new flux, that is the boundary flux Jb, the critical and threshold flux equations may be merged in one set, and may be written as:

$$dm/dt = -\alpha \qquad ; Jp(t) \leq Jb \qquad (1)$$

$$dm/dt = -\alpha - \beta\,(Jp(t) - Jb) \qquad ; Jp(t) > Jb \qquad (2)$$

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 [$h^{-1}\ bar^{-1}$], represents the fouling behaviour 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)
- m, expressed in [$l\ h^{-1}\ m^{-2}\ bar^{-1}$], represents the membrane permeability;
- Jp, expressed in [$l\ h^{-1}\ m^{-2}$], represents the permeate flux.

Eq.1 is the most relevant one, since only reversible fouling triggers and therefore the membrane longevity results maximized. In this respect, operating below the Jb value is sufficient to guarantee long-term performances. In a second step, the value of α determines how long the membrane may operate without cleaning procedures. Cleaning membranes represent a cost and an operation stop which is certainly not desired to certain extent. Therefore, low α value membranes are preferred to high α value ones.

In this work, a small review about applications of UF and NF membrane processes will be listed and studied, in order to check whatever membrane is more suitable to perform the case study feed stream treatments. One one side, UF should exhibit higher permeabilities, leading to higher performances and less membrane area (investment costs); on the other side, UF may be more prone to fouling issues. The results will lead to possible justification on the different membrane behaviours as a function of the different feed streams.

2. Experimental data

Experimental data of UF and NF membranes employed in different processes are reported in Table 1.
In the last column of Table 1, the optimized membrane area surface requirement (A) needed to operate the membrane system for the treatment of 1m^3 h^{-1} of feed stream for 3 years, below the Jb value, with a washing cycle period equal to 1h by adopting the methods developed by Stoller and Ochando Pulido, is reported.
Since investment costs are directly proportional to A, the value of this parameter gives a straight indication of economic and technical optimization.

Table 1: Experimental data of selected wastewater streams

Process	Membrane	J_b [l h^{-1} m^{-2}]	TMP [bar]	α [l h^{-2} m^{-2} bar^{-1}]	A [m^2]
High salinity drilling water	UF	202.9	20	0.0085	5.10
	NF	157.4	20	0.0060	6.47
Olive mill wastewater (2 phase)	UF	8.2	9	0.0160	122.10
	NF	11.8	8	0.0070	84.80
Olive mill wastewater (3 phase)	UF	3.1	4	0.0239	322.68
	NF	12.2	4	0.0084	82.00
Whey solution	UF	14.7	3	3.63	78.92
	NF	15.4	8	0.54	69.26
Humic Acid solution	UF	72.7	2	5.0	23.76
	NF	47.6	2	175.0	371.01
Landfill Leachate	UF	30.4	17	10.08	204.25
	NF	106.9	20	1.60	41.35
Pharaceutical industry ww	UF	90.0	5	0.067	11.45
	NF	70.0	5	0.320	15.89

3. Results and Discussion

From the data in Table 1 it is possible to observe that in case of an α value different than zero, in most investigated cases, beside treating Humic Acid solutions, the NF membrane appears to be more suitable than UF.
Possible justifications of this observed behaviour may be only hypothesized. The authors wish to present some different explanations:

- Local boundary flux values exceeded: Oringer and al. introduced in a previous work a nice concept, that is the local critical flux. In other words, they express critical fluxes for single pores and hypothesized that every pore may have its own critical pore flux value. Therefore, fouling may be a statistical consequence of some pores exceeding critical pore conditions, given also by the not homogeneous distribution of feed and pressure over the membrane, thus triggering fouling. In a second step, since some pores will be blocked, fluxes may increase on nearby pores, overcoming again critical pore flux values and promoting the growth of fouling over several pores. This concept can easily fit boundary flux, since the latter shares with the critical flux main concepts. If this is true, as soon as permeate fluxes are on average high, most probably the range of fluxes is wide spread and such as may statistically trigger fouling due to overcoming single pore boundary fluxes. This phenomena my trigger easily in presence of larger pores, that is UF rather than NF.

- Stoller et al. analyzed in a previous work how fouling, among other factors, is a function of particle size and concentration. In this work, particle size distribution was put in relationship to the boundary flux, and fitting equations were determined. Moreover, a rule of thumb was given, that is particles with a size of 1/10 to 10 times the pore size is those affecting pore blocking and therefore fouling (Figure 1). MF pores are in the size range of many macromolecules in many industries concerning biotech, food and manufacturing. NF has smaller pore sizes, thus even if characterized by lower permeability values, it may over-perform UF in the moment that the concentration and size of the molecules in the feed stream are outside the danger range. This is especially true if molecules agglomerates: as soon as the agglomerate forms, it will grow in size and therefore may reach the danger size for the membrane. On contrary, the same phenomena will keep NF safe, since smaller particles will agglomerate to larger ones and therefore will not affect the membrane pores.

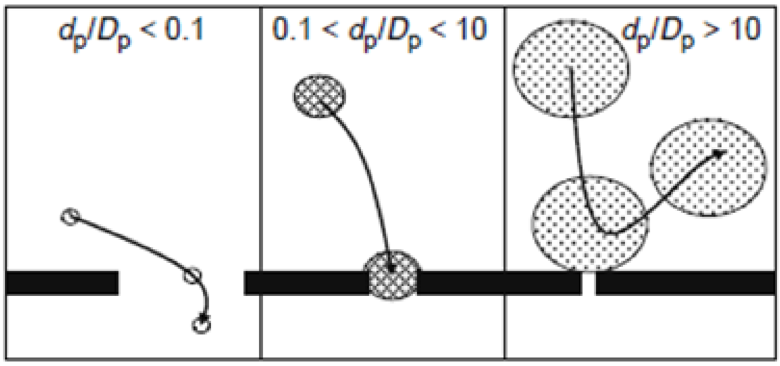

Figure 1. Pore blocking mechanism as a function of the particle size

- Severe gelification: the experience of high permeate fluxes leading to severe fouling was previously observed on polymeric nanosieves. Despite the name, these are tight UF membranes. In this case, the nanosieves were prepared by nanoneedles, and once formed, punched through a polymeric dense film. The result was a dense membrane exhibiting nanopores, which perfectly follow the pattern on the stamp. For the first time, polymeric UF membranes exhibits the same pore size and density throughout the membrane, and hope was that this could lead to improved performances and longevity. Unfortunately, despite the amazing fabrication results, both performances and longevity sensibly decreases. The main reason was too high permeate fluxes crossing the membrane, resulting to yield local recovery values that high to leads the concentrate stream on top of the membrane to overcome the gel concentration. Not capable to move along with the bulk stream, the gel starts to deposit over the surface and to cover the pores, resulting in severe fouling that decreases the fluxes almost instantaneously. The passage from the gel state to irreversible fouling is short, thus in the longer run the membrane will definitively loose its performances. Since gelification is triggered more easily by longer molecules put tightly together, this phenomenon is more likely to happen on UF; in case of NF, between this relatively big molecules, smaller ones will keep them apart, lowering their local concentration and, as a consequence, hindering gel formation by steric means.

Most probably, the justification of the better performances of MF affected by boundary fluxes at α values not equal to zero is at least a combination of the hypothesis here given separately. This aspect merits further investigation and should be exploited in future work.

4. Conclusions

This study reports the use of UF and NF for many real process and wastewater streams, in order to check if there is a membrane representing the best choice for membrane process designers.

The results show that not always UF appears to be a good choice, leading in some cases to higher membrane surface requirements if compared to NF, even if characterized by a smaller pore size and reduced performances.

The main issue appears to be membrane fouling, that appears to be more severe in case of UF membranes if compared to NF membranes. As a consequence, in the long term the initial performances of UF membranes may be quickly nullified, and the use of these membranes leads to higher membrane area requirements to maintain fluxes at or above the target (project) ones.

References

Bacchin P., Aimar P., Field R.W., 2006, Critical and sustainable fluxes: Theory, experiments and applications, J. Membr. Sci. 281, 42.

Badrnezhad R., Mirza B., 2014, Modeling and optimization of cross-flow ultrafiltration using hybrid neural network-genetic algorithm approach, J. Ind. Eng. Chem. 20 (2), 528-543.

Baker R.W., 2004, Membrane Technology and Applications, John Wiley & Sons Ltd, England.

Bavasso I., Vilardi G., Stoller M., Chianese A., Di Palma L., 2016, Perspectives in Nanotechnology Based Innovative Applications For The Environment, CET 47, 55-61.

Cheremisinoff P.N. (1995), Handbook of Water and Wastewater Treatment Technology, Marcel Dekker Inc., New York.

Cicci A., Stoller M., Bravi M., 2013, Microalgal biomass production by using ultra- and nanofiltration membrane fractions of olive mill wastewater, Water Res. 47, 4710.

Di Palma L., Petrucci E. - Treatment and recovery of contaminated railway ballast, Turkish J Eng Env Sci, 38, 248-255, 2014, doi:10.3906/muh-1404- 9.

Field R.W., Wu D., Howell J.A., Gupta B.B., 1995, Critical flux concept for microfiltration fouling, J. Membr. Sci. 100, 259.

Field R.W., Pearce G.K., 2011, Critical, sustainable and threshold fluxes for membrane filtration with water industry applications, Adv. Colloid Interface Sci. 164, 38.

Gueye M.T., Di Palma L., Allahverdeyeva G., Bavasso I., Petrucci E., Stoller M., Vilardi G., 2016, The Influence of Heavy Metals and Organic Matter on Hexavalent Chromium Reduction by Nano Zero Valent Iron in Soil CET 47, 289-295.

Gueye T.M., Petrucci E., Di Palma L., 2015, Chemical reduction of hexavalent chromium (vi) in soil slurry by nano zero valent iron, Chemical Engineering Transactions, 43, 655-660 DOI: 10.3303/CET1543110

Iaquinta M., Stoller M., Merli C., 2009, Optimization of a nanofiltration membrane process for tomato industry wastewater effluent treatment, Desalination 245, 314.

Le-Clech P., Chen V., Fane T.A.G., 2006, Fouling in membrane bioreactors used in wastewater treatment, J. Membr. Sci. 284 (1–2), 17.

Lim A.L., Rembi B., 2003, Membrane fouling and cleaning in MF of activated sludge wastewater, J. Membr. Sci. 216, 279.

Manttari M., Nystorm M., 2000, Critical flux in NF of high molar mass polysaccharides and effluents from the paper industry, J. Membr. Sci. 170, 257.

Ochando-Pulido J.M., Stoller M., Di Palma L., Martínez-Ferez A. (2016), On the optimization of a flocculation process as fouling inhibiting pretreatment on an ultrafiltration membrane during olive mill effluents treatment, Desalination, Volume 393, Pages 151–158;

Ochando-Pulido J.M., Stoller M., Di Palma L., Martinez-Ferez A. (2014). Threshold performance of a spiral-wound reverse osmosis membrane in the treatment of olive mill effluents from two-phase and three-phase extraction processes. Chemical Engineering and Processing: Process Intensification, Vol. 83, P. 64-70. DOI: 10.1016/j.cep.2014.07.006

Ognier S, Wisniewski C, Grasmick A. Membrane bioreactor fouling in sub-critical filtration conditions: a local critical flux concept. J Memb Sci 2004;229

Ruzmanova Y., Ustundas M., Stoller M., Chianese A., 2013a, Photocatalytic treatment of olive mill wastewater by n-doped titanium dioxide nanoparticles under visible light, CET 32, 2233-2239.

Ruzmanova Y., Stoller M., Chianese A., 2013b, Photocatalytic treatment of olive mill wastewater by magnetic core titanium dioxide nanoparticles, CET 32, 2269-2275.

Stoller, M., Ochando Pulido, J.M., Di Palma, L., Ferez, A.M., (2015). Membrane process enhancement of 2-phase and 3-phase olive mill wastewater treatment plants by photocatalysis with magnetic-core titanium dioxide nanoparticles, Journal of Industrial and Engineering Chemistry 30, 147 – 152

Stoller M., Ochando-Pulido J.M., 2012, Going from a critical flux concept to a threshold flux concept on membrane processes treating olive mill wastewater streams, Procedia Eng. 44, 607.

Stoller M., 2013, A three year long experience of effect ive fouling inhibition by threshold flux based optimization methods on a NF membrane module for olive mill wastewater treatment, CET 32, 37-42.

Stoller M., Ochando-Pulido J.M., 2013, Comparison of Critical and Threshold Fluxes on Ultrafiltration and Nanofiltration by Treating 2-Phase or 3-Phase Olive Mill Wastewater, CET 32 (2013), 397-403.

Stoller M., Bravi M., 2010, Critical flux analyses on differently pretreated olive vegetation waste water streams: some case studies, Desalination 250 (2), 578.

Stoller M., De Caprariis B., Cicci A., Verdone V., Bravi M., Chianese A., 2013, About proper membrane process design affected by fouling by means of the analysis of measured threshold flux data, Sep. Purif. Technol. 114, 83.

Stoller M., Ochando-Pulido J.M., 2014, About Merging Threshold and Critical Flux Concepts into a Single One: The Boundary Flux, Sci. World J., ID:656101.

Stoller M., Ochando Pulido J.M., 2015, The boundary flux handbook, ISBN 9780128015896.

Stoller M., 2016, About the Validation of Advanced Membrane Process Control Systems in Wastewater Treatment Applications, CET 47, 385-391.

Stoller M., Azizova G., Mammadova A., Vilardi G., Di Palma L., Chianese A., 2016, Treatment of Olive Oil Processing Wastewater by Ultrafiltration, Nanofiltration, Reverse Osmosis and Biofiltration, CET 47, 409-415.

Stoller M., Ochando Pulido J.M., Di Palma L., 2014, On The Relationship between Suspended Solids of Different Size, the Observed Boundary Flux and Rejection Values for Membranes Treating a Civil Wastewater Stream,Membranes, 414.

Stoller M., Di Palma L., Merli M., 2011, Optimisation of batch membrane processes for the removal of residual heavy metal contamination in pretreated marine sediment, Chemistry and Ecology 27, 171.

Vyas H.S., Bennett R.J., Marshall A.D., 2002, Performance of cross flow MF during constant TMP and constant flux operations, Int. Diary J. 12, 473.