About the limits of microfiltration for the purification of wastewaters

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Abstract

In the past, microfiltration was widely used as a pretreatment step for wastewater stream purification purposes. Experiences performed during the last years shows that microfiltration fails to maintain its performances for longer period of times. Many case studies demonstrate that the adoption of microfiltration leads to the failure of the overall process; the severe fouling of the microfiltration membranes leads to high operating costs with the consequence to make the treatment of the wastewater economically unfeasible. The boundary flux concept is a profitable tool to analyze 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 content, 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 membranes appear to be suits better to the needs, even they exhibit lower permeate fluxes compared to microfiltration. Key to this choice is that ultrafiltration appears to resist better to fouling issues, with a limited reduction of the performances as a function of time. In other words, it appears that ultrafiltration exhibit higher boundary flux values and lower sub-boundary fouling rates. In this work, after a brief introduction to the boundary flux concept, for many different wastewater streams (more than 20, produced by the most relevant industries in food, agriculture, manufacture, pharmaceutics), the boundary flux and sub-boundary fouling rate values of different microfiltration and ultrafiltration membranes will be discussed and compared. The possibility to successfully use microfiltration as a pretreatment step strongly depends on the feedstock characteristics and, in detail, on the particle size of the suspended matter. In most cases, microfiltration demonstrates to be technically unsuitable for pretreatment purposes of many wastewater streams; as a consequence, the adoption of microfiltration pushes operators to exceed boundary flux conditions, therefore triggering severe fouling, that leads to economic unfeasibility of the process in long terms.

Keywords: membranes, fouling, boundary flux, wastewater treatment, microfiltration

1. Introduction

Microfiltration (MF) usually is used as a pre-treatment for other subsequent membrane separation processes and as a post-treatment step for granular media filtration to eliminate suspended solids. Typical pore sizes of microfiltration ranges from about 0.1 to 10 µm (Barker, 2004). In this range, multiple coarse particles such as sediment, algae, protozoa or large bacteria are withdrawn (Cicci *et al*., 2013). On the other hand, dissolved material and smaller particles such as nanoparticles and salt ions, passes through the membrane (Di Palma, 2014; Bavasso, 2016; Gueye, 2015; Gueye, 2016). The liquid phase of the feed flow passed though the membrane at moderate pressure values and high fluxes (Cheremisinoff, 1995). Appealing to MF is the low required membrane area to treat higher volumes of feed (Stoller, 2013). This is especially true when new MF membranes are employed (Vyas, 2002). Water and wastewater treatment are two main applications for MF (Lim, 2003, Le-Clech, 2006; Ochando Pulido, 2014; Ochando Pulido 2016). The permeate stream, after treatment using a micro-filter, reaches recovery values up to 90-98%, highest in membrane technology. The most prominent use of MF membranes is the treatment of potable water supplies, being a key step in the primary disinfection of the feed water stream. Protozoa Cryptosporidium and Giardia Lamblia, which are responsible for numerous disease outbreaks and show a gradual resistance to traditional disinfectants, are immediately withdrawn without use of additional chemicals such as in other processes (Ruzmanova, 2013ab). Similarly, the MF membranes can be used in secondary wastewater effluents to remove turbidity and provide disinfection. At this stage, coagulants (iron or aluminum) may potentially be added to precipitate species such as phosphorus and arsenic which would otherwise have been dissolved. Sterilization of beverages and pharmaceuticals is another application of MF membranes. In the past, heat was used to sterilize milk, juice, wine and beer in particular, with a loss in flavor and nutrients. At the same time, pharmaceuticals have been shown to lose their effectiveness upon heat treatment. MF membranes as a method to remove bacteria and other undesired suspensions from liquids without heat solves these problems. Furthermore, MF membranes are finding increasing use in areas such as petroleum refining, for the removal of particulates from flue gases. The key requirements for this technology are the ability of the membrane modules to withstand high temperatures and to provide a very thin sheeting (thickness < 2000 angstroms) to increase the flux. A major phenomenon that limits the performances of MF is membrane fouling (Stoller, 2010). The exceptional performances of MF, 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. Field *et al*. (1995, 2011) 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 J_b, the critical and threshold flux equations may be merged in one set, and may be written as (Stoller, 2014):

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

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

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} 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).

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 J_b value is sufficient to guarantee long-term performances. In a second step, the value of α determines how long the membrane may operate without clening procedures. Cleaning membranes represent a cost and a 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 MF membrane processes will be listed and studied, in order to check if MF is effectivley the best choice, or if other membrane types such as tight MF or ultrafiltration (UF) are more siutable. Moreover, the results will lead to possible justification of MF miss behaviours and some guide lines will be given within the text.

2. Experimental data

Experimental data of MF membranes employed in different processes are reported in Table 1 (Stoller, 2015). For each system, an alternative membrane is given at the same feed stream flow rate, composition and temperature. The alternative is a tight MF or a UF membrane. The relevant data of the alternative solution is given in Table 1, for comparison purposes. 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 J_b value, with a washing cycle period equal to 1h. by adopting the methods developed by Stoller and Ochando Pulido, is reported (Stoller, 2016). Since investment costs are directly proportional to A, the value of this parameter gives a straight indication of economic and technical optimization (Stoller, 2013).

3. Results and Discussion

From the data in Table 1 it is possible to observe that in the case of an α value of the MF membrane equal to zero, there is no need to seek alternatives: the process, operated below Jb, will not develop fouling at all. As expected, the excellent productivity performances of the MF membrane are preserved, and corresponds to the best possible ones. In case of an α value different than zero, in most investigated cases, the UF membrane appears to be more suitable. In some cases, MF fails to b capable to target the required capacity for long time, and fouling is such severe to seek to infinite membrane area (∞ in Table 1): in this case, the only way to operate the plant is to foresee washing cycles with a period in between of less than 1h. Only in one case (oil in water emulsion) the MF permeability is that high that it stand out UF despite incresed fouling. In other words, the UF membrane is less prone to fouling than the MF one as soon as reversible or irreversible fouling triggers. Possible justifications of this observed behavior may be only hypothesized. The authors wish to present four different explanations:

Table 1. Experimental data and calculated membrane area requirements for a capacity of 1 m^3 h^{-1}

Process	Membrane	J_b [l h^{-1} m^{-2}]	TMP [bar]	α [l h^{-2} m^{-2} bar^{-1}]	A [m^2]
Diary fluids	MF	21.5	0.3	27.30	75.13
	UF	**22.0**	**0.3**	**12.00**	**54.34**
Expanded polystyrene (EPS)	MF	5.58	2.5	6.44	∞
	UF	**5.93**	**2.5**	**2.00**	**1075.26**
Landfill Leachate MBR WW	MF	30.4	17.5	10.08	∞
	UF	**106.9**	**20.0**	**1.60**	**13.35**
Oil in water emulsions	**MF**	**130.0**	**2.5**	**0.00**	**7.69**
	UF	30.0	0.5	0.00	33.33
PMMA suspension	MF	48.7	5.0	7.10	75.75
	MF tight	**61.7**	**5.0**	**3.50**	**22.62**
Polymer in WW	**MF**	**253.5**	**1.0**	**0.00**	**3.94**
	UF	177.8	1.0	0.00	5.62
Raw rice wine	MF	18.0	1.0	4.30	72.99
	MF tight	**54.3**	**1.0**	**6.70**	**21.00**
Sodium alginate solution	MF	7.3	2.5	8.44	∞
	UF	**7.6**	**2.5**	**2.40**	**625.00**
Whey solution	MF	14.7	3.0	3.63	262.46
	UF	**15.4**	**8.0**	**0.54**	**90.25**

- Membrane surface roughness: MF exhibits higher roughness values compared to other ones. Higher surface roughness give rise to increased pressure drop along the membrane and increased thickness of the laminar sublayer. As a consequence, deposited material will not suffer severe suspension forces to the bulk, thus halting and staying over the membrane surface and the membrane pores (Figure 1).

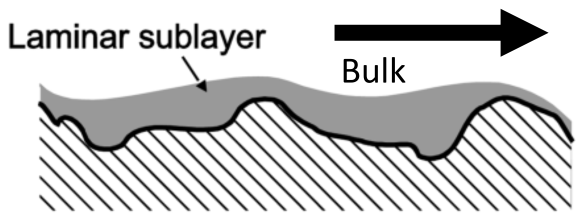

Figure 1. Laminar sublayer formation due to roughness

- Permeate fluxes are too high: the experience of high permeate fluxes leading to severe fouling was previously observed on polymeric microsieves. In this case, the microsieves were prepared by nano- or microneedles, and once formed, punched through a polymeric dense film. The result was a dense membrane exhibiting micropores, which perfectly follow the pattern on the stamp. For the first time, polymeric MF 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 were too high permeate fluxes crossing the membrane, resulting to yield local recovery values that high to let the concentrate stream on top of the membrane almost dry. Not capable to move along with the bulk stream, deposits starts to cover pores and membranes, resulting in severe fouling that decreases the fluxes almost instantaneously.
- Local boundary flux values exceeded: Oringer and al. (2004) 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.
- Stoller *et al.* (2014, 2015) analyzed in a previous work how fouling, among other factors, is a function of particle size and concentration. In this work, particle size distribution were 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 are 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. UF has smaller pore sizes, thus even if characterized by lower permeability values, it may over-perform MF 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 UF safe, since smaller particles will agglomerate to bigger ones and therefore will not affect the membrane pores.

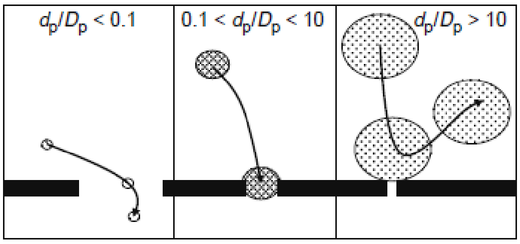

Figure 1. Pore blocking mechanism as a function of the particle size

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 three hypothesis here given separately. This aspect merits further work and should be exploited in the next future.

4. Conclusions

This study reports the use of MF for many real process and wastewater streams, in order to check if this membrane represent the best choice of membrane process designers. The results shows that not always MF appears to be a good choice, leading in some cases to higher membrane surface requirements if compared to other membranes characterized by a smaller pore size. As a rule of thumb, MF is suggested only if the relevant α value of the system is equal to zero; in all other cases, a tight MF or a UF membrane is suggested. In this latter case, UF exhibits increased productivity and longevity of the membrane.

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