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Optimized Design of Wastewater Stream Treatment Processes by Membrane Technologies

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Wastewater treatment by membrane technologies is gaining more and more importance and the relevant market is increasing. This trend is mainly justified by novel and high-performance membrane materials, a wider number of successful applications by membrane technologies and the progressive reduction of the investment and operating costs.
The main drawback of membrane technology is membrane fouling, that reduces the membrane performances along the time and leads to a premature substitution of the membrane modules. In the last years, a better understanding of the fouling phenomena has sensibly increased the confidence in this technology. This is especially true for wastewater treatment processes based on membranes. In this case low operating costs are mandatory, thus the membrane modules should not be frequently replaced.
This work briefly covers the theory and measurement procedures of the critical, threshold and boundary flux, with the aim of process optimization and control design. The goal is to operate membranes modules by avoiding irreversible fouling for a long period of time (several years). The importance of specific pretreatment processes, such as flocculation and photocatalysis, adopted to reduce fouling phenomena will be also discussed. Moreover, the design of advanced control systems for batch membrane and some examples of wastewater treatment (olive mill wastewater and the effluents from the tannery industry) will be reported.

1. Introduction

In the last decades, water is becoming more and more a valuable resource. This is especially true considering that the relative small amount of fresh water, that is 3 % of the total quantity of water on earth, is being increasingly polluted by human activities. This trend is in contrast with the need of high quality water required by production processes, and as a consequence, a more severe purification grade to be pursued.
Water lack affects in particular agricultural irrigation, which uses 70 % of the total water consumption worldwide. On the other hand, there is an opportunity to use regenerated wastewater for irrigation purposes. Recent technological breakthroughs in wastewater treatment and reclamation for water reuse are addressed on the use of membrane technology, due to their easiness, relatively low cost, high performances and selectivities. Moreover, the modular nature of membrane technology allows easy upgrade and/or revamping of existing wastewater treatment plants.
In the past years, ultrafiltration (UF) and nanofiltration (NF) membranes have been increasingly implemented in water treatment processes such as groundwater and surface water (Van der Bruggen and Vandecasteele, 2003), desalination of brackish water and seawater (Paugam et al., 2004), decontamination of wastewater of different nature including carwash (Boussu et al., 2007), textile and tannery (Stoller et al. 2013), pulp and paper (Mänttäri and Nystörm, 2000), pharmaceutical (Wei, 2010) and agro-food industries such as dairy, beverage, winery, tomato (Iaquinta et al., 2009) and olive oil from 2-phase (Ochando Pulido et al., 2012) or 3-phase processes (Stoller et al., 2013), among others. In particular for wastewater treatment applications, membranes are currently being used as a tertiary advanced treatment for the removal of dissolved species such as not biodegradable organic pollutants, phosphorus, nitrogen compounds, colloidal and suspended solids, and human pathogens, including bacteria, protozoan cysts and viruses.

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The biggest technical drawback for the implementation of membrane technologies in wastewater treatment plants is still membrane fouling. This latter is caused by the accumulation of colloids, soluble organic compounds and microorganisms on the membrane surface and inside the pores. These phenomena are unavoidable, but it can be of reversible or irreversible nature. If irreversible fouling takes place, it cannot be removed by membrane cleaning procedures anymore and leads quickly to the necessity of the process shut-down. Therefore, the optimal operation of membrane processes should be targeted to attain only a reversible fouling in order to ensure constant performances over a long period of time, without any run stop Stoller and Chianese, 2006).

This paper will report a suitable method, based on the boundary flux theory, to reach this target. The knowledge of the boundary flux values permits to avoid irreversible fouling by applying suitable operating conditions. The core of the proposed method is to increase, if possible, by proper pretreatment processes, the boundary flux up to a maximum value, so as to design the process on the basis of this value and to leave the automatic control of the process to an advanced control system. Some design examples of possible wastewater treatment processes by membranes for the purification of olive mill wastewater streams (2-phase and 3-phase) and the effluents from the tannery industry will be reported.

2. The boundary flux concept

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, it can be subdivided in three main typologies: a reversible fouling, a semi-reversible fouling and an irreversible fouling which, once formed, it cannot be eliminated by any procedure. The latter is the main cause of membrane failure concerning productivity. In all cases of tangential cross flow membrane separations, all three types of fouling will unavoidably appear.

In a first stage (Field et al., 1993) and the next year, (Belfort et al., 1994) started to study the experimental and theoretical behaviour of fouling in MF and UF membranes, respectively. The first theoretical model giving some explanation on membrane transport phenomena of colloidal particles was proposed by the research group of (Bacchin et al., 1996). The existence of a critical flux was theoretically proven and explained, and a first definition was given: below the critical point, no fouling occurs. In the following years, (Field et al., 1995) suggest an empirical approach to the concept of the critical flux for MF membranes, and the validity of the findings was extended to UF and NF membranes.

The existence of different fouling types was observed in some works such those published by (Bacchin et al. , 2006), on the basis of phase changes and (Ognier et al., 2004), considering local membrane conditions. Fouling triggers different liquid/gel phases locally over the membrane layer and in the membrane pores due to the concentration profiles intensified by the polarization phenomena. In these conditions, some authors observed that the critical flux concept is not strictly valid for all membrane separation processes, in particular when high concentrated feedstock are used: fouling cannot be completely avoided during operation, even at very low operating conditions. (Le Clech et al., 2006) reported long-term fouling in the treatment of wastewater by membrane bioreactors (MBR), even when operating below the critical point. This behavior was confirmed in the treatment of dairy wastewater with NF membranes by (Luo et al., 2012) and recently in the treatment of olive mill wastewater (OMWW) with UF and NF membranes by (Stoller and Ochando-Pulido, 2012).

To overcome this limitation in the definition of critical flux, (Field and Pearce, 2011) introduced for the first time the concept of the threshold flux. Summarizing the concept briefly, 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-dependent high fouling rates can be observed.

Finally, both critical and threshold flux concepts, which share many common aspects, were merged by (Stoller and Ochando, 2014) into a new concept, that is the boundary flux. The boundary flux concept does not extend by addition of new theory or knowledge the critical and threshold flux concepts. On the contrary, it tries to simplify the use of these concepts by the use of one common term.

The main difficulty in determining the boundary flux values (J_b) relies in the impossibility of theoretical prediction, thus experimental estimation by time consuming experiments at a certain time moment is necessary. However, several pressure cycle and stepping protocols have been developed in order to measure critical, threshold and boundary flux values efficiently. The unavoidable development of fouling over the membrane surface leads to changes to the boundary flux value. Moreover, different boundary flux values can be measured on the same system, depending on various factors, such as the membrane type, the membrane surface roughness and mean porosity, the hydrodynamic conditions and the effluent composition and concentration. Boundary flux values are a function of the feed stream composition, and this is especially true for agricultural wastewater streams treatment by membranes, since the entering feedstock composition is not constant during the same campaign. Direct treatment by membranes of raw effluents has been reported to lead to rapid formation of membrane fouling. Furthermore, the use of batch membrane processes in order to

limit the amount of required membrane area, and thus saving investment costs, leads again to sensible feedstock changes during operation. As a consequence, in batch systems, boundary flux values never remain constant. This fact of low constancy represents a major difficulty in tuning the optimal operating conditions for the process and to use the boundary flux values for membrane process design and control purposes.
The boundary flux concept merges both critical and threshold flux concepts for simplification purposes, taking into account the similarities between them. Referring to one single concept, it will reduce sensibly the incorrect use of both the critical and threshold flux concepts. By introducing a new flux, that is, the boundary flux J_b, the previous equations may be written as (Stoller and Ochando Pulido, 2015):

$$dm/dt = - \alpha; \qquad \text{when} : J_p(t) \leq J_b \qquad (1)$$

$$dm/dt = - \alpha + \beta\ (J_p(t) - J_b) ; \qquad \text{when} : J_p(t) > J_b \qquad (2)$$

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

3. Results and Discussion

Three different examples and calculations are hereafter presented on three different systems, which are: the treatment of olive mill waste water, exiting a 2-phase and 3-phase production process (OMWW2 and OMWW3, respectively), and tannery wastewater streams.
The performed calculations are based on the previous performed assumptions, which are: all membrane processes are batch wise; inhibition of fouling is mandatory (and, as a consequence, working always in sub-boundary flux conditions); the plant capacity is taken to be equal to 10 m^3 day^{-1}.
Results are reported in Tables 1-3 as a function of the control type, if the permeate flow rate (FC) or the operating pressure (PC) results to be fixed by a proper set-point, in detail for the tratment of these wastewater streams:
2-phase and 3-phase olive mill wastewaters membrane plant treatment design:
The significant boost of the olive oil industrial sector in the last years has brought to an undesired side-effect on the environment: the produced amounts of olive mill effluents have accordingly increased, in particular due to the update of the batch press method by modern continuous centrifugation-based equipment. An average-sized olive oil factory generates between 10 and 15 m^3 of wastewater daily, called olive mill wastewater (OMWW) and exiting the centrifuges. In addition to this, 1 m^3 of wastewater derived from the washing of the olives per processed ton (olives washing wastewater, OWWW) are produced. The yearly production of these effluents is of several millions of cubic meters.
In this regard, membrane technology offers compact modular nature, high efficiency and moderate investment and maintenance expenses. In Table 1 and Table 2 the membrane plant treatment design - comprising the membrane area and total costs evaluation - for OMWW2 and OMWW3 is reported, respectively. For both feedstocks, the organic matter content measured by the COD concentration is taken as key parameter. Two different tailored pretreatments (Stoller et al., 2013) were applied on the raw OMWW2 and OMWW3 feedstreams: gridding (cut-size 300 µm) and UV/TiO_2 photocatalysis (Stoller et al., 2014). Proper pretreatment processes sensibly increases boundary flux values accordingly (Stoller, 2013). The feedstock was driven to an UF membrane process and subsequently to NF. The feedstocks' characteristics and membrane properties, as well as the operating conditions adopted, are hereafter reported in Table 1 and Table 2.

Table 1: Membrane area and total costs evaluation for the treatment of 1m^3 h^{-1} of OMWW2

Feedstock	Key parameter	COD	COD
	Value in feed stream	11.1 g L^{-1}	6.0 g L^{-1}
	Pretreatments	Gridding and photocatalysis	From UF permeate
Membrane properties	Membrane type	UF	NF
	Membrane model	SW	SW
	Membrane ID	GM	DK
	Membrane supplier	Osmonics	Osmonics
	Pore size	2.0 nm	0.5 nm

	mw [L h^{-1} m^{-2} bar^{-1}]	5.2		2.5	
Process properties	T [°C]	20		20	
	v_F [L h^{-1}]	550		550	
	π [bar]	0.0		0.0	
	Operation time [h]	4		4	
	Operation cycles [-]	500		500	
	R [%]	48.5		76.6	
Boundary flux data	Boundary flux type	threshold		threshold	
	α [L h^{-2} m^{-2} bar^{-1}]	0.011		0.005	
	Δw% [%]	0.001		0.001	
	J_b [L h^{-1} m^{-2}]	10.0		14.3	
	TMP_b [bar]	10.0		9.0	
Results	Control type	FC	PC	FC	PC
	Membrane area [m^2]	74.2	68.8	50.3	47.4
	Investment costs [€ m^{-3}]	4.83	4.50	3.30	3.11
	Operating costs [€ m^{-3}]	0.54	0.54	0.49	0.49
	Total costs [€ m^{-3}]	5.37	5.04	3.79	3.60
Note	Polyphenols might be recovered from the NF concentrate				

Table 2: Membrane area and total costs evaluation for the treatment of 1m^3 h^{-1} of OMWW3

Feedstock	Key parameter	COD		COD	
	Value in feed stream	15.2 g L^{-1}		12.6 g L^{-1}	
	Pretreatments	Gridding and photocatalysis		From UF permeate	
Membrane properties	Membrane type	UF		NF	
	Membrane model	SW		SW	
	Membrane ID	GM		DK	
	Membrane supplier	Osmonics		Osmonics	
	Pore size	2.0 nm		0.5 nm	
	mw [L h^{-1} m^{-2} bar^{-1}]	5.2		2.5	
Process properties	T [°C]	20		20	
	v_F [L h^{-1}]	600		600	
	π [bar]	0.0		0.9	
	Operation time [h]	4		4	
	Operation cycles [-]	500		500	
	R [%]	23.0		76.0	
Boundary flux data	Boundary flux type	threshold		threshold	
	α [L h^{-2} m^{-2} bar^{-1}]	0.0553		0.0191	
	Δw% [%]	0.001		0.001	
	J_b [L h^{-1} m^{-2}]	7.6		14.9	
	TMP_b [bar]	6.0		8.0	
Results	Control type	FC	PC	FC	PC
	Membrane area [m^2]	113.1	96.7	49.7	46.1
	Investment costs [€ m^{-3}]	6.36	5.45	3.30	3.07
	Operating costs [€ m^{-3}]	0.33	0.33	0.43	0.43
	Total costs [€ m^{-3}]	6.69	5.78	3.73	3.50
Note	Polyphenols might be recovered from the NF concentrate				

Tannery wastewaters membrane plant treatment design:
Leather tanning is a wide common industry all over the world. In leather processing, water is one of the most important medium, almost 40-45 *L* water *kg*$^{-1}$ raw-hide or skin is used by tanneries for processing finished leathers. Because the tannery process requires a large use of a wide variety of chemicals added at different stages of the process, the tannery wastewater treatment is complex. The major problems of tannery wastewater are due to the high concentrations of pollutants and a great variety of composition. The composition of tannery wastewater presents considerable dissimilarities in the concentration range of

pollutants both of inorganic (chlorides, with concentration ranging from several hundred to over 10,000 *mg* L^{-1} Cl^-; sulphate (VI), ammonium ions and sulphide ions, exhibiting concentration that ranges from tens to several hundred *mg* L^{-1}) and organic (the COD value is usually several thousand *mg* L^{-1} O_2). The composition of organic pollutants in tannery wastewater is complex. Proteins, mainly collagen and their hydrolysis products - amino acids derived from the skin - are predominant, while other such as fats are in low concentrations.
In these conditions, the application of membrane technology appears to be advantageous for the tannery manufacturer, even if the economic benefit of chromium recovery is not taken into account: the treatment and discharge of the wastewater stream is solved, with a minimum total cost savings of about 21 %, if compared to the fixed fees of the external biological treatment plant. The treatment process by membranes limits the disposal of concentrates to external services to 5 %, permitting the discharge of 90 % of the initial wastewater volume in surface waters and reusing 5 % as chromium-rich concentrate at no cost.

Table 3: Membrane area and total costs evaluation for the treatment of 1m^3 h^{-1} of tannery WW

Feedstock	Key parameter	COD	
	Value in feed stream	2.0 g L^{-1}	
	Pretreatments	Primary treatment processes	
Membrane properties	Membrane type	NF	
	Membrane model	SW	
	Membrane ID	DK	
	Membrane supplier	Osmonics	
	Pore size	0.5 nm	
	mw [L h^{-1} m^{-2} bar^{-1}]	2.5	
Process properties	T [°C]	20	
	v_F [L h^{-1}]	600	
	π [bar]	0.0	
	Operation time [h]	4	
	Operation cycles [-]	450	
	R [%]	95.0	
Boundary flux data	Boundary flux type	threshold	
	α [L h^{-2} m^{-2} bar^{-1}]	0.00014	
	Δw% [%]	0.001	
	J_b [L h^{-1} m^{-2}]	4.4	
	TMP_b [bar]	6.0	
Results	Control type	FC	PC
	Membrane area [m^2]	150.6	143.0
	Investment costs [€ m^{-3}]	8.37	7.94
	Operating costs [€ m^{-3}]	0.33	0.33
	Total costs [€ m^{-3}]	9.00	8.27
Note	Cr is recovered back in the concentrate and might be used again in process.		

4. Conclusions

In this work the possibility to use membrane technologies as core technology for wastewater treatment processes is discussed. A reliable control of the fouling issues, which sensibly reduce the membrane performances as a function of time, appears to be mandatory to reach technical and economical feasibility.
The boundary flux model can help the successful design and control of membrane processes inhibiting irreversible fouling issues. By proper pretreatment processes, the boundary flux values should be maximized. After this, the boundary flux values as a function of a key parameter and time must be measured and determined or searched in the available bibliography and handbooks. The knowledge of these data can be used for the design of advanced control systems able to guarantee that the membrane systems always work below boundary flux conditions. In this way, only reversible fouling forms, and it can be eliminated with simple standard membrane cleaning procedures. Moreover, constant membrane performances and high longevity of the membrane modules can be achieved, leading to competitive investment and operating costs compared to conventional treatment processes.

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