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Description of the Biofouling Phenomena Affecting Membranes by the Boundary Flux Concept

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Membrane fouling, showing up with a significant reduction of process productivity and membrane lifetime, is one of the main issues in membrane technologies and has been successfully described by the boundary flux concept. Although the concept was applied for both organic and inorganic fouling, biofouling enjoys partial treatises in literature. In this work, a model extending the boundary flux concept to biofouling issues was developed. A population dynamics-based model considering the development of a fouling layer originated by attached growing biomass on the surface of the membrane using nutrients and substrates available in the processed feed has been developed. The manuscript highlights the critical aspects of the developed model and the possible connection points between it and the boundary flux concept.

1. Introduction

Biofouling, i.e. the accumulation of living material (or remnants of the decomposition thereof) on the surface of process equipment, is a key problem in the filtration of process waters, and expecially wastewaters, by using membranes. With the increasing use of membrane processes to gain competitive advantages with respect to other separation processes or to increase capacity of existing facilities, biofouling has rapidly shown to be able to curtail the expected potential. Many studies have dealt with membrane fouling and have led to the introduction of such fundamental concepts as the critical flux (Field, 1995), i.e. the upper bound of transmembrane pressure below which membrane permeability does not suffer from a time-related decay, and the threshould flux, i.e. the upper bound of transmembrane pressure for which membrane permeability decay exhibits a time-transmembrane pressure decoupling. Many studies have assessed that the effect of the particle size on the boundary flux cannot be experimentally determined, since an accurate analysis strictly requires well-defined and surface similar particles even though with different sizes (Field and Aimar, 1993). This appears to be a great deal, especially in the treatment of actual wastewaters (WWs). Within them, dissolved particles naturally lead to fouling and biofouling issues because of their heterogeneity. This comes to be an essential point in order to realise an appropriate membrane process design properly inhibiting fouling occurrences. In the last years, some researchers have focused the treatment of this wastewater by means of batch membrane processes especially for the ultrafiltration (UF) (Stoller et al., 2013,a) and nanofiltration (NF) (Stoller et al., 2013,b), which are both widely used in membrane bioreactors and biotechnologies. Fouling issues can be effectively moderated by the application of the critical and threshold flux concepts, as deeply studied by Field and Pearce (2011). Furthermore, evidence exist that both the critical and threshold fluxes may exist on specific wastewaters, although the former may go undetected because it falls below the region of economic membrane management policy. Recently, Stoller et al. (2013,c) unified the concepts of critical and threshold under a single novel concept, that is, the boundary flux, which attempts at estimating an irreversible fouling-safe value of transmembrane pressure for an assigned system. The design size of membrane separation systems is highly dependent on long-term efficiency. However, in all these and other works, the issues on the boundary flux concept concerning biofouling were not investigated. Biofouling is a phenomenon which severely affects such systems requiring either a very significant overdesign or a very premature replacement of separation modules, and the proper application of the boundary flux concept may be of great benefit for these systems.

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In this contribution, a first step to extend the boundary flux concept to biofouling will be accomplished and we deal with the issue of establishing a simple, fundamental, predictive model describing the formation of a biofilm on cross-flow membrane systems owing to the significant content of metabolisable substances naturally dissolved within municipal WWs. Attachment, inhibited and non-inhibited growth of *Escherichia coli* bacteria naturally present within the WW, death of bacterial biomass subjected to nutritional shortage, were adopted as the phenomena describing the biofilm evolution and "secondary membrane" formation. Finally, a simple model basing on the formation of biofouling cakes acting as a secondary membrane layer was successfully developed in order to describe a possible arrangement of viable and non viable bacteria.

2. The biological model

The developed model describes the formation of a layer of cells at top of the membrane surface. Cells collectively act as a secondary membrane and filter the wastewater themselves much as a trickling filter does, using the dissolved substrates, nutrients, and oxygen for replication and maintenance purposes. Cell adhesion is subjected to a lag, referred to the time required for propagules to adapt and stick on to the surface; thereafter replication, promoted by substrates, nutrients and oxygen and could be partially inhibited by accumulated carbon dioxide, and possibly acetate. The latter ones bring about the formation of a layer of living cells becoming thicker and thicker and eventually consuming the limiting required growth component, be it substrate, nutrient, or oxygen. Viable cells have a cylindrical shape with roughly emispherical-shaped ends and pack themselves with many empty spaces due to their convex shape.
When the medium concentration is insufficient for cell growth at the membrane surface, a first layer of cells dies. In many attached growth contexts of wastewater engineering, this usually entails the detachment of the whole attached layer of living biomass because the decayed biomass is unable to support the weight of the overlying living layer. However, this is not the case in membrane biofouling, since the pressure determined by continuous operation and the entrainment action determined by the permeation flux maintain the stability of the whole combined layer made by live and dead cells. Dead cells are expected to undergo breakdown and release cell debris and colloidal cellular substances which may or may not be able to permeate the membrane depending on the fragment, molecular and pore size. Substances which are colloidal in nature, in the changed washing liquid environment, may become unstable and flocculate in the proximity of the surface or within the pores. Overall, it is expected that, while small molecules may be entrained in the permeate flow, a large part of the remaining breakdown materials simply pack themselves as layers occupying all of the available space, so that interstitial spaces are gradually lost. A finite-thickness layer of live cells turn into a uniform layer of coagulated material with a fraction of the initial thickness. Figure 1a shows a possible overview of the phenomenon in a macroscopic context extending the schematic plant previously proposed by Stoller and Bravi (2010).

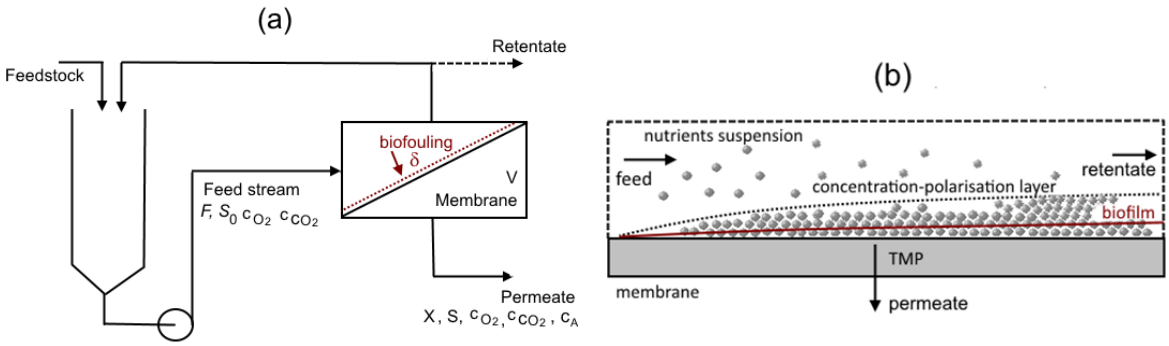

Figure 1: Schematic illustration of flows and quantities relevant to biofouling build-up in the adopted macroscopic context (a) and in the control volume (b).

Concerning the mathematical model, a few assumptions about the control volume (Figure 1b) as well as the main products have been made. More specifically, the latter ones are carbon dioxide (CO_2), acetate (A) and biomass. When dealing with the living biomass exploiting oxygen and nutrients, it has to be considered that some cells progressively turned to die when O_2 becomes a limiting factor. When the glucose as substrate is highly concentrated, especially for municipal WWs, an amount is fully oxidised to CO_2 as a product of microbial metabolism. In addition, the substrate may also be converted into acetate acting as a growth-

inhibitor (Roeva and Tzonkov, 2006). The composition of the biomass is assumed as elemental and directly followed from balanced growth condition. The proposed kinetics equations have been established from a "secondary" model describing cell-growth dynamics as a function of environmental conditions. Half-saturation, yield and maintenance coefficients values as well as gas mass transfer coefficients are in agreement with those previously proposed by Roeva and Tzonkov (2006) and all reported in Table 1. The equation (1) has been used for the functional form of biomass growth rate under glucose and dissolved oxygen consumption, carbon dioxide accumulation and the inhibiting effect of acetate (Galvanauskas et al., 1998):

$$\mu = \mu_{\max} \frac{S}{K_S + S} \frac{c_{O_2}}{K_{O_2} + c_{O_2}} \frac{k_A}{k_A + c_A} \tag{1}$$

where μ_{max} is the maximum specific growth rate, k_A the acetate inhibition constant of growth and K_s and K_{O_2} are the saturation constants for respectively glucose and oxygen.

Table 1: Significant parameters used in the model

Parameters	Unit	Value	Parameters	Unit	Value
μ_{max}	h^{-1}	0.519	$Y_{S/X}$	$g_S\ g^{-1}$	16.0
K_S	$g\ L^{-1}$	0.27	$Y_{A/X}$	$g_A\ g^{-1}$	23.4
K_{O_2}	$g\ L^{-1}$	0.02	$Y_{O_2/X}$	$g_{O_2}\ g^{-1}$	20.6
k_A	$g\ L^{-1}$	53.6	$Y_{CO_2/x}$	$g_{CO_2}\ g^{-1}$	29.6
$k_{LCO_2max}a$	h^{-1}	79.81	A_S	m^2	0.5
m_S	$g_S\ g^{-1}\ h^{-1}$	0.08	ρ_d/ρ_b	$kg_{Xd}/\ kg_X$	1.4

The proper mathematical model is based on the mass balance of each component and is collectively described by the following equations:

$$\frac{dX}{dt} = \mu X - \frac{F}{V} X - m Y_{X/S} X \tag{2}$$

$$\frac{dX_D}{dt} = m Y_{X/S} X_D \tag{3}$$

$$\frac{dS}{dt} = -\frac{\mu}{Y_{X/S}} X + \frac{F}{A_S \delta}(S_0 - S) \tag{4}$$

$$\frac{dc_{O_2}}{dt} = -\frac{\mu}{Y_{c_{O_2}/X}} X + k^b_{LO_2} a(c^*_{O_2} - c_{O_2}) - \frac{F}{A_S \delta}(c^*_{O_2} - c_{O_2}) \tag{5}$$

$$\frac{dc_{CO_2}}{dt} = \frac{\mu}{Y_{c_{CO_2}/X}} X + k_{LCO_2} a(c^*_{CO_2} - c_{CO_2}) - \frac{F}{A_s \delta}(c^*_{CO_2} - c_{CO_2}) \tag{6}$$

$$\frac{dc_A}{dt} = \frac{\mu}{Y_{A/X}} X - \frac{F}{A_S \delta} c_A \tag{7}$$

Equations (2) to (7) describe respectively the partial balances of the concentration of the viable biomass (2), dead cells (3), substrate (4), oxygen (5), carbon dioxide (6) and acetate (7). Two further equations concern the increasing thickness of the biologic layer (8) and the decay of oxygen by the advective transport within the same (9).

$$\frac{d\delta}{dt} = \frac{1}{A_S}\left(\frac{F}{\rho_b}(S_0 - S) + \mu \frac{X\delta}{\rho_b} - m \frac{Y_{X/S} X \delta}{\rho_b + \rho_d}\right) \tag{8}$$

$$\frac{dk^b_{LO_2} a}{dt} = -\frac{k^b_{O_2} a}{\tau_D} \tag{9}$$

where ρ_b and ρ_d are assumed as average densities for respectively elemental living layers and dead cells. Under the consideration that diffusive transports may be negligible for the long times, the parameter τ_d, as the characteristic time for diffusion within the biofilm, was tentatively supposed equal to 200 h. The maximum oxygen mass transfer coefficient $k_{bO2\ max}$ within the biomass coincides with its boundary conditions (Table 2). Equation set (2) to (9) includes acetate balance and describe the most general model considering inhibition and may be simplified by replacing Equation (3) at the steady-state and setting $c_A\ (t=0) = 0\ mg\ L^{-1}$. Overall, boundary conditions imposed for the simulation are all reported in Table 2.

Table 2: Boundary conditions at t = 0 h

Species	Unit	Value	Equation	Species	Unit	Value	Equation
X	$g\ L^{-1}$	0	(2)	CO_2	$mg\ L^{-1}$	0.78	(6)
X_d	$g\ L^{-1}$	0	(3)	A	$g\ L^{-1}$	0	(7)
S	$mg\ L^{-1}$	3800	(4)	δ	mm	0	(8)
O_2	$mg\ L^{-1}$	7.2	(5)	$k_{bO2\ max}a$	h^{-1}	101.02	(9)

3. Results and discussion

Since the microorganisms belong to the natural contaminant populations of the processed WWs, biofouling phenomena occur naturally so that preventive inhibition is often physically difficult. Their tendency to take part in the colonisation of membrane surfaces is related to their concentration in the WWs which dictates the likeliness of their attachment at the membrane surface where they settle to their replication. In addition, their multiplication capability is also related to the rate at which a sparse colony could turn into a dense and thick layer. Many attempts have been made in order to devise membrane systems less likely to be colonized. There are attempts to inhibit colonization on the membrane by surface modifications getting more hydrophobic, more charged, more smooth or antibacterial, but are not capable in the long term run to avoid biofouling. In some cases, the very same biochemical metabolism of the chemical inhibition can be an useful approach. Particularly, when dealing fed-batch cultivation of *E. coli* (Galvanauskas et al., 1998), it was found thereof that acetate is produced by *E. coli* on glucose both as an intermediate product and as a by-product. This is a significant information concerning a form of biofouling "self-control".

Figure 2a shows the time profile of the main quantities involved during the biofouling of a membrane surface under conditions of controlling substrate content. As can been seen, dissolved oxygen, initially close to the saturation value, undergoes a marked drop until shortage of oxygen and inhibitory effects by acetate slow down and change metabolism.

When the layer becomes sufficiently thick that the permeating substrate is reduced to half of the initial value of the biomass, a significant concentration of acetate has developed. The latter one influences the basal layers of the live biomass, further reducing their respiration rate. This leads to the decrease of both the consumption of oxygen and the release of carbon dioxide, whilst a fair amount of the carbon inflowing with the substrate is released in the permeate in the form of acetate.

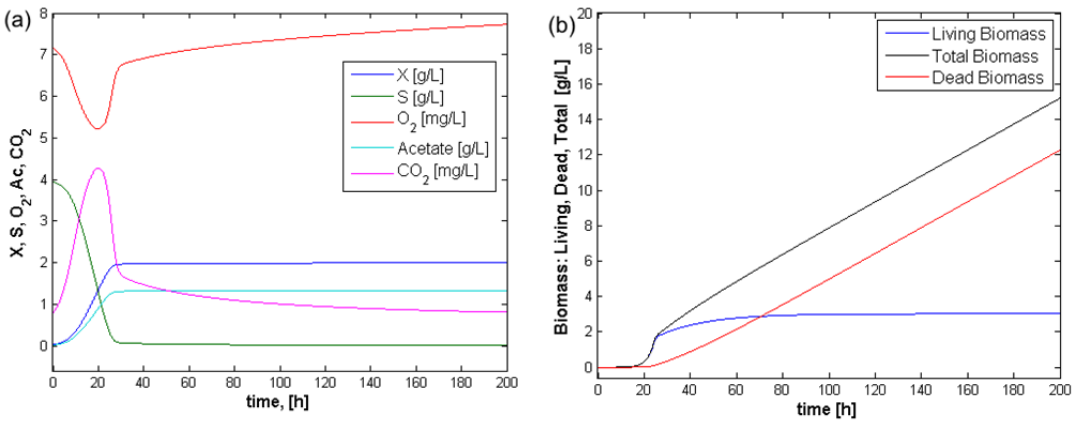

Figure 2: Time profile of live biomass, substrate, dissolved oxygen, dissolved CO_2, acetate (a) and biomass growth, biomass death and overall development of a biofouling layer (b).

Live biomass is constant after little less than 40 h. but this should not be interpreted as a constancy of the biomass altogether, rather as an equilibrium between the growth of new biomass and the death of biomass in the deeper layers of the developed fouling under substrate shortage. This fact is clearly visible in Figure 2b, which makes a distinction between live and dead biomass.
When substrate is unable to support maintenance of the deepest layers of the formed biofouling, cells undergo endogenous metabolism, then die. Contrary to what is commonly observed in biofilter equipment, they remain in place under the trans-membrane pressure, degrade and transform into a gelled, ordinary fouling layer that grows in thickness and elevates the “ground floor” where the live biomass fouling layer stands. Overall, this brings about a continuous growth of the overall fouling layer.
The initial set of substrate, nutrients and oxygen is able to support a layer of live biomass with a well-defined thickness, which may be denoted as “critical” (δ_{crit}). Apart from the very special case of perfectly balanced liquid feed, there will be one limiting component that will determine the transition from simple biofouling and mixed biofouling. The nature of the limiting component, its initial feedstock and its half-saturation constant will dictate the exact shape of the transition region between the first part and the second part of the fouling layer thickness growth.
By degrading their structure, dead cells fill empty spaces left by their original structure and decouple the original secondary membrane into a tertiary, thicker membrane with a denser structure, which occupies less space. Therefore, for any given volume of new live biomass formed, an equivalent volume of live biomass degrades and recovers a fraction of its initial volume. This is apparent in Figure 3a, where it can be seen that, while the layer thickness develops initially very quickly, the build-up slows down and the build-up rate eventually tends to an asymptotic lower rate.

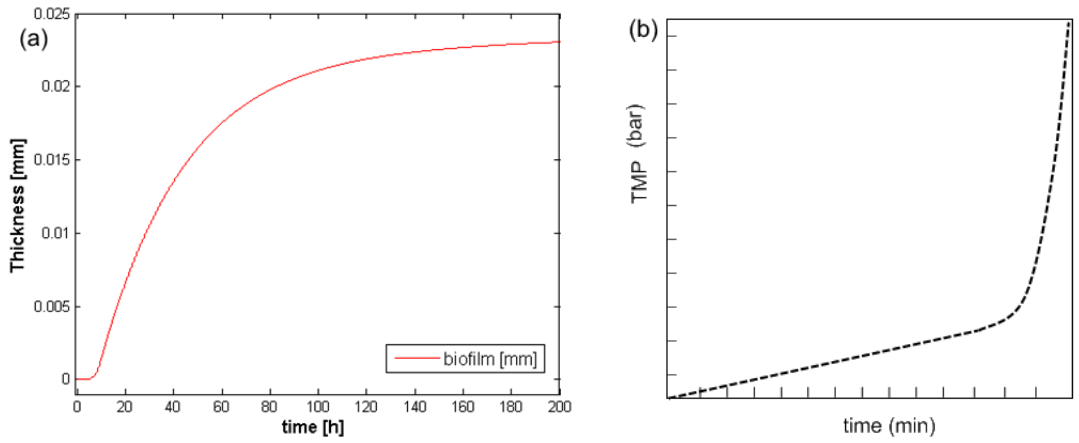

Figure 3: Time profile of the overall thickness of the biofouling layer (a) and qualitative trend of long-term filtration for constant flux operations (b).

The change in the meso-scale nature of the layer turns into a change of the average permeability of the entire layer. In fact, while the layer of live biomass has a porosity which owes to the convex shape of the stacked cells and, after the onset of dead biomass, creates a constant resistance to flow, the gelled layer growing at the base of the superficial live layer has an intrinsically lower permeability. Moreover, since the gelled layer is the only layer exhibiting a net linear growth after a certain time, it dictates the change of permeability of the total fouling layer accumulated on the membrane surface. The phenomenon emerging from Figure 3b has been reviewed by Le-Clech et al. (2006). More accurately, a typical experimental trend of permeation rate over time is shown. After an initial period characterised by a slow decrease of permeability, a different behaviour is observed with a much steeper decrease of permeability (Miller et al., 2014).

4. Conclusions

The boundary flux concept, built from both the critical and threshold flux theories, is an important progression in membrane knowledge in order to be properly used during membranes plant design. The results of the present study indicate that a simple mathematical model may be considered as a valuable prediction of naturally-occurring biofouling phenomena. We have also dealt with the likeliness of the resulting biofilm to affect membrane surfaces with particular attention of the live cells turning to die under nutrients shortage. In defiance of reversible fouling, biofouling build-up obeys more complex mechanisms which may be difficultly

prevented. Future studies should be addressed at validating the model experimentally and identifying the main parameters responsible for a quick biomass growth occurring after the microbial lag-phase.

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