Review

Critical and sustainable fluxes: Theory, experiments and applications

P. Bacchin [a,*], P. Aimar [a], R.W. Field [b]

[a] *Laboratoire de Génie Chimique, Université Paul Sabatier, 31062 Toulouse Cedex 9, France*
[b] *Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, UK*

Abstract

Over the last 10 years, numerous membrane filtration data have been viewed through the lens of the concept of critical flux. This concept, used in a number of different ways often without explicit redefinition, is here clarified both theoretically and from an experimental viewpoint. A link is made with the concept of sustainable flux and an approach given for the determination of the apparent sustainable flux. To retain the utility of the critical flux concepts, it is emphasised firstly that the strong form and weak form of the critical flux, J_{cs} and J_{cw}, must be evaluated via a check on whether or not the overall resistance has remained invariant. Secondly, the critical flux for irreversibility, J_{ci}, has a sound theoretical basis; it represents the shift from repulsive interaction (dispersed matter—polarised layer) to attractive interaction (condensed matter—deposit). The various methods for measuring critical flux and the influence of membrane and suspension properties on critical flux are reviewed. Dispersive forces that are the key to the existence of a critical flux are discussed. The concept of a critical concentration for phase transition is also introduced. For theoreticians and experimentalists, this and the clarified concept of a small set of critical fluxes will continue to provide a valuable framework. But in addition, and especially for membrane users dealing with industrial process streams, the concept of a sustainable flux (which has evolved from critical flux thinking) is of a great utility. Above the sustainable flux (dependent on hydrodynamics, feed conditions and process time), the rate of fouling is economically and environmentally unsustainable.
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Keywords: Fouling; Critical flux; Colloid; Ultrafiltration; Nanofiltration; Microfiltration; Reverse osmosis

Contents

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* Corresponding author. Fax: +33 5 61 55 61 39.
 E-mail address: bacchin@chimie.ups-tlse.fr (P. Bacchin).

1. Introduction

It has been suggested that in some membrane filtration systems there may be a critical flux below which fouling does not occur. This concept is now over 10 years old and it is timely to review the theoretical principles and the experimental observations that underlie this concept. It is also useful to consider how this important concept and the concept of sustainable flux might be of use in understanding and improving the operation of membrane filtration systems. As an illustration of its popularity, Fig. 1 shows the growing evolution over the last 10 years of the

number of publications in journals satisfying the research criteria "critical flux* and (fouling or membrane)". Data was taken from Science Citation Index in January 2006. In the same figure, the number of these papers as a fraction of those dealing with fouling in membrane science (satisfying the research criteria "fouling and membrane") is also plotted. This relates to the impact of the concept. In recent years, 10–20 papers per year were produced using the critical flux concept and this represents around 10% of the scientific production on fouling in membrane science. This research area is expanding and now represents a significant fraction of works dealing with fouling. This output also has a good impact factor: the 135 papers being cited 1250 times over these years. Table 1 lists papers concerned with this concept that have had more than 30 citations. The first three

Fig. 1. Numbers of publications around critical flux concept and their relative percentage to paper dealing with fouling in membrane science last 10 years.

Table 1
Papers on the concept of a critical flux with more than 30 citations

Publications	Number of citations since its publication
Field et al. [1]	152
Howell [2]	86
Bacchin et al. [3]	73
Li et al. [4]	49
Chen et al. [5]	42
Bacchin et al. [8]	35
Wu et al. [6]	32

of them corresponds to the first ones to define a critical flux in 1995.

This paper seeks to summarise the literature on 'critical' flux especially with regard to colloidal filtration, to summarise methods of measurement and to refine and clarify terms used so that they might be more useful. The literature contains many usages of the term "critical flux", each constructed in order to satisfy a particular view of the author(s). One is reminded of Humpty–Dumpty (in the book "Alice through the Looking Glass" by Lewis Carroll), 'When I use a word, it means exactly what I want it to mean, neither more nor less'. The almost arbitrary redefinition of critical flux is not actually helpful and we must recognise that there is an idea, which is to be brought out of the wilderness and secured. As Samuel Baker put it 'A definition is the enclosing of a wilderness of an idea within a wall of words'. It is time to disentangle various concepts that have arisen around the critical flux postulate and repair the wall of its definition. Then we may be able to answer the questions, "Is the critical flux concept just a fashion or is it useful?" and "What related terms (e.g. sustainable flux) are now useful?"

Before examining critical flux, it is important to understand some of the ways in which membrane flux is reduced below that of the corresponding pure water flux (or more generally pure solvent flux). The reduction can be divided into two separate parts.

Firstly concentration polarisation is a natural consequence of the selectivity of a membrane. This leads to an accumulation of particles or solutes in a mass transfer boundary layer adjacent to the membrane surface that can affect the flux. Dissolved molecules accumulating at the surface reduce the solvent activity and this reduces the solvent flow through the membrane. This can be represented as a reduction in the effective transmembrane pressure driving force (TMP) due to an osmotic pressure difference between the filtrate and the feed solution adjacent to the membrane surface. This phenomenon is inevitable, but is reversible with a reduction in TMP and hence flux.

Secondly, there is fouling, build-up of material (e.g. adsorbed macromolecules, gels or deposited particles on the membrane surface), which may take the following forms:

- *Adsorption*: Adsorption occurs when attractive interaction between the membrane and the solute or particles exist. A monolayer of particles and solutes can grow even in the absence of permeation flux leading to an additional hydraulic resistance. If the degree of adsorption is concentration dependent then concentration polarisation exacerbates the amount of adsorption.
- *Pore blockage*: When filtering, pore blockage can occur leading to a reduction in flux due to the closure (or partial closure) of pores.
- *Deposit*: A deposit of particles can grow layer by layer at the membrane surface leading to an additional hydraulic resistance. This is often referred to as a cake resistance.
- *Gel*: The level of concentration polarisation may lead to gel formation for certain macromolecules.

It is noted that due to slow kinetics, certain colloids may not form during a period of laboratory study but may form during plant operation. Dispersive forces that are key to the existence of a critical flux are discussed in the next section after a brief historical review.

2. Critical flux concept: background and first definition

Broadly speaking, the critical flux has been defined in two ways. Either as the flux at which the transmembrane pressure starts to deviate from the pure water line (the strong form of critical flux) or as the first permeate flux for which irreversible fouling appears on the membrane surface. The critical flux can be generally defined as the "first" permeate flux at which fouling become noticeable; being then well differentiated from limiting flux, which is perhaps the oldest concept in cross-flow filtration. It will be recalled that the limiting flux (See, for example, classic work by Michaels [12] and Porter [13]) represents the maximum stationary permeation flux which can be reached when increasing transmembrane pressure with a given solution or suspension for a given set of hydrodynamic conditions. Now as a contextual introduction, some prior history will precede further discussion of the critical flux concept.

2.1. State of the art leading to the critical flux concept

Historically, the first publication giving the idea of a possible "threshold" flux when filtering a colloidal suspension has to be attributed to Cohen and Probstein [14] in 1986. In this publication, the authors noted that permeate flux obtained during reverse osmosis of ferric hydroxide was very high compared to the one expected from a balance between convection and classical dispersive forces (diffusion, lateral migration, shear induced diffusion, . . .) and called this the "colloid flux paradox". They advanced the idea that such a behaviour could be due to surface interaction between colloidal particles. In 1989, Mcdonogh et al. [15] pursued this idea and reported experiments with silica particles where permeate flux was affected by changes of ionic strength. This underlines the role played by surface interaction. In a 1994 review, Belfort et al. [16] detail fouling mechanisms and included in their discussion a section about colloid capture by a membrane, which is, however, separated from the main one dealing with particle transport. They concluded that progress has been made in "identifying the importance of colloidal and particle fouling and the proper description of colloid–membrane interaction" but that there still exists a need to develop "quantitative understanding of the possible interactions that can occur between (. . .) particles in a complex process streams".

2.2. First definitions and features

In 1995, the first three papers to define the critical flux concept were published. Firstly, a theoretical model proposed by Bacchin et al. [3,17] balanced surface interaction, diffusion and convection. This gives a physical explanation for the "colloid flux paradox". When compared to other transport phenomena, surface interaction are shown to be responsible for fluxes which are well above the ones given with other transport phenomena (diffusion, shear induced diffusion and lateral migration)
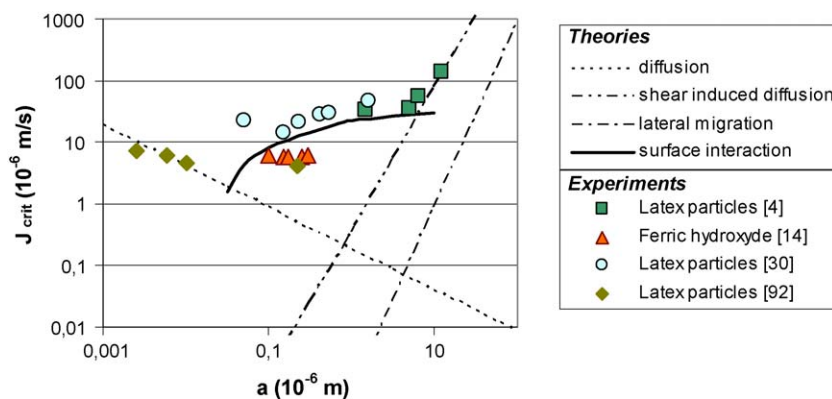
Fig. 2. Calculation of a critical flux induced by colloidal surface interaction and comparison with flux being obtained accounting for Brownian diffusion, shear induced diffusion, lateral migration and tubular pinch effect (from ref. [14]). Calculations (Reynolds number of 1500) are compared to experimental value of flux for colloids (symbols). Surface interaction can be an explanation for the "colloid flux paradox".

for particle size between 10 nm and 10 μm (Fig. 2). From this modelling, a critical flux is defined as "the flux below which no fouling occurs" and its existence is theoretically proven and physically explained by transport phenomena induced by surface interaction: the critical flux is the flux required to overcome particle repulsion and lead to the coagulation on the surface. This definition has the clear merit of being related to a physical mechanism and "criticality" is the point at which the repulsive barrier is overcome.

The second paper took a purely empirical approach. Field et al. [1] defined "a flux below which a decline of flux with time does not occur; above it fouling is observed". As shown in Fig. 3, there are two forms of this flux: strong and weak. The strong form is the flux at which the transmembrane pressure starts to deviate from the pure water line, which is of course linear. For the weak form, there is the assumption that there is very rapid fouling on start-up and so the flux–TMP relationship is below that of the pure water line. The critical flux (weak form) is the point at which this line becomes non-linear.

Thirdly, Howell [2] depicted "a flux below which there is no fouling by colloidal particles" which allows then the definition of "sub-critical flux operation of microfiltration". In so far as this definition avoids reference to fouling by macromolecules that might also be present, and that their effect could increase

with time, this definition can now be seen retrospectively, as a harbinger of the concept of a sustainable flux. The sustainable flux is usually defined in relation to a flux policy (that might be implicit rather than explicit) in which fouling is minimised to avoid frequent cleaning.

2.3. Clarification and new definitions

It is important before going further to clarify definitions of critical flux that will be linked to methods of measurements (Section 3), experimental features (Section 4) and theory (Section 5). Above it was noted that the term critical flux had been used in mainly two ways, *either* as the flux at which the flux–transmembrane pressure curve starts to deviate from linearity *or* as the first permeate flux for which irreversible fouling appears. Definitions have been given at different levels. Some are from a physical (deterministic) point a view (typically defined as the flux that leads to coagulation close to and then deposition upon the membrane) whilst others are from an experimental (naturalistic) point a view. The latter were typically defined as the flux leading to a first deviation from a linear variation of flux with TMP.

A clarification will be first made in this section according to the type of transport phenomena involved in the mass deposition. A corresponding classification, based on the classical flux–TMP-fouling equations is also given in Appendix A, for those readers who are more used to this latter type of approach. Some further links to the theory will be given in the modelling section.

2.3.1. Transport phenomena and membrane fouling

From a general point of view, the net radial flux of material towards the membrane is the combination of a convective flux and of fluxes, which tend to remove material away from the wall, and which derive from "dispersive" effects:

$$N = JC - D\frac{dC}{dy} + p(\zeta) + q(\tau) \qquad (1)$$

where D is the Brownian diffusion coefficient, $p(\zeta)$ represents the term for migration of the solutes/particles due to surface interac-
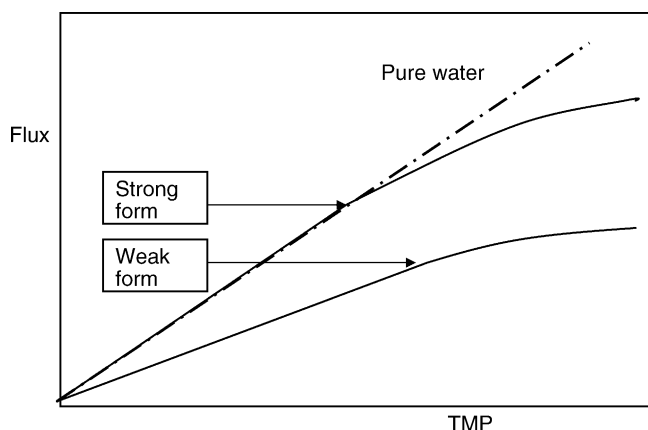

Fig. 3. Forms of critical flux as originally defined by Field et al. [1].

tions between the membrane and solutes/particles surfaces and $q(\tau)$ represents the effect of the local hydrodynamics on the mass flux. The possible settlement of non-buoyant particles onto the membrane surface will not be considered.

Now, $p(\zeta)$ can be positive, in the case of electrostatic attraction between membrane surface and solute/particles. This situation corresponds to adsorption of the solute onto the membrane, creating a sink term. It can progress at a rate, which is limited either by diffusion or by the adsorption kinetics, until the adsorption layers are complete. A steady state has then been reached, but which does not formally depend on the flux J, except insofar as the flux influences the concentration polarisation and hence the concentration of solute immediately adjacent to the membrane surface. In the case of a solute/particle–membrane repulsion, $p(\zeta)$ is negative. The consequences of this have been developed by several authors ([15,3], Bowen et al. [18]). The particle–membrane repulsion is efficient as long as the migration so induced is of the same order of magnitude as the convective flux.

$q(\tau)$ is the term for the effect of the local hydrodynamics on the mass flux. It depends, but not exclusively, on the shear forces. It can be a migration, if the dominant mechanism is a migration (e.g. lateral migration), or diffusive in nature (i.e. requires a concentration gradient) as in the case of turbulent diffusion or shear induced diffusion. This term has been discussed extensively in a review [16] and several papers, such as those of Li et al. [11].

In operation, a deposition on the membrane continues as long as N is strictly positive. If for some reason, N comes to be nil, then the net mass deposition stops, membrane fouling also stops and the main system parameters (flux J and membrane selectivity) reach a steady state, provided the other operating parameters are kept constant. An interesting way of measuring the relative importance of the dispersive mechanisms as compared to convection by filtration, is to analyse the changes in the radial Peclet number of the system, an analysis which has been promoted by Vasan and Field [19], Zeman and Zydney [20].

As noted in another section of this paper, it is sometimes experimentally difficult to make a difference between the conditions for which N is nil, and those for which the flux is at steady state ($\mathrm{d}J/\mathrm{d}t = 0$ or, as in Appendix A: $\mathrm{d}R_{\mathrm{experimental}}/\mathrm{d}t = 0$), this is because the impact of the deposit on flux may be small compared with the accuracy/sensitivity of the experimental measurements.

Eq. (1) has the merit of accounting for several classes of dispersive mechanisms, which is especially important when several classes of solutes/particles are simultaneously present in a fluid. However, the mechanisms do not have the same magnitude for all classes of solutes/particles, especially in respect to their size and surface charge. The first example is the one of small solutes, ions and molecules, for which the terms $p(\zeta)$ and $q(\tau)$ can be neglected, to give the familiar convection/diffusion equation. But other cases can be simplified as well (if one considers that terms $p(\zeta)$ and $q(\tau)$ are not concentration dependant), as shown in Table 2.

We see in Table 2 that according to the class of solute/particle, the steady state flux is expected to depend on different parameters. As soon as the terms $p(\zeta)$ or $q(\tau)$ can be expressed as the product of a velocity and concentration, then a consequence is that the steady state flux is approximately equal to this velocity; the migration due to surface forces in one case, the migration due to shear forces in another case. These simplifications must not hide the complexity of transport phenomena in a concentrated, often multi-phase flow, and so they are only indicative of the relative importance of parameters, and should not be used for a quantitative analysis.

From a system analysis point of view, Eq. (1) predicts that a steady state flux is reached only for colloids and particles, and this without accounting for the behaviour of concentrated media. However, for solutes and macromolecules, when the physics of the fluid are combined with the transport phenomena, the flux limitations, observed for so many years in ultrafiltration or reverse osmosis, can be described. This was done in the osmotic pressure model by Kedem and Katchalsky [21], applied to reverse osmosis, and in the gel theory model by Porter [13] or Michaels [12] applied to ultrafiltration. The concentration of the solute in the fluid boundary layer changes its properties. In the case of macromolecules, the reduction of the water chemical activity develops an osmotic pressure that partially balances the applied pressure. Also the proximity of solutes to each other at high concentration leads to their interconnections, which gradually form a gel (i.e. a new phase), covering the membrane surface. This latter model refers to the value of the

Table 2
Relative magnitude of the dispersive transport phenomena forces appearing in Eq. (1), as a function of the categories of solutes/particles concerned

Type of solutes/particles	Most relevant type of membrane filtration	Brownian Diffusion	p	q	Implicit form for steady state flux ($N=0$)
Ion/molecule	Reverse osmosis/nanofiltration	Large	Small	0	$J_{\mathrm{ss}} = k \ln\left(\dfrac{C_m}{C_{\mathrm{b}}}\right)$ (2)
Macromolecule	Ultrafiltration	Medium to large	Small to medium	0	Combination of Eqs. (2) and (3) as seen in Eqs. (7), (8) and (9) in Section 5
Colloids	Ultrafiltration/microfiltration	Small	Large	Small	$J_{\mathrm{ss}} \approx \dfrac{p(\zeta)}{C_{\mathrm{b}}}$ (3)
Particles	Microfiltration	0	Small	Large	$J_{\mathrm{ss}} \approx \dfrac{q(\tau)}{C_{\mathrm{b}}}$ (4)

The information is indicative, and should be checked for particular applications especially when non-ideality is important.

Table 3
Definitions of critical flux

Definitions	Abbreviations	Discrimination between		Determination based on analysis of
Strong form of critical flux	J_{cs}	No fouling	Any kind of fouling	Linearity of flux–TMP variation
Weak form of critical flux	J_{cw}	Fouling independent of solvent transfer	Fouling driven by solvent transfer	
Critical flux for irreversibility	J_{ci}	Reversible fouling	Irreversible fouling	Irreversibility
Sustainable flux	–	Sustainable flux	No sustainable flux	Rate of fouling

flux for which a gelation would occur as the "limiting flux" in micro or ultrafiltration, and this term is commented on in another section of this article. These two models, developed by visionary colleagues are now well-accepted, at least as phenomenological explanations. However, only recently has attention been paid to the non-ideality of suspensions (whether of colloids or of particles), as described in Section 5.

These studies show that in addition to the transport phenomena, which formally separate the "non-deposition" operating conditions from the "deposition" operating conditions, an increase in concentration of macromolecules, colloids or particles by accumulation in the boundary layer leads to drastic changes in the collective properties of such particles: their diffusion coefficient, osmotic pressure and furthermore their stability are modified. It is observed that even for fluxes below the steady state as defined in Table 2, the fluid near to the membrane can reach such a concentration that its stability is challenged, and this locally initiates the formation of aggregates, which in turn, soon deposit on the membrane.

2.3.2. Critical flux

The classification described in the previous paragraph can be used to define, from a theoretical point of view, what is critical and what is not in a membrane system. In other parts of this paper, we try to correlate these theoretical definitions to the data that can be accessed experimentally, and to the consequences on the optimum operation of a plant. Table 3 gives a summary that links to Appendix A.

Basically, two categories of events, described in the previous paragraph, can be considered as critical:

1. The transition of a filtration system between a situation for which $N = 0$, and a situation for which $N > 0$ (a nuclear reactor is critical when the rate of neutron production is equal to the rate of neutron loss). There are two sub-classes.
   (a) If adsorption is negligible, this borderline separates the non-deposition conditions from the fouling conditions, but does not refer to the reversibility of the situation as a criterion. The corresponding conditions depend on the solute/particle–membrane material interactions (whatever the kind of other interaction considered). Whether or not a small net deposit of material onto or within the membrane will lead to a measurable flux decline is not inferred by this definition. However, it will necessarily impact the experimental determination of such critical conditions. The corresponding flux then corresponds to the *strong form of critical flux*, also defined in terms of fouling resistances in Appendix A.

   (b) In the presence of adsorption, as mentioned in the comment about $p(\zeta)$, the steady state is reached after adsorption is completed. Therefore, a strong form of the critical flux cannot be defined (since even with a nil flux, fouling would occur). However, mass deposition by convection can occur in addition to adsorption, and the particular value of flux below which such deposition would cease may be viewed as the *weak form of the critical flux*. The link with the original definition of the weak form of the critical flux is discussed in Appendix A.

2. The transition between dispersed solutes/particles and aggregates on the membrane: the borderline here refers to an irreversible transformation in the processed fluid, and essentially relies on the fluid properties in the vicinity of the membrane surface. This transition occurs for a critical concentration (or volume fraction), which is triggered by the filtration flux (for given operating conditions). From an experimental point of view, searching for the limits of system reversibility amongst the operating conditions, will allow this critical point to be determined (to the accuracy of the experimental measurement devices). Here, on both sides of the transition, system parameters (such as flux) may be changed with time, but recovering the initial properties (membrane permeability and selectivity) requires a different action (e.g. cleaning). If flux is the controlled variable, it corresponds to the *critical flux for irreversibility* as also defined in terms of fouling resistance in Appendix A and illustrated in Fig. 4. The term reversibility is used in the same sense as in thermodynamics. However, a phase transition in a real chemical system has its own kinetics, which may be fast or slow at the time scale of the experiments/plant operation. Depending on the magnitude of this time scale, some phase transitions can be observed here and ignored there. This issue, which is more important for the experimental study of critical flux, is then commented in Section 3.

2.3.3. Limiting and critical fluxes

Limiting flux is perhaps the oldest concept in cross-flow filtration which represents the maximum stationary permeation flux which can be reached when increasing transmembrane pressure with a given solution or suspension [12,13]. It represents an important characteristic of membrane operation, especially in UF/MF. For this limit, further increases in TMP do not increase flux. The limiting flux can correspond to a flux for which the fouling saturates the filtration capacity of the membrane. Towards the opposite end of the operating envelope, the critical flux is defined as the flux for which fouling first occurs (it is then
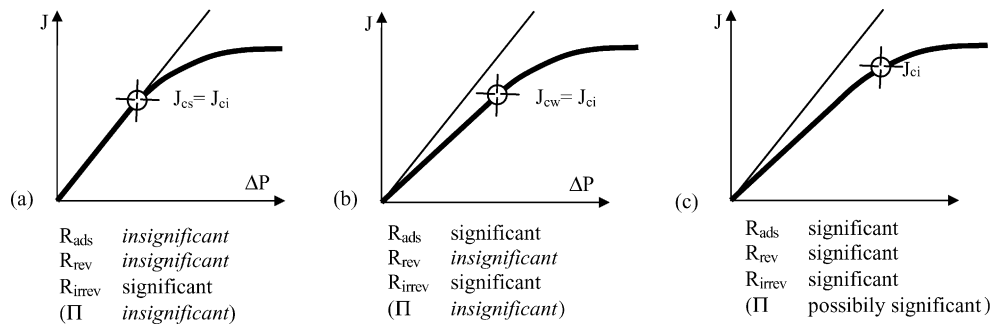
Fig. 4. Relationship between different critical flux definitions for three types of fouling behaviour. Only for the UF of macromolecules is the osmotic pressure term potentially significant.

the maximum flux for which no fouling occurs). Critical and limiting fluxes are well-differentiated concepts in their definitions. Unlike the limiting flux, the critical flux is a criterion for the transition between concentration polarisation and fouling. The latter can be related to fouling occurring locally on the membrane surface whereas the former relates to the system as a whole and to a plateau as discussed in Section 6. The existence of a critical flux distribution along a membrane surface has been considered [22] to propose a possible link between critical and limiting fluxes.

More or less all the studies on critical flux, whether experimental or theoretical, refer explicitly or not, to one of the above definitions in Section 2.3.2. The "limiting flux" as defined in the early "gel theory" also relates to the second definition, although its experimental evidence was not connected to the occurrence of a "critical" situation (the macromolecule turning into a gel) on the membrane.

3. Methods of measurement

The critical flux has mainly been obtained from flux–TMP measurements often by flux or pressure stepping. Also observations have been deduced from particle mass balances and by direct observation through the membrane (DOTM). The various methods are introduced together with critical comments on implementation including the quality (accuracy and reliability) to cost (length of experiment and complexity).

3.1. Deductions from flux–pressure observations

Flux–pressure experiments can be made either by imposing a flux and measuring a pressure or by imposing a pressure and measuring a flux. They have different advantages and inconveniences.

A constant pressure allows determination of a steady state flux (the filtration system is self regulated as fouling decreases the flux thus reducing the rate of fouling), which lead to reliable results with no time dependence (*if* a sufficient duration for each pressure step is used). With this method the steady state flux and then the steady state hydraulic resistance should be determined and compared with that of a clean membrane. On the other hand, constant flux experiments lead, in the presence of fouling phenomena, to a continuously increasing pressure with running time

because of a (quasi) constant fouling rate. This latter method is able to give (for a fixed flux) the fouling rate (the variation of the resistance with time). This dynamic data allows one to have an idea about the sustainability of the process, whereas the former method gives steady state data that is also needed when scaling-up filtration processes.

In general constant pressure experiments can be recommended when working with suspensions, containing components that show little tendency to adsorb onto the membrane, as steady state permeate fluxes will be achieved. On the other hand, constant flux experiments are well adapted to reveal fouling phenomena with complex suspensions as steady state fluxes may not be achievable. Indeed it is important to note that time scale is important. A flux may appear to be steady over a short time scale but in reality over a few days or weeks it is not. Indeed all of the methods of measuring critical flux only detect that the fouling rate is below a threshold of sensitivity for the method and the time scale used. This point needs to be held in mind especially for those applications (e.g. water treatment) where the operating period between cleans can be long and/or a sudden change is fouling rate is to be suspected (Aimar [23]).

3.1.1. Flux–pressure profile

With a suitable value for the permeability of the membrane either constant pressure or constant flux operation can be used to determine the critical flux. However, for UF membranes and dilute feeds it has been found [6] that it is very difficult to control the TMP at a low enough value to measure the strong form of the critical flux and therefore that constant flux operation was to be preferred. Constant flux operation (with measurement of TMP) is readily achieved by pumping the permeate. The TMP should remain constant with time at each flux, as any increase indicates fouling and therefore that the critical flux has been exceeded. Ideally, the total resistance should be calculated at each step to check whether the resistance has remained constant.

Constant pressure experiments have also been used, for example, by Gesan-Guiziou et al. [24]. An indication of fouling is then given by flux decline. So with certain feeds permeate pumping is not essential but for very sensitive determination of critical flux constant flux operation is recommended because the sensitivity of the TMP measurement allows small changes due to any trace fouling to be detected. Another example of constant pressure operation involved magnesium hydroxide suspensions and
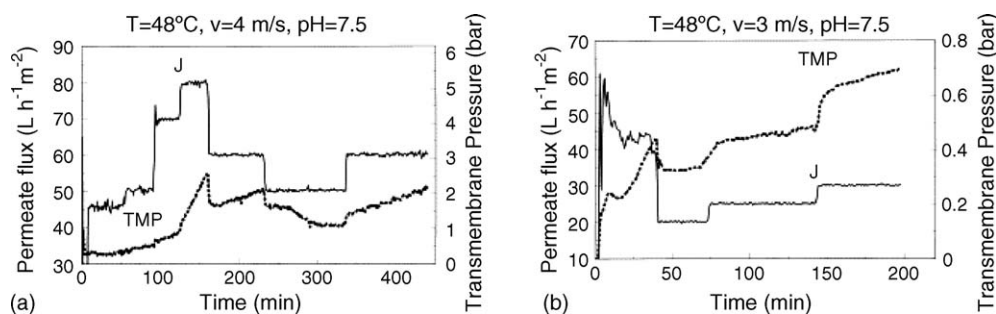
Fig. 5. Flux–TMP profiles for lactic acid fermentation broth [27]. Reproduced with permission from H. Carrere.

a sintered metal membrane, Fradin and Field [25]. For a linear response between flux and TMP, membrane conditioning was required. This involved operation of the membrane at a low flux and with a dilute suspension for a few hours prior to operation with feeds of interest. When membrane conditioning of this type is involved, any critical flux found is now best viewed as being indicative of a critical flux for irreversibility, J_{ic} as defined in Appendix A.

For both modes, the critical flux is the point where the flux–TMP relationship becomes non-linear. If flux–TMP gradient is lower than that of clean water but linear then this critical flux is of the weak form. Whilst reference was made to clean water, one could for UF/MF membranes, beneficially substitute buffer solution because the use of pure water can lead to very thick Gouy–Chapman double layers and an electro-viscous resistance in the membrane pores (Huisman et al. [26]). This effect can be effectively removed by using electrolyte (higher ionic strength).

It is important that the flux is initially sub-critical and then increased to the critical flux. If initially the flux is too high then irreversible fouling at the higher flux will affect any subsequent measurements. From Fig. 5a, Milcent and Carrere [27] concluded that the "critical flux" was $50 \, l/m^2$ h. At $50 \, l/m^2$ h, TMP does appear to have stabilised however this graph cannot be used to determine J_{crit} without some cross-checking of resistance because the flux was previously much higher. Indeed if one examines the TMP curve one may note that there has been some irreversible fouling as TMP is much higher than when it was at the same flux previously. For the lower cross-flow velocity (Fig. 5b), the value attributed to J_{crit} was given as $20 \, l/m^2$ h but the same reservations hold. Also there appears to be a slight increase in TMP at this flux, which means it is above the critical flux. The values determined do relate to a significant change in behaviour but do not satisfy the definition of critical flux as originally defined. There is insufficient evidence to determine whether the fouling is reversible and so the values given cannot be taken to be values of the critical flux for irreversibility. Repetition of the experiments approaching the flux values from below would have been, with hindsight, of greater interest.

Although during flux stepping experiments, an increase in TMP at a given flux indicates fouling, the converse, namely an observably constant TMP at a constant flux, is not enough to prove sub-critical flux operation. For example, Persson et al. [28] claimed stable fluxes up to $110 \, l/m^2$ h but it can be seen from

the flux–TMP profile (Fig. 6) that some fouling has occurred by $80 \, l/m^2$ h. There can be a flux above the critical value at which pressure will appear to remain constant with time because the new steady state is rapidly obtained. For this reason, resistance calculation at each point is recommended.

It has been noted that the plotting of raw data for J and TMP alone cannot allow the objective determination of the critical flux. To avoid subjective or arbitrary determinations, we recommend that resistance be calculated (but even so, one should remember that the equipment has a threshold of sensitivity). Other groups have chosen to calculated dTMP/dt for a series of fixed fluxes and when some arbitrary criteria
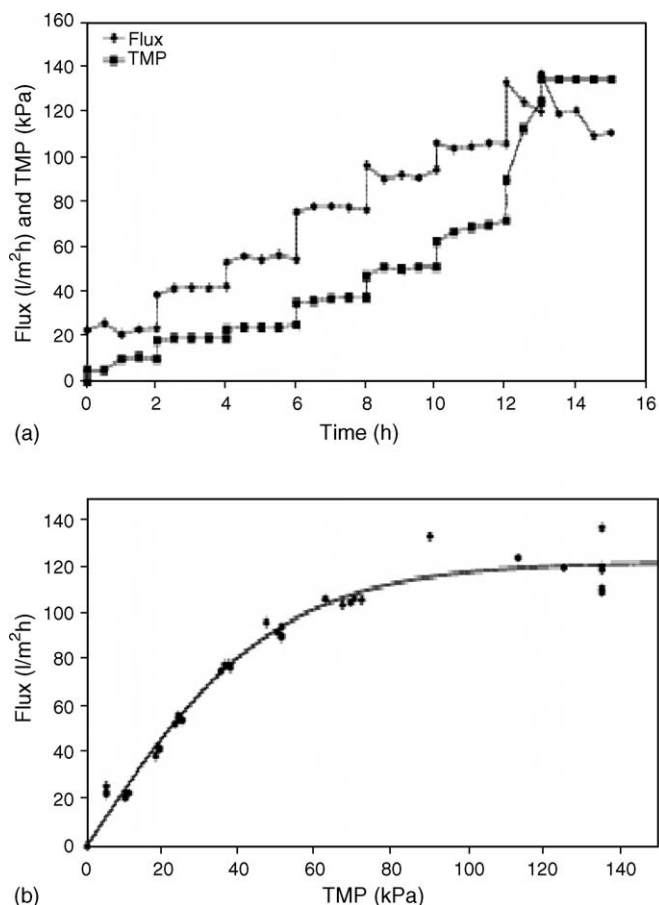

Fig. 6. Flux–TMP relationship for lactic acid fermentation broth with a ceramic MF membrane [28]. Reproduced with permission from G. Zacchi.
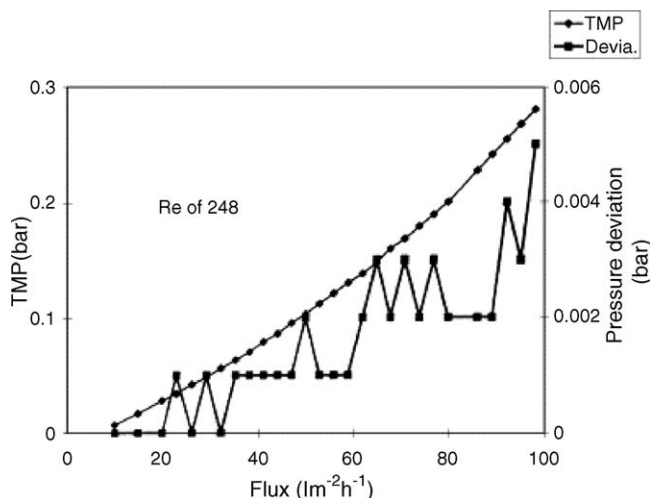
Fig. 7. The absolute increase in transmembrane pressure between the two points is plotted as a function of the increasing flux. The total transmembrane pressure is also shown (0.15% BSA, pH 9.7, Re 248). Source: Fig. 7 of ref. [6] (It is noted that the original caption in ref. [6] there is an error, there should not have been a cross-reference to another figure.).

(e.g. dTMP/dt < 1 kPa/min) is exceeded then they have asserted that a critical flux has been exceeded. This has the merit that the threshold is clearly mentioned but this approach might well be thought to be more akin to the concept of a sustainable flux (see Section 3.4).

3.1.2. Flux stepping and flux cycling

The simplest form of this technique is a set of increasing pressure steps followed by a set of decreasing steps, e.g. Chen et al. [5]. They showed that above the "critical" flux a significant hysteresis occurred but the deviation from linearity was not made clear. The stepwise filtration procedure has been commonly used to determine "critical" filtration conditions for a variety of fluids, e.g. Gesan-Guiziou et al. [29], Kwon et al. [30], Manttari and Nystrom [31]. An identical step-by-step procedure but regulated on the permeate flux was used by Wu et al. [6]. They described two types of experiments. One is a series of increasing flux steps (e.g. Fig. 5 in ref. [6]), the other involved a series of up-and-down steps. The latter is a series of flux cycles and is illustrated in Fig. 7. In the latter the sensitivity of the TMP measurement allows small changes due to any trace fouling to be detected. For example, when examining the filtration of BSA solution with a 50 k MWCO membrane (pH 7.4, 0.15% (w/w), Re 248) use was made of this procedure where flux was increased and then decreased to a previous value in a series of steps. At step 1, once J_1 was set and the process had reached a steady state (in this case it took 40 s) the transmembrane pressure was recorded as TMP_1. If this was the first step, the flux was then increased to a slightly higher value and the flux was again recorded. After this step, the flux was set back to J_1 and another value of TMP was recorded as TMP'_1. The difference between TMP_1 and TMP'_1 was called the deviation. If deviation equalled zero, it was presumed that no fouling had occurred. The flux was then increased to J_3 before being moved back to J_2. If the difference between TMP_2 and TMP'_2 was zero, it was presumed that no fouling had occurred. Fig. 7 illustrates the flux, the TMPs and the deviation at each stage for the process; upto stage 7 the amount of fouling is close to the limit of detection.

As illustrated in Fig. 7, the transition to irreversible fouling occurs either at the same point as the deviation from linearity or it occurs at a higher flux. Clearly a check of reversibility is required. This can be done using flux stepping if the flux is increased by two steps and then decreased by one and TMP measured at each step. If the TMP, when the flux is decreased, is not the same as when the flux was previously at that level, irreversible fouling has occurred and the critical flux for irreversibility has been exceeded. This technique has been used by Metsamuuronen et al. [32]. Their experiments were run for only 9 min, which is only sufficient to indicate "critical" flux. Certainly it is worth checking that the critical flux indicated in short times is stable over longer periods of time. In most early works including that of some of the co-authors' this was not done. Some recent theoretical work indicates the importance of time especially for macromolecules and this point will be expanded upon later.

Critical fluxes obtained by mass balance (see Section 3.3) are always inferior (around two times less) than the one obtained by analysing results of a flux step method. Whilst one may question the "critical" flux values obtained from profiles and deduce different values, there is a need for improved techniques (and clearer definitions) if different values are obtained by different people from the same data. A more accurate critical flux determination can be obtained by analysing the reversibility of the fouling for each step of pressure or flux. To this end the procedure of filtration with pressure steps composed of alternative increasing and decreasing step initiated by Wu et al. [6] has been developed further by Espinasse et al. [33]. This last method (illustrated in Fig. 8) allows continuous quantification of fouling reversibility so permitting very accurate measurement of two critical fluxes: the "critical flux for irreversibility", J_{ci} as
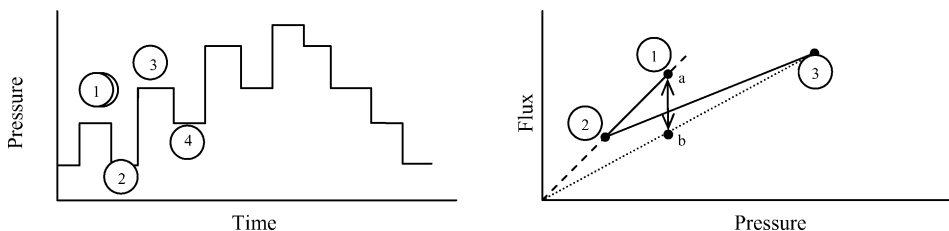

Fig. 8. Pressure step used for an accurate determination of critical flux. Comparison of permeate flux/pressure obtained in steps 4 and 1 permits conclusion as to degree of fouling irreversibility in pressure step 3 [33].
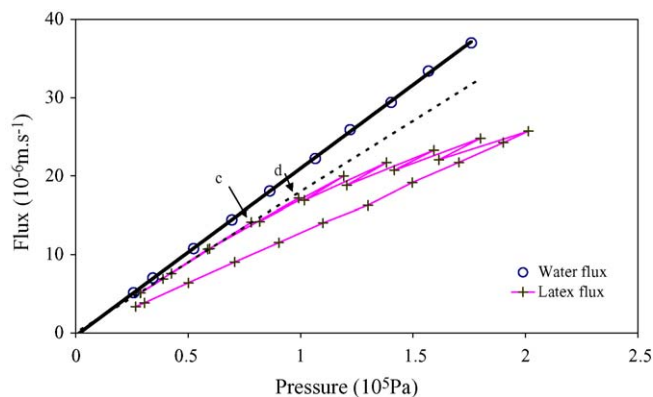
Fig. 9. Relationship between applied flux and transmembrane pressure according filtration procedure in Fig. 8 for water (circle) and PVC latex: points c and d corresponds to the range of critical flux (first irreversible fouling) [33].

well as the strong form of critical flux, J_{cs}. The authors dissociated the irreversible and reversible part of fouling for each pressure step. If reversible fouling is associated with the osmotic pressure contribution, then Fig. 9 shows an increase of osmotic pressure from the start of the filtration. However the increase due to the irreversible part of fouling was measured only above a flux of around 14×10^{-6} m/s. This flux is the critical flux for irreversibility (J_{ci}). The behaviour corresponded to that shown in Fig. 4c.

Whether fouling is reversible and hence whether the transition to irreversibility has been exceeded is readily determined by this technique but repetition of experiments is highly desirable. Also the flux–pressure history may influence the transition to irreversibility. If the flux is increased gradually to a given level, the cake can be much looser and more likely to re-disperse than if that same flux had been imposed immediately.

3.2. Direct observation through the membrane

Some have suggested the term "cake formation flux" but this cannot be measured directly from the flux–pressure relationship as the changes might not be attributable to cake formation. Whether it is, can partially be answered by results from direct observation through the membrane. In DOTM, a microscope is used to look through an Anopore membrane, which is transparent when wet. Deposition of particles on the membrane surface (or their absence) can be observed. Authors [4,11] have used this technique and have shown that the variations in pressure caused by deposition can be very small. As illustrated in Fig. 10, the point of first deposition is *not* the point of a large change in resistance.

Clearly DOTM is a very sensitive way of detecting particle deposition but it is restricted to transparent membranes and modules with a transparent section on the permeate side. Nevertheless, this technique where applicable has been the only one that can be used for direct observation of the initial deposit on the membrane. Also it has to be noted that these direct observation have always been made on particle of a relatively large size (*circa* 10 μm in diameter). Although the use of UV observation may in the future permit the observation of smaller particles of

a few microns in diameter. Electron micrographs have proven the non-existence of deposit on a membrane after sub-critical operation [5].

3.3. Mass balance

By monitoring the concentration of particles in the outlet stream, Kwon et al. [30] measured a critical flux based on a particle mass balance. Firstly, the passive adsorption of particles at no flux was measured. Then any additional reduction in particle outlet concentration was attributed to deposition. Once the deposition rate at several fluxes had been found, a graph of flux against deposition rate was plotted. The critical flux was then found by extrapolation; it is the flux at which the deposition rate is zero. This could be expected to relate to a "cake formation flux". However, the critical fluxes were also measured using TMP increases at constant flux and found to be up two times larger. Whilst this is in agreement with the statement in Section 3.2 that noted that the point of first deposition is *not* the point of a large change in resistance, the factor of two is open to doubt. The flux–TMP relationship is not linear below the supposed critical fluxes. For example, in Fig. 11 (corresponding to filtration of 0.816 μm diameter latex), the given critical flux is around 120 l/m² h for all pore sizes. But by 80 l/m² h, all the profiles have become non-linear which suggests the given critical flux is at least 40 l/m² h too high. So the point of transition that was determined will have corresponded to a different phenomenon.

Gesan-Guiziou et al. [24] claim they found their critical flux from a mass balance and TMP stepping simultaneously but they do not say whether these values agreed or if they used an average of the two. Bowen et al. [34] have used a similar technique. They found the fractional deposition after 4 h of operation at several different fluxes. By plotting these, they could extrapolate to find the flux at which there was no deposition but they did not find a critical flux for all the membranes they used. The mass balance technique does not distinguish between strong and weak forms of critical flux and gives no information about reversibility per se. Its use is only recommended in conjunction with another technique. Also it must be remembered that whilst it is suitable as a complementary technique for particulates, it is not directly applicable to macromolecules where a measurable quantity of solute will accumulate (polarise) near the membrane in the concentration polarisation layer.

3.4. Determination by fouling rate analysis

As noted by Le Clech et al. [35], a zero rate of TMP increase may never be obtained during trials with real and synthetic sewage. Thus use of the flux-step or any other method to determine critical flux will yield a result that it may not exist. In their work the result is that if it exists, the value is less than 2 l/m² h. The useful results from experiments in this area relate to the *rate* of fouling, given by the derivative of the transmembrane pressure, dTMP/dt, for constant flux experiments. Significant differences above and below clearly defined fluxes have been found. These points of change are significant and relate to the operational and economic sustainability of a membrane process.
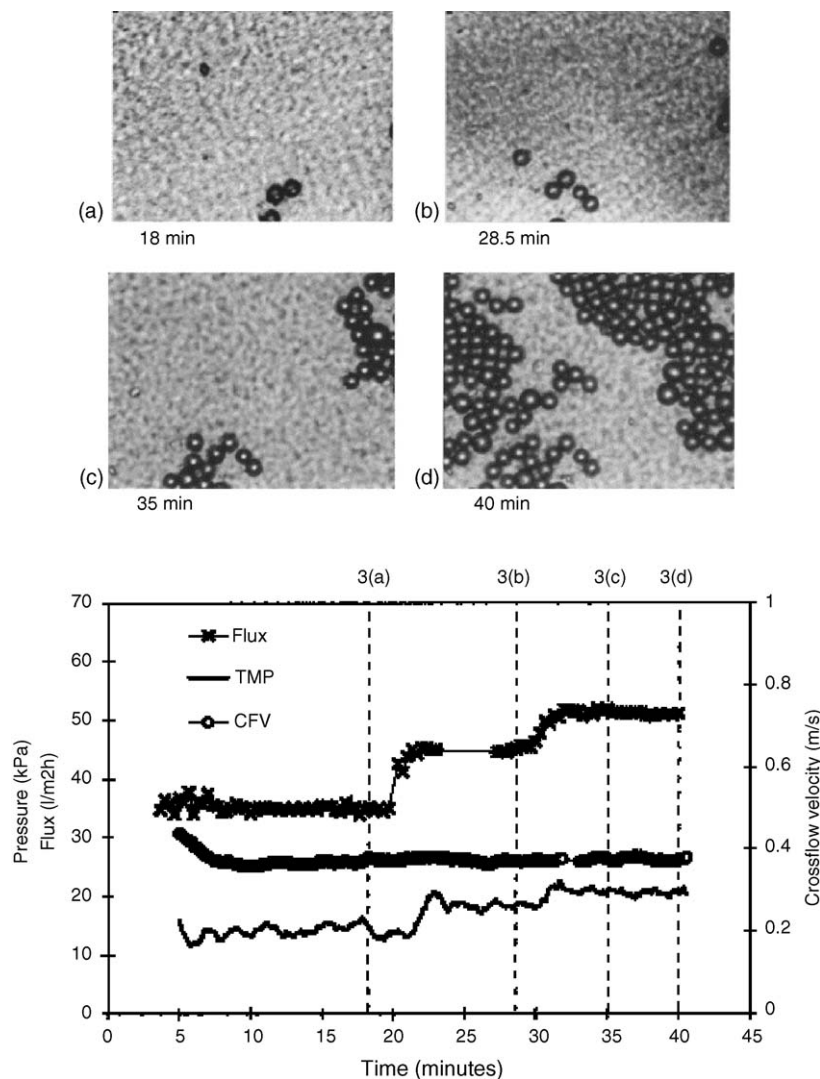
Fig. 10. Particle deposition images (a–d) and the flux and cross-flow conditions (e) for filtration of 11.9 μm latex particles. The time when the images were taken is denoted by the vertical broken lines in (e) [4]. Reproduced with permission from A.G. Fane.

As discussed in Section 6, the term *sustainable flux*, J_{sus}, will be more appropriate if a distinction is being made between low and high fouling rates. It is conceivable that the rate of fouling approach will identify both a value J_{sus} and a critical flux.

Fig. 11. TMP–flux profile for various membrane pore sizes [43]. Reproduced with permission from S. Vigneswaran.

Indeed referring back to Fig. 4, three points of change might be significant: two critical fluxes (J_{cs} or J_{cw} and J_{ci}) as illustrated in that figure and at a higher flux a value of J_{sus}.

3.5. Comparison of techniques for critical flux measurement

The various measurement techniques have different advantages and disadvantages; a summary is given in Table 4. According to the definitions given in Section 2, the weak and strong form of critical flux can be defined by a deviation from water flux line. The irreversibility form of critical flux can be fully determined by methods with continuous up-and-down flux or pressure steps. The mass balance method could be a useful complement to these methods with a determination of deposited mass. However, for complex suspensions, the analysis of the criticality via fouling rate, has become increasingly common, e.g. for submerged membrane bioreactor, Jefferson et al. [36]. This method has potential in other systems. Indeed it could be argued that the fouling rate, especially for multi-component systems, is of key

Table 4
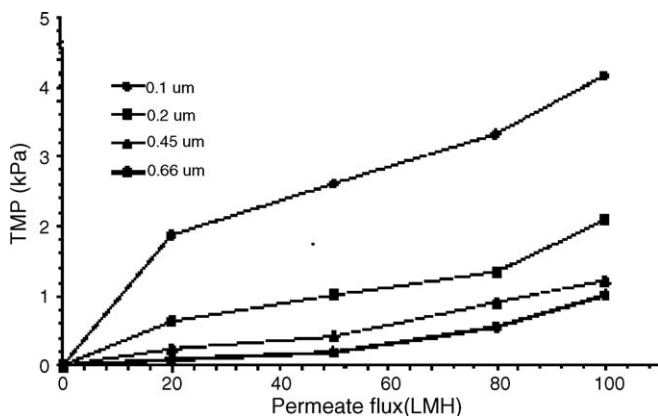Methods of measurement for critical flux: a comparison

Method	Advantages	Disadvantages	Form measured	Suitability
Flux–pressure profile: deviation from linearity (Section 3.1.1)	Simplicity	Can be subjective. No link with reversibility	Strong and weak form J_{cs}, J_{cw}	Feeds with low osmotic pressure
Flux or pressure vs. time: flux stepping (Section 3.1.2)	With up and down steps, fouling hysteresis found. Resistance should be determined for each step	Unlike flux cycling, points of transition to irreversibility can be missed	Strong and weak form J_{cs}, J_{cw}	Feeds with low osmotic pressure; if correction is to be made for osmotic pressure flux cycling is to be preferred
Flux or pressure vs. time: flux cycling (Section 3.1.2)	Rigorous when allowance made for osmotic pressure	Time consuming and complex	All forms J_{cs}, J_{cw} and J_{ci}	All kinds of feed
Direct observation through the membrane (Section 3.2)	Direct observation of flux giving deposition. Potential for measuring J_{ci} yet to be exploited	Limited to particulate feeds and membranes that are transparent when wet	Linkage to J_{cs}, J_{cw} or J_{ci} not obvious, but value determined is significant	Particulate feeds
Mass balance (Section 3.3)	Linked to a complementary parameter, the deposited mass	Needs to be used in conjunction with another method	Linkage to J_{cs}, J_{cw} or J_{ci} not obvious, but value determined is significant	Particulate feeds
Determination by fouling rate analysis (Section 3.4)	If a flux for "low fouling" is not found then determination of dP/dt (under fixed fluxes) may identify a point of sustainable flux. Absolute "no fouling" corresponds to a critical flux	Can be subjective. No link with reversibility	Strong and weak form J_{cs}, J_{cw} also J_{sus}	All feeds

importance. Industry often operates at an acceptable fouling rate between cleans as this allows a higher permeability to be used throughout a run. Such a practice clearly links to the concept of a sustainable flux but it has no precise definition. If it were taken to be the industrially acceptable flux, which is determined from economic considerations, then its value would change as the balance between capital and running costs changed. An alternative approach is considered in Section 6.

4. Experimental features

The first experimental findings linked to the critical flux concept were by Field et al. [1] and Howell [2] who used a wide range of different colloidal suspension (yeast, dodecane–water emulsion and calcium carbonate slurry). Experimental determination of critical flux made with suspensions of clays with different ionic strength have proven the important link between the critical flux value and suspension stability so underling the role taken by particle repulsion [17]. Many studies have since proven the existence of a "critical" flux (the inverted commas are used to show that the values determined might relate to the sustainable flux rather than the critical flux) for different fluid and filtration conditions.

The wide range can be viewed in Table 5 as consisting of three subsets (colloidal dispersion, macromolecular solution and complex fluid) for which the increasing level of complexity can explain the difficulties in reaching accurate and reliable critical flux values.

Table 6 summarises the operating conditions for these principal determinations of "critical" flux. Objectives of most of these publications were focused on the determination of fouling mechanisms so as to have a good choice of operating conditions.

The way determinations can be made and the tools develop to experimentally access "critical" flux has been covered in Section 3. The sensitivity of "critical" flux to operating conditions is now reviewed (suspensions properties, Section 4.1, hydrodynamics, Section 4.2 and membrane properties, Section 4.3) and the consequences on process productivity and selectivity is detailed Section 4.4.

Table 5
Range of dispersion and solution used in experiments dealing with critical flux measurements

Colloidal particles	
Gold sol	[37]
Silica particles	[6,5,38–40]
Titanium dioxide	[41]
Latex	[24,29,30,4,11,33,42–44]
Clays	[8,45–47]
Macromolecular solution	
Proteins	Lactalbumin: [48–50]
	Myoglobin: [32,50]
	γ-Lactoglobulim and IgG: [48,50–52]
	Lysozyme: [53,50]
Bovine serum albumin	[6,51–55]
Natural organic matter or humic substances	[34,56–60]
Emulsion, liquid droplets	[1,61]
Complex fluids	
Yeast cells	[6,32,11,62–64]
Skimmed milk	[29,50,65–70]
Water and waste water	[71–75]
Lactic acid broth	[27,28,76,77]
Bioreactors sludge	[7,9,10,78–87]
Pulp and paper mill	[31,88,89]

Table 6
Critical flux measurements: some experimental features

| Suspensions	pH	Ionic strength	Concentration	Re	Membrane	Jcrit (l/h m^2)	Authors
Paper mill effluent	7.7	–	150 ppm	2 m/s	Desal 5	32	Mänttari and Nystrom [31]
Paper mill effluent	6.5	1.6 mS/cm	COD 1550 mg/l	3.1 m/s	Desal 5	50	Mänttari et al. [89]
Biologically treated wastewater	7.9	1.62 mS/cm	COD 80 mg/l	3 m/s	Carbosep M14	100	Vera et al. [73]
Activated sludge	–	–	COD 1200 mg/l (solid cc 10 g/l)	4 m/s	Kerasep 0.1 μm	115	Defrance and Jaffrin [78]
Activated sludge	–	–	3–10 g/l	2300	Millipore plane membranes	65	Madaeni et al. [84]
Lactic acid fermentation broths	6.2		Bacterial concentration = 2.6 g/l	4 m/s	Kerasep 0.1 μm	50	Milcent and Carrere [27]
Lactic acid fermentation broths		–	1.7 g/l dry weight	10.8 m/s	0.2 mm ceramic tubular membrane	90	Persson et al. [28]
Skimmed milk	–	–	–	5.4 m/s, 3.8 m/s	Kerasep 0.1 μm	60	Gésan-Guisiou et al. [66]
Natural organic matter	8	0.01 M	20 mg/l	0.4 m/s	NF 70	20.2	Seidel and Elimelech [57]
BSA	7.4	–	0.15% (w/w)	248	PES 50 kDa	32	Wu et al. [6]
BSA	7.4	–	0.15% (w/w)	580	PES 50 kDa	55	
BSA	7.4	–	0.15% (w/w)	248	PES 100 kDa	21	
Silica X30	9.7	–	0.5%	580	PES 50 kDa	70	Wu et al. [6]
Silica X30	9.7	–	0.5%	580	PES 100 kDa	52	
Silica X30	9.7	–	0.5%	580	PS 0.2 μm	50	
Silica 0.53 μm	3	0.001 M	0.16% (w/w)	5 m/s	Membralox	30	Huisman et al. [38]
Yeast	–	–	5 g/l	Bubbling	Polypropylene hollow fiber	10	Chang and Fane [62]
BSA	3, 4.8, 9	0.02	0.1% (w/w)	704	0.2 mm trak-etched	220	Chan and Chen [53]
Yeast	7.4		5%	580	PES 50 kDa	23	Wu et al. [6]
Yeast	7.4		5%	580	PES 100 kDa	12	
Silica 12 nm	7.5	–	0.4%	3740	PS 10 kDa	200<, <280	Chen et al. [5]
Silica 12 nm	7.5	–	0.4%	1860	PS 10 kDa	220	
Silica 12 nm	7.5	–	0.4%	740	PS 10 kDa	120<, <160	
Silica 12 nm	5		0.4%	2570	PS 10 kDa	180<, <210	
Silica 12 nm	3		0.4%	2570	PS 10 kDa	130<, <160	
Myoglobin	6	0.01 M	100 mg/l	373	Regen. cellulose 30 kDa	70	Metsämuuronen et al. [32]
Myoglobin	7	0.01 M	100 mg/l	373	Regen. cellulose 30 kDa	60	
Myoglobin	7	0.01 M	100 mg/l	496	Regen. cellulose 30 kDa	120	
Myoglobin	7	0.01 M	200 mg/l	496	Regen. cellulose 30 kDa	120	
Myoglobin	8	0.01 M	100 mg/l	373	Regen. cellulose 30 kDa	105	
Myoglobin	8	0.01 M	300 mg/l	373	Regen. cellulose 30 kDa	65	
Yeast	4<, <6	0.01 M citric buffer	100 mg/l	373		100<, <120	Metsämuuronen et al. [32]
Yeast	4<, <6	0.01 M citric buffer	1 g/l	373		50<, <60	
Yeast	4<, <6	0.01 M citric buffer	10 g/l	373		20	
Clay (bentonite)	–	0.00001 M	0.3 g/l	1500	AC 10 kDa	27	Bacchin et al. [8]
Clay (bentonite)	–	0.0001 M	0.3 g/l	1500		18	
Clay (bentonite)	–	0.001 M	0.3 g/l	1500		11	
Latex PVC 123 nm	–	0 M	0.71 g/l	2000	Tubular ceramic 10 kDa	25	Espinasse et al. [33,42]
Latex PVC 123 nm	–	0 M	0.71 g/l	4000		43	
Latex PVC 123 nm	–	0 M	0.71 g/l	6000		58	
Latex PVC 123 nm	–	0.01 M	0.71 g/l	6000		43	
Latex 190 nm	7	0 M	4.9 g/l	11350	Tubular ceramic 0.1 μm	120	Gesan-Guiziou et al. [24]
Latex 190 nm	7	0 M	4.9 g/l	3800		35	
Latex 190 nm	7	0 M	4.9 g/l	7700		80	
Latex 190 nm	7	0 M	1.8 g/l	3800		47	
Latex 190 nm	7	0 M	0.4 g/l	3800		140	
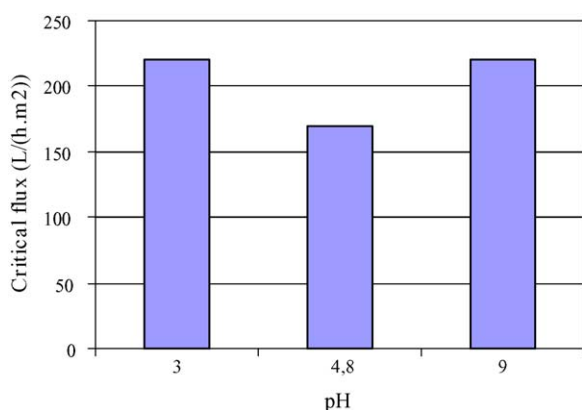
Fig. 12. Effect of the pH on the critical flux obtained during flux stepping, experiments using 0.1 wt.% solutions BSA. A minimum is observed near the IEP of BSA [53].

4.1. Effect of suspension properties on critical flux

4.1.1. Suspension stability

As soon as surface interaction was highlighted as being mainly responsible for the critical flux of colloidal suspensions [3] numerous works were undertaken to study the effect of suspension properties. Principally, these are pH, which changes the solute charge, and ionic strength that varies the surface repulsion through charge screening. Globally an increase in pH above the isoelectric point (IEP) gives an increase in the critical flux. By way of illustration, firstly it has been found that there is an increase in the weak form of critical flux from 60 to 105 l/h m^2 for myoglobin as pH is increased from 7 to 8 (Metsammuren et al. [32] in Table 4). Secondly, for silica the following rise was found: circa 145–195 l/h/m^2 as pH increased from 3 to 5 (Chen et al. [5] in Table 4). A minimum in the critical flux has also been determined for BSA suspension for a pH near the IEP as presented in Fig. 12 (Chan and Chen [53]). Consistent with this, it has been observed with whey protein concentrate and sodium caseinate suspensions (Youravong et al. [69]) that there is an increase in critical flux for both protein suspensions with increasing pH.

Regarding ionic strength, an increase of ionic strength below the critical concentration for coagulation decreased the critical flux both in clays suspension [8] and for latex particles (Kwon et al. [30], Espinasse [42]). Also addition of electrolyte decreased the critical flux for sodium caseinate with a more pronounced influence for CaCl$_2$ than for NaCl. These experiments directly illustrate the role of the ionic strength and the pH on the repulsive surface interaction that can explained through DLVO theory. They underline again the direct correlation between the stability of the suspension and the critical flux.

Surface hydrophobic interaction has also been shown to be important in more complex suspensions. The effect of Ca^{2+} concentration on critical flux has been underlined during NOM nanofiltration (Seidel and Elimelech [57]). The formation of Ca-NOM binding leads to a change in interaction between NOM macromolecules: the stability is decreased by a change in confor-

mation when calcium is added which exposes the hydrophobic part of NOM. As a consequence a decrease in the critical flux is observed.

The mechanism of precipitation or crystallisation of a solute can be seen as resulting from the presence of a solute with low stability. For example, an increase of pH beyond a threshold value in a membrane bioreactor used for denitrification (Ognier et al. [85]) resulted in an important decrease in critical flux. This resulted in the deposition of carbonate calcium precipitate on the membrane. So again the important decrease in critical flux results from suspension instability.

4.1.2. Suspension concentration

Many studies show a decrease in the critical flux when the suspension concentration rises. As an example, Gesan-Guiziou et al. [24] observed a rapid decrease of the critical flux with increasing concentration of suspensions of latex. From 0.4 to 2 g/l, the critical flux values decreased from 140 to 47 l/h/m^2. For higher concentrations, the critical flux was almost constant at around 30 l/h/m^2 for concentrations from 3 to 8 g/l. The same trend was observed for latex suspensions by Kwon et al. [30]. However, the plotting of the permeate flux as a function of the logarithm of the concentration is not linear and so does not satisfy the film model. As a consequence, neither the film nor the gel model can explain the mass accumulation. Variation of diffusion coefficient or viscosity (Aimar and Sanchez [90]) and the presence of surface interaction [3] can be responsible for these discrepancies. As explained in earlier work (Field and Aimar [91]), a constant surface concentration is not to be expected. The effect of concentration in a complex suspension can exhibit similar behaviour, e.g. activated sludge concentration [84]. Sometimes the effect of increasing concentration of bacterial cells in fermentation broth [28] leads to only slight decreases in critical flux.

4.1.3. Suspension size

The effect of the particle size on the critical flux is difficult to determine experimentally as it is necessary, for an accurate analysis, to have particles with different size but the same surface properties. A study [30] was made with polystyrene latex particles of seven different sizes from 0.1 to 10 μm. Experimental determination of critical flux both based on the TMP increase for constant flux experiments and on a mass balance on particles in the retentate showed a minimum in the critical flux for particles size of about 0.2 μm (Fig. 3). The value of critical flux observed is higher for particles of 0.1 mm (Fig. 4). This trend (minimum of critical flux for size around 100 nm) was found theoretically by Harmant and Aimar [92] and explained (Fig. 13) by a coupling of different critical flux mechanisms of diffusion (higher for smaller particles) and surface interaction (higher for bigger particles). Such a minimum can also be related to the transition between the formation of gel layer (for small particles) and a deposit (for bigger particles) [93]. Experiments made by Li et al. [11] for larger particles also showed an increase of critical flux with particle size. These results will be compared to back-transport mechanisms in the section dedicated to model analysis Section 5.
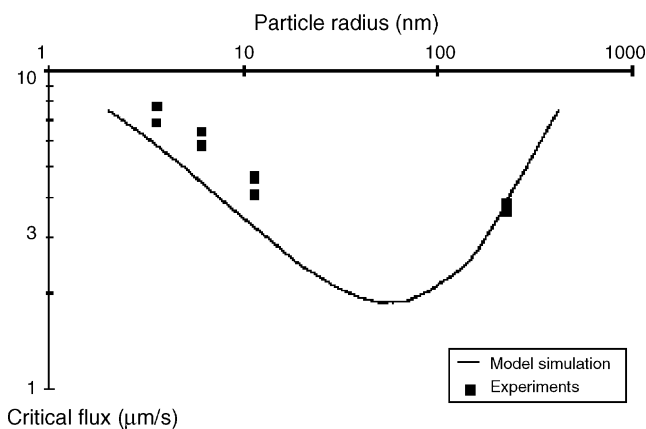
Fig. 13. Effect of particles size on the critical flux obtained with latex particles (symbols). These experiments are compared to simulation accounting surface interactions showing a minimum in critical flux for 100 nm particles [92].

4.2. Effect of hydrodynamics on critical flux

Hydrodynamics at the membrane surface have a major influence on variations in critical flux values: an increase in the strength of the hydrodynamics being synonymous with a critical flux rise. Furthermore, the sensitivity of critical flux to hydrodynamic conditions can explain the distribution of critical fluxes (and then of fouling) along a membrane surface.

4.2.1. Hydrodynamic and global critical flux

Tangential flow at the membrane surface induces a variation of critical flux, which has typically been expressed as a power law of the Reynolds number in numerous papers dealing with critical flux. Such a trend is found in all studies dealing with effect of the cross-flow velocity on critical flux but a common exponent for this power law cannot be deduced from these works. It has to be noted that a large cross-flow velocity can cause only a small increase in critical flux if the pressure drop along the membrane surface becomes significant [84]. For the same TMP, the transmembrane pressure at the inlet of the membrane surface when the velocity and hence feed-side pressure gradient are high is itself high. This leads to a local permeate flux, which can be superior to the critical value and hence local fouling.

Experiments have also been made with different hydrodynamic promoters: cross-rotational and vibratory shear enhanced processes (Al Akoum et al. [65], Huuhilo et al. [88]), gas sparging (Sur and Cui [63], Cabassud et al. [45], Chang and Fane [62], Bouhabila et al. [10]), washing period (Defrance and Jaffrin [78]), agitator-induced flushing (Ahn and Song [94]).

A critical ratio linking the permeate flux and the hydrodynamics has theoretically to be related to the mass transfer coefficient or boundary layer thickness, δ [3,95]. The critical ratio is then a critical Peclet number ($J\delta/D$). Gesan-Guisiou et al. [66] expressed their hydrodynamic criteria in terms of a critical wall shear stress; the experimental results on ultrafiltration of skimmed milk showed a linear variation of critical flux and wall shear stress (Fig. 14). The slope of this line, which has been found to 0.95 l/h m^2 Pa for skimmed milk [66] and 18 l/h m^2 Pa for latex particles [24], represents a critical ratio independent of hydrodynamic conditions and only a function of suspension
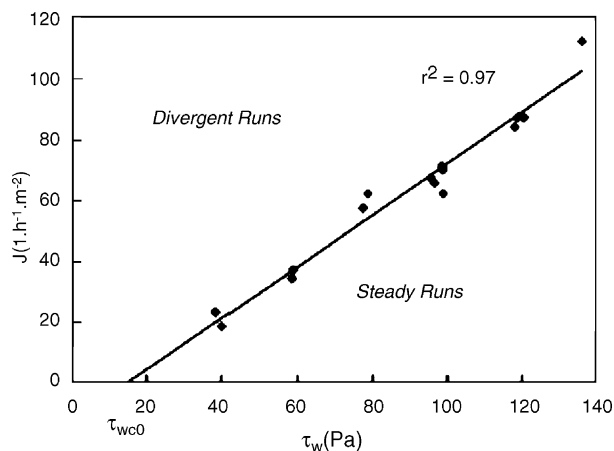

Fig. 14. Critical flux plotted against the wall shear stress. Filtration of skimmed milk realised on a 0.1 μm Kerasep membrane [66]. Reproduced with permission from G. Gésan-Guiziou.

properties. The intercept with x-axis is interpreted as a critical erosion shear stress below which a critical flux does not exist for a given solution–membrane combination. These two last approaches using a critical Peclet number or a critical ratio "flux over wall shear stress" are convergent as the wall shear stress and boundary layer thickness can be theoretically linked through the Fanning friction factor.

4.2.2. Critical flux distribution along the membrane

Critical flux can be reached preferentially at certain points along a membrane surface. Experimental illustration of this behaviour has been observed during filtration near sub-critical flux showing an important distribution of deposited mass along the membrane surface during biomass filtration for a membrane without spacers (Fig. 15 from ref. [80]) or during desalination by reverse osmosis with spacer filled channels (Schwinge et al. [96]). Such a trend can be fully explained by a distribution of critical flux along the membrane surface; the real critical number is not the critical flux but a critical Peclet number ($J\delta/D$) [3]. Indeed, the boundary layer thickness grows along the membrane leading to a decrease in mass transfer coefficient. So if one considers that there is a constant critical Peclet number
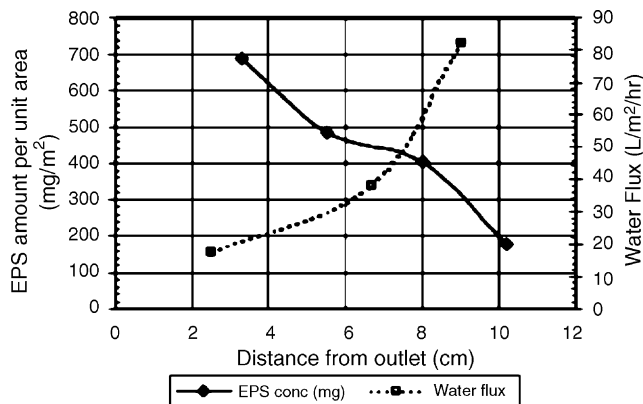

Fig. 15. Spatial distribution of extra polymeric substances (EPS) and water flux along a membrane channel (Cho and Fane [80]). Illustrations of the distribution of a critical flux along the membrane surface. Reproduced with permission from A.G. Fane.

then it follows that there is a decrease in critical flux from the membrane inlet to outlet. This distribution explains why a cake grows from the outlet where the mass transfer coefficient is unfavourable compared to that at the inlet [93,95]. The trends illustrated by Fig. 15 are readily explained in terms of a critical Peclet number thus emphasizing the role of this critical number to describe fouling conditions in tangential filtration. Some recent models for submerged hollow fibre modules integrate the critical flux and its distribution along the membrane to optimise the fibre length and radius (Chang et al. [97]).

4.2.3. Analogy in dead end filtration

In the absence of tangential flow along the membrane (i.e. dead end filtration) a critical flux cannot be observed if the critical factor is a critical wall shear stress. However, a critical filtered volume ([92], Bacchin et al. [98]) has been found for dead-end filtration of certain fluids. Indeed, for dead end filtration of a colloidal suspension or natural water [59], a deposit appears on the membrane only after a given filtered volume (the critical filtered volume). Such a concept presents the same phenomena with regard to the formation of an irreversible coagulated deposit as when, in cross-flow filtration, the critical flux for irreversibility is not exceeded. Thus for true colloidal suspensions there is a link to dead-end operation.

4.3. Effect of membrane properties on critical flux

Membrane properties, such as porosity and pore size (or molecular weight cut-off) have been experimentally investigated in addition to the effect of the membrane materials properties (surface charge or hydrophilic effect).

4.3.1. Effect of membrane porosity and cut-off

The geometric structure of the membrane (porosity, cut-off, pore shape, . . .) has been shown to be important for critical flux. Wu et al. [6] observed for a PES membrane a decrease of the critical flux when the membrane cut-off is increased (Table 6). As proposed by the authors, the change in critical flux could be the difference in surface properties (such as charge) but could also be the results of a change in local porosity and hence in local permeate velocity. The latter would modify locally the balance between drag force and surface interaction responsible for the critical flux. This effect might be particularly important for macromolecules. Recently, during the ultrafiltration of colloidal latex suspension it was observed that the initial permeability of tubular ceramic membranes has little effect on the critical flux value [24]. However, experiments realised on a membrane pre-coated with an irreversible deposit induced an important decrease in critical flux.

Experiments have been recently performed on microsieves, i.e. membrane with well-defined pore made by controlled etching. Bromley et al. [99] have shown five-fold higher critical flux with slotted pores that with a circular pores. These results clearly indicate the impact of the local structure at the membrane surface on the critical flux. Furthermore, other experiments with microsieves realised by Kuiper et al. [100] with circular pores but different porosity have shown that porosity can play an impor-

tant role in the development of the cake layer at the membrane surface. For high porosity, i.e. pore very close to each other, steric hindrance can occur between particles and prevented their deposition on the whole membrane surface. Even if critical flux is exceeded the deposit cannot develop on the whole surface. Such a system might well have a critical flux for irreversibility, J_{ci}, in excess of a conventional critical flux J_{cs} or J_{cw}.

A membrane with a higher porosity will have a better distribution of the permeate flux on the porous surface (lower value for local maximum permeate flux) and should lead to an increased global (averaged over the whole surface) critical flux.

4.3.2. Effect of membrane materials

Huisman et al. [38] ran experiments on silica filtration using three membranes having the same cut-off but made with different membrane materials (titania, zirconia and α-alumina). No noticeable difference in the value of critical flux was observed even when membrane zeta potential was changed from positive to negative. The effect of a membrane surface being hydrophobic or hydrophilic or even the effect of a membrane cleaning did not show consequences for the determination of critical flux [31]. The only difference noted in favour of hydrophilic membranes [32] can be explained by the fact that the hydrophilic membrane exhibited higher porosity, which can be the cause of a higher value in critical flux (as detailed above). Chan and Chen [53] emphasise this conclusion in a study focused on the precake formation, which showed evidence of the importance of membrane morphology for the limiting mechanisms only during sub-critical experiments. A time-lag for a first appearance of fouling resistance was introduced dependent on the kinetics of protein aggregation and aggregate deposition. Finally, it has to be noted that the critical flux for irreversibility was defined as the permeate flux above which a multi-layer fouling occurs (Section 2.3 and 5.5). Thus almost by definition membrane surface properties can have only little effect on the value of J_{ci}.

4.4. Consequences of critical flux on process efficiency

4.4.1. Consequences on productivity

As already discussed above, critical flux is a concept of importance to optimise filtration productivity. Indeed, fouling leads to a loss of productivity. Fouling may only be reduced by the adoption (if applicable) of membrane back-washing adapted (additional cost and lost in energy and/or permeate production) or an increase in shear at membrane surface (additional energy cost due, for example, to increased cross-flow velocity). The possibility opened by sub-critical operation is then very challenging. A lot of works cited above have shown results of filtration without fouling and hence no loss in productivity over a long period of time. One of the main applications of sub-critical operations is the filtration of bioreactors sludge, which can work at low flux. Numerous publications have been made in this area. As an example, Gander et al. [7] report that there is evidence from MBRs to support the critical flux hypothesis as many submerged plate and frame plants run at a transmembrane pressure inferior to 0.4×10^5 Pa (0.4 bar) with no noticeable steady state flux decline.
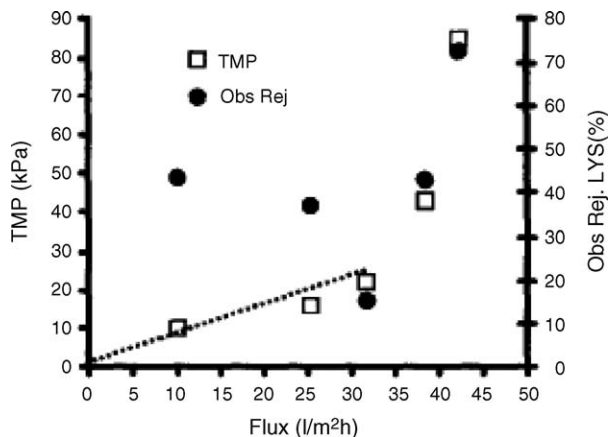
Fig. 16. Filtration of a binary mixture of proteins. A minimum of observed rejection in the smaller protein is observed when critical flux is reached [51]. Reproduced with permission from V. Chen.

4.4.2. Consequences on selectivity

Some papers use the determination of a critical flux to improve the fractionation by avoiding an additional rejection due to a deposit on the membrane. Studies on membrane selectivity have soon been used to verify the concept of critical flux, i.e. the presence of a deposit on the membrane surface. However, Chen et al. [5] who was expecting an increase of rejection above or below the critical flux, observed no such variation in rejection. They explained this trend by two concomitant phenomena: an increase in flux can both be responsible for a deposit and then an additional resistance to the solute transfer (increase in rejection) and the cause of the increase of solute concentration at the membrane (decrease in observed rejection). Gésan-Guisiou et al. [66] note an important increase in retention of both β-lactaglobulin and α-lactalbumin when operating at fluxes above the critical flux when filtering skimmed milk. These results were confirmed at different value of tangential flow and explained by authors as the consequences of an irreversible deposition of casein micelles, micro-organisms and entrapped or retained soluble proteins at the membrane surface. In 2002, Chan et al. [51] showed in a study combining fouling and selectivity determination during filtration of a solution of two proteins, a minimum of observed rejection in the smaller protein near the critical flux (Fig. 16): the initial decrease of rejection with permeate flux can be explained by the increase of the membrane concentration and the following increase by the appearance of the deposit leading to an additional resistance for protein transfer. As underlined by Howell et al. [48], controlled flux operation can be a solution to achieve high fractionation via membrane processes by taking advantage of the fact that when the flux increases the rejection of high molecular weight decreases (because of the fouling layer) whilst that of lower molecular weight materials decreases (because of the polarisation concentration).

5. Theoretical development and explanation

As introduced in Section 2.3.1, the causes for the existence of a critical flux are based on back transport mechanisms, which can be either surface interaction or hydrodynamic phenomena, such

as lateral migration or shear induced diffusion (Figs. 2 and 13). Lateral migration or shear induced diffusion have led to the development of models well before the appearance of the critical flux concept. Also the review of 1994 [16] has been complemented by Li et al. [11]. We will therefore focus our discussion of recent models on the effect of surface interaction during ultrafiltration, which are well adapted for describing colloidal fouling.

5.1. Mass balance in a boundary layer

The first "modified film model", as it was call by the authors, was developed by McDonogh et al. [15]. Surface interactions in the boundary layer (where δ is the mass boundary layer thickness) are accounted for through the force of repulsion due to osmotic pressure, p_{elec}, caused by the accumulation of ions between charged planes. Such a model corresponds to a term $p(\zeta)$ (introduced in Section 2.3 (Eq. (1)) as the term for migration of the solutes/particles due to surface interactions) written as:

$$p(\zeta) = \frac{D_0}{\delta} \int_0^\delta \frac{p_{elec} A}{k_B T} \, dx \tag{5}$$

This model describes the gap between the film model due to surface interaction and allows one to calculate the rise of steady state flux induced by an increase of zeta potential. These results were compared to steady state flux measurements. The same approach was developed in 1995 by Buffham and Cumming [101] in a model where the boundary layer assumptions was avoided by using the modified film model with a Berman axial flow (Berman [102]) and a mass balance along the channel section. Although this work includes, the notion of a metastable equilibrium indicating whether particle deposition is more or less likely, the term "critical" is intentionally avoided. The authors cite the reason as being: "there does not appear to be a critical phenomenon in the sense that a very small change in permeation rate causes the concentration profile to change from one for which deposition would be most unlikely to one for which deposition is almost certain". However, the fluxes they considered are lower than those considered experimentally. Also it has to be noted that this definition is now be used to depict a critical flux.

In Bowen et al. [18], improvements are made in the way surface interaction act on mass transport: the effect of the surface interaction is taken into account through the variation of the collective diffusion coefficient, D_c, accounting for multiple interactions between particles in a cell model Bowen and Jenner [103]. The terms accounting for diffusion and surface interaction in Eq. (1), are then combined into one term, the collective diffusion coefficient, D_c, so recognising that the particles are close enough to each other for surface interaction to modify their random motion:

$$D_0 \frac{dC}{dy} + p(\zeta) = D_c(\zeta, C) \frac{dC}{dy} \tag{6}$$

where the collective (or gradient) diffusion coefficient is a function of the colloidal osmotic pressure, Π (incorporating the

effect of the particle concentration and surface interactions), through the generalised Stokes Einstein (Einstein [104]) which has been further discussed on different level by Van den Broeck et al. [105], Petsev and Denkov [106], Russel et al. [107] and Bowen et al. [108]. The equation for the steady state flux should then be modified to account for the collective diffusion coefficient or the osmotic pressure as follows:

$$J_{ss} = \frac{D_0}{\delta} \int_{c_b}^{c_m} \frac{D_c(c)}{D_0} \frac{dc}{c} = \frac{D_0}{\delta} \int_{\Pi_b^*}^{\Pi_m^*} \frac{K(\phi)}{\phi} d\Pi^* \tag{7}$$

where K is the hindered settling coefficient describing the effect of concentration (or the volume fraction ϕ) on the permeation drag force. This equation can help to account for surface interaction for solutes, which exhibit diffusive properties, such as macromolecules or colloids.

In 1996, Jonsson and Jonsson [109] developed the same kind of model based on a depiction of the effect of surface interaction through a thermodynamic force due to the osmotic pressure gradient in a cell model accounting for multi-interactions. The model is developed in a boundary layer thickness and with a boundary condition based on the osmotic pressure at the membrane. The transition between polarisation concentration and deposit or gel on the membrane is then explained as the consequence of the fact that the concentration at the membrane can reach a critical volume fraction for which the osmotic pressure has a maximum. The paper indicates that "the operating conditions under which the critical precipitation concentration (the gel or cake concentration) is reached can also be calculated" but no results were presented in this work. The same year Bhattacharjee et al. [110] included the effects of concentrated and interacting solutes in the convection–diffusion equation via a structure factor for interacting particles. This model allows then a realistic description of the behaviour of concentrated solutions near a membrane. However, all calculations were made for volume fractions at the membrane that were too low to determine critical fouling conditions. More recently, a modified film model with a two dimensional flow (Berman) was published by Bacchin et al. [93] where critical flux is given through Eq. (7) by considering a critical osmotic pressure [109]:

$$J_{crit} = \frac{D_0}{\delta} \int_{\Pi_b^*}^{\Pi_{crit}^*} \frac{K(\phi)}{\phi} d\Pi^* \tag{8}$$

The boundary condition was given by the osmotic pressure at the wall but a criteria for deposition was added giving a cake resistance when a critical osmotic pressure was reached. This model depicts both a critical flux and cake growth at the membrane surface (Fig. 17) and validates the more accurate concept of critical Peclet number [3,95].

It is interesting to note, when assuming that a solute undergoes similar interaction with a wall rather than with counter-ions (i.e. small charged solutes), that a simplified convection–diffusion–electrophoretic migration model can be developed (Rabiller-Baudry et al. [111]) where the electrophoretic migration is directly given by the electrostatic potential of the wall. If the boundary layer thickness is thick compared
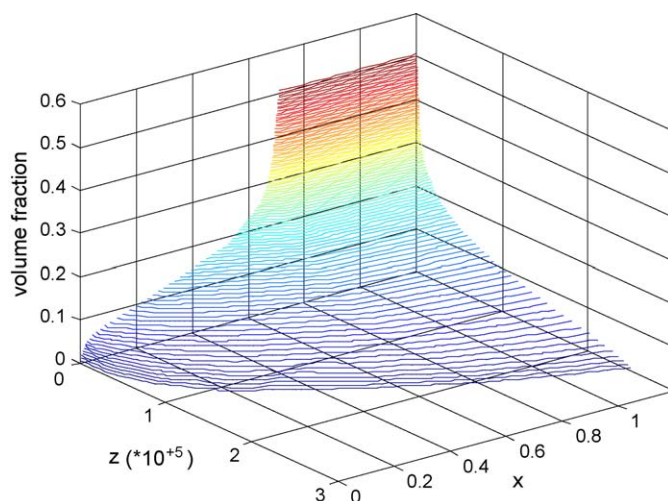

Fig. 17. Modelling of the colloid volume fraction near the membrane surface (at $z=0$) and along the membrane channel (entrance at $x=0$). A deposit forms at a critical volume fraction (around 0.5). For a flux above the critical flux, a zone of the membrane surface located at the outlet of the membrane channel is covered by the deposit [93].

to the Debye length, it is interesting to note that the solution is a relationship whereby the steady state flux is given by the classical film model to which an extra term, accounting for the electrostatic contribution, has been added:

$$J_{ss} = \frac{D_0}{\delta} \ln\left(\frac{c_m}{c_b}\right) + \frac{m_i \zeta}{\delta} \tag{9}$$

where m_i is ψ the electrophoretic mobility of the charged solute and ζ is the zeta potential of the membrane. These simplified theoretical developments shows that the steady state flux for macromolecules or colloids can then be depicted with a classical film model (Eq. (2) in Table 2) where surface interaction are accounted via an additional term (as in Eqs. (5) and (9)) or via an integral (Eq. (7)).

5.2. Force equilibrium and Lagrangian approaches

Fouling can also be described through a mechanical approach based on a force balance on a particle. Petsev et al. [112] published in 1993 a theoretical model based on a force equilibrium accounting for the surface interaction force acting on a particle in a body-centred cubic or hexagonal geometry. By balancing this force with the permeate drag force and a thermodynamic force to account for diffusion, a dead end filtration law allows one to define the concentration profile above the membrane. A critical time is introduced to define the moment at which coagulation occurs on the membrane: "the hydrodynamic drag force, ..., tends to compress the particle layer, so that again at a given moment coagulation can occur". In 1994, Palecek and Zydney [113] developed a simplified equilibrium between the drag force on the proteins associated with the filtrate flow and the intermolecular repulsive interactions between the proteins in the bulk solution and those in the protein deposit on the surface of the membrane. This work was compared to experimental results of steady state flux obtained when filtering protein at pH's away

from the isoelectric point. However, this model needs to include an assumption on the distance between the protein and the membrane to estimate the limiting permeate flux. Harmant and Aimar [114,92] developed a model based on the construction of layers of particles during dead end filtration. These constructions respect the balance between convective, diffusive and surface interaction forces estimated in a hexagonal geometry. It was shown that above a critical filtered volume, the sum of the drag force exerted on the accumulated layer lead to the coagulation of the first layer at the membrane surface.

In 1999, Bowen et al. [115,108] and later [116] proposed a 2-D model using a finite element approach to calculate the force between a spherical colloidal particle and a cylindrical membrane pore accounting for the hydrodynamic force (resulting from permeation but not that from cross-flow) and surface interactions. They found that a potential barrier exists at the pore entrance preventing a particle from entering the pore. Critical values of pressure gradients across the membrane pore were then been calculated. Kim and Zydney [117] developed similar modelling but accounted for Brownian diffusion. Small differences are in the pore geometry (slit-shaped pore versus cylindrical pore) and in the calculation procedures. A "critical filtration velocity" (similar to the critical flux concept) was found (Fig. 18) but diffusion and particle–particle interaction were not accounted for. Later when accounting for the effect of particle–particle interactions, Kim and Zydney [118] showed that inter-particle forces can push the particle over the energy barrier and then significantly reduce the magnitude of the critical filtration velocity required for particle transmission into the pore.

5.3. Deposition rate modelling

Another kind of model is based on the writing of the total mass flux continuity (with convective, diffusive and interactive mass flux as discussed in Section 5.1) and using a boundary
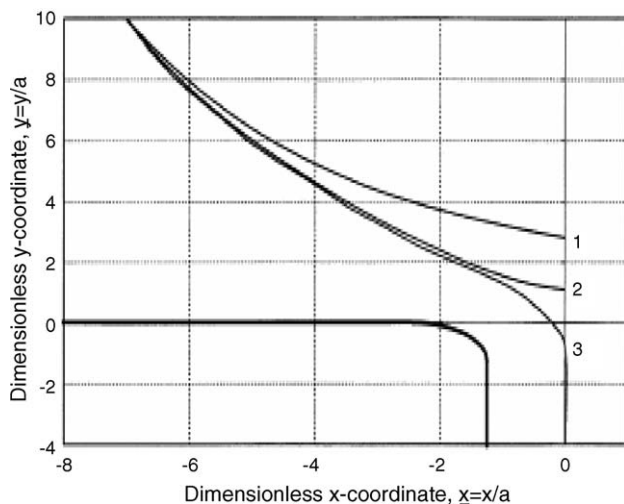

Fig. 18. Effect of filtration velocity on the particle trajectories for charged colloids: (1) $V_f = 0.001$ m/s, (2) $V_f = 0.01$ m/s and (3) $V_f = 0.05$ m/s. Filtration conditions (3) is above the critical flux [117]. Reproduced with permission from A.L. Zydney.

condition of perfect sink on the solid surface (nil concentration at the interface). The basic assumption is that all particles arriving at the collector surface are irreversibly and quickly captured and disappear from the system. Such a boundary condition originally applied by Smoluchowski [119] to describe fast coagulation and later used for determination of the stability ratio by Verwey and Overbeek [120] is often used to solve deposition problems (Adamczyk et al. [121]). These kind of models differ from models based upon steady state mass balance (Section 5.1), wherein the mass flux is nil, in the way they can describe the variation of the mass transfer (the deposition rate) versus operating conditions.

Such a model has been developed [3] to describe the deposition problem during ultrafiltration fouling. This approach allows determination of the operating conditions promoting deposition on the one hand and no fouling on the other. Operating conditions are described through a Peclet number combining in one expression both the effect of permeate flux and cross-flow velocity (through the boundary layer thickness), and in a second expression the stability of the suspension. A critical Peclet number is then defined to border the fouling and no fouling zones:

$$Pe_{crit} = \frac{J_{crit}\delta}{D_0} = \ln\left(\frac{V_B}{\delta}\right) \qquad (10)$$

where J_{crit} is the critical flux, D_0 the diffusivity at infinite dilution of the suspension, δ the boundary layer thickness for mass transfer induced by the cross-flow velocity and V_B is the potential barrier due to repulsive interaction which can be link to DLVO theory. This approach with boundary layer assumptions was developed by Song and Elimelech [122] for a channel using a Bermann velocity profile. This paper underlines the important interplay between classical transport phenomena and interaction mechanisms but does not directly comment on critical phenomena for filtration.

5.4. Phase transition

The description of the fouling from preceding approaches always faces the problem of dense suspensions at a membrane surface, which lead to important changes in dispersion properties (variations in transport properties, such as diffusion or viscosity), but also in dispersion structure (ordered and disordered phase) or in state of matter (dispersed, fluid-like phase to solid phase). Early on this was assumed in the famous model proposed by Michaels [12], suggesting that the wall concentration could reach a "gelling" concentration, thus turning the solution into a gel. In the same way, the work by Petsev et al. [112] and Jonsson and Jonsson [109], incorporating surface interactions into the expression of the osmotic pressure versus volume fraction, showed that because of short range van der Waals attraction, the osmotic pressure can reach a maximum for a given value of the volume fraction. Beyond this value, the suspension is not stable anymore (particles attract each other): the osmotic model had gained a maximum concentration, perfectly compatible with the "gel" model. Bowen and Williams [123] facing the problem of the maximum concentration for the viscosity description, suggested using the perturbation theory to account for the

interaction energy between particles. This can lead one to depict transitions between disorder/ordered colloids [108]. An explanation for critical flux based on phase diagrams of suspensions could then be a transition between fluid-like phase (dispersion) and a solid-like phase (deposit) occurring at the membrane (Bacchin and Aimar [124]). This approach still mainly qualitative, but based on well-documented phase behaviour, allows the description of phase changes within the boundary layer. Chen et al. [125] developed a Monte Carlo simulation of dead-end filtration to investigate the influences of permeation flux as well as inter-particle interactions on the volume fraction of the particle deposit. From their simulations, the authors identified three possible criteria for phase transition: weak form of the critical flux, particle contact and irreversible adhesion of particle. All of these works link the critical flux to a critical transition of the system (called spinodal decomposition by a physicist) and so give a semantic argument to justify the adjective "critical". Such approaches to phase transition are a challenge in membrane science as these considerations are both useful in membrane formation (in polymeric membrane formation by phase inversion) and a problem during membrane application (as seen above with fouling). However, it is an incredibly complex area (see, for example, ref. [107]) because a phase transition in a real chemical system has its own kinetics, which may be fast or slow at the time scale of the operator [23]. Depending on the magnitude of this time scale, some phase transitions can be experimentally observed here and ignored there: this issue, which is more important for the experimental study of critical flux, is commented in Section 3. But, theoretical models should also consider the kinetic aspects of phase transition (which has been theoretically developed in 2001 through the jamming phase concept Trappe et al. [126]) in order to develop tools, which can account for the effect of time scale on the transition process.

5.5. Models analysis

These different studies have lead to important progress in the consideration of a new transport phenomenon to explain fouling in membrane processes: namely surface interaction. Today this has to be considered as important as molecular diffusion, shear induced diffusion and lateral migration. It is interesting to note that even very different modelling approaches (mass balance, force model or deposition rate) have lead to similar descriptions of critical conditions for filtration—the aggregation of the colloidal suspension at the membrane (Table 7). Physically, the critical flux can then be linked to the permeate flux and the respective drag force needed to overcome the repulsive barrier generated by interactions existing between colloidal particles. Above this critical value of the permeate flux, aggregation occurs in the suspension close to the membrane surface leading to a multi-layer deposit. The term critical has a scientific "semantic" significance here: critical is already used when surface interaction controls an aggregation phenomena – critical concentration for coagulation – [119] or for the critical deposition concentration Van de Ven [127] for the deposition kinetics on a collector. In these area, the term "critical"

corresponds to the fact that the system shifts from repulsive interaction between particles (dispersed matter—stable state) to attractive interaction (aggregate—unstable state) when a critical electrolyte concentration is reached. In the same way, the critical flux represent the flux above which the accumulated mass at the membrane shifts from repulsive interaction (dispersed matter—polarised layer) to attractive interaction (condensed matter—deposit) [124]—the matter undergoes a phase transition Section 5.4.

At this point, it is important to have in mind that critical flux can be seen similarly:

- As a permeate flux inducing the concentration at the membrane to reach a critical concentration leading to a phase transition.
- As a permeate drag force overcoming the dispersive forces (because of colloidal or hydrodynamic interaction) between particles.

Thermodynamic and mechanistic approaches both underline the critical flux demonstrating then the specificity of the filtration of colloidal dispersions; it raises interest for modelling in this area (Section 5): just a small variation in operating conditions (particle size or surface charge, pH, ionic strength, concentration, pressure, cross-flow velocity, permeation rate, etc.) induces important changes in the working point and so in the way the process has to be operated.

The concept of critical flux is sometimes used for larger particles (around 10 μm) that are large relative to colloidal suspensions. However, the mechanisms responsible for this phenomena are then essentially shear induced diffusion or lateral migration as predicted by comparison of the effect of various transport phenomena on the critical flux (Table 2; Fig. 2).

Experimental results of critical flux observed by direct observation of mass accumulation through the membrane for latex particles and yeast cells (size superior to 3 μm) [11] were compared to calculation of shear induced diffusion and showed good agreement for larger particles (6 and 12 μm). However, for 3 μm, the experimental critical flux was well above the one calculated. This difference can be explained by surface interaction, which can generate for colloidal suspension a higher flux than those calculated using classical models (diffusion, shear induced diffusion and lateral migration) as seen in Fig. 2. These results confirm the fact that in moving from 1 to 10 μm the main phenomena for particle transport shifts from surface interactions to hydrodynamic causes.

The strength of the surface interaction models is their ability to explain the effect of suspensions properties, such as pH or ionic strength, which take a role in determining particle interaction and so control the formation of fouling layers. Critical operating conditions can then be theoretically deduced from physico-chemical properties of suspension. Their main weakness is the new degree of complexity and the inability to provide direct predictions (above all for complex fluids) from microscopic properties of the suspension (size, zeta, ionic strength, ...). One of the causes of this weakness and discrepancy between predictions and observations is that the

Table 7
Different models used to describe the effect of surface interactions on fouling

Authors	Type	Transport phenomena					Main assumptions	Explication for critical conditions
		Diffusion	Interaction induced diffusion	Surface interaction	Convection	Cross-flow		
McDonogh et al. [15]	Mass balance	$-D\nabla c$		$-\frac{D}{kT}c\nabla V$	$+Jc$	Boundary layer assum.	Wall concentration	No
Petsev et al. [112]	Force equilibrium		Interaction induced force		$+F_{conv}$		Dead end filtration	Critical time for dead end filtration
Palecek and Zydney [113]	Force equilibrium			$+F_{int}$	$+F_{conv}$		Wall volume fraction Interactive force calculated at a given distance to the interface Absence of cross-flow force	No
Bacchin et al. [3]	Deposition	$-D\nabla c$		$-\frac{D}{kT}c\nabla V$	$+Jc$	Boundary layer assum.	Perfect sink	Critical flux
Buffham and Cumming [101]	Mass balance	$-D\nabla c$		$-\frac{D}{kT}c\nabla V$	$+Jc$	$+v_{xy}c$	Wall concentration	Metasble equilibrium
Song and Elimelech [122]	Deposition	$-D\nabla c$		$-\frac{D}{kT}c\nabla V$	$+v_{xy}c +$ lift velocity		Perfect sink	No
Jonsson and Jonsson [109]	Mass balance		$-D_c(\phi)\nabla c$		$+Jc$	Boundary layer assum.	Steady state	Operating conditions for critical precipitation concentration
Bowen et al. [18]	Mass balance		$-D_c(\phi)\nabla c$		$+Jc$	$+v_{xy}c$	Permeate flux at the membrane Parabolic concentration profile	No
Harmant and Aimar [114]	Force equilibrium	Diffusive force		$+F_{int}$	$+F_{conv}$	No cross-flow	Dead end filtration	Critical accumulated mass
Bowen et al. [115] Bowen and Sharif [116]	Lagrangian approach			$+F_{int}$	$+F_{hydro}$	2-D	One particle in dead end filtration	Critical pressure gradient and Critical filtration velocity
Bhattacharjee et al. [110]	Mass balance		$-D_c(\phi)\nabla c$		$+Jc$		Multiple interaction and radial distribution function accounted	
Bacchin et al. [93]	Mass balance		$-D_c(\phi)\nabla c$		$+Jc$	$+v_{xy}c$	Steady state	Critical flux
Kim and Zydney [117]	Lagrangian approach	Stochastic force		$+F_{int}$	$+F_{hydro}$	2-D	One particle in dead end filtration	Critical filtration velocity

theoretical description of concentrated soft matter suspensions is not sufficient, today, to be integrated into transport models.

6. Discussion

6.1. The notion of critical fluxes

As noted at the beginning of Section 3.1, the strong form and weak form of the critical flux, J_{cs} and J_{cw}, must be evaluated via a check on whether or not the overall resistance has remained invariant. Results for J_{cs} could be written as: "Below a value of J^*, within the accuracy of the experimental system and for the length of the experiments, the hypothesis that the overall resistance remained the membrane resistance was not disproved and therefore J^* is taken to be J_{cs}, the critical flux (strong form)." This indicates that J_{cs} is not absolute and more sensitive equipment might give a lower value. One is reminded of the models for Bingham fluids. For such fluids, data can be extrapolated to give an *apparent* yield stress, τ_y but with more sensitive equipment and an appropriate experimental time one can measure a shear rates at stresses below the apparent yield stress. Thus, τ_y, like J_{cs}, is indicative of behaviour and useful for modelling over certain ranges. J_{cs} is, inter alia, a function of the mass transfer coefficient at the membrane surface.

The critical flux for irreversibility, J_{ci}, needs a sophisticated approach as mentioned in Section 3.1.2. It was linked to a critical Peclet number in Section 4.2.2, 5.1 and 5.3 since it is the balance between convection and diffusion, which leads to a critical concentration. This approach is mainly applied to depict filtration of colloidal dispersions but can also be linked to solubility limits thus leading to the application of the critical flux concept in reverse osmosis [39,40,96], Schwinge et al. [128]. So whilst one could argue that for reverse osmosis and ultrafiltration of colloidal suspensions that the critical fundamental factor is a concentration, this is not the case with particulate systems. For these, critical shear stresses have been measured. Also from a design point-of-view, flux is a directly controlled variable or a variable indirectly controlled via TMP. Thus it is useful to retain the notion that there is a critical flux.

In doing so, we must avoid following Humpty–Dumpty and seek to grasp the precision of definition required by Baker (Section 1). Henry Brooks Adams noted that 'words are slippery and thought is viscous' so this is not an easy task. Regarding the three forms of critical flux, communication will be helped by more precision about what is measured and the evaluation of overall resistance. Conceptually, J_{ci}, has a firm scientific base but the strong form and weak form of the critical flux, J_{cs} and J_{cw} should be viewed as technologically useful constructs. Much of the literature on limiting flux can be viewed in the same way.

6.2. Measuring critical fluxes

Progress in measurement could come from the development of miniaturised and standardised filtration procedures with automated flux or pressure stepping allowing a continuous determi-

nation of the degree of irreversibility of the fouling. In this way, it will be possible to achieve accurate determination allowing, for a given suspension, to discriminate between membranes and to have a value, which can be a parameter of importance for a process development. In Section 3.1.2, disappointment was expressed that there is a factor of two difference between the critical fluxes obtained by mass balance (Section 3.3) and those obtained by analysing results of a flux step method. At this point, we are not withdrawing the observation that there is a need for improved techniques (and clearer definitions) but membranologists should remember that the critical Reynolds number for pipe flow (the value of which indicates the transition from laminar to turbulent flow) is generally quoted as having a range, mainly because inlet conditions are important. For example, Schetz and Fuhs [129], label 2000–4000 as being the range for transition flow. When critical Peclet numbers for the same solutions/suspensions but different equipment are compared, modest differences are to be expected.

Timescales of measurement are important if the suspension coagulates slowly. In the area of rheology, there is a very useful dimensionless number, the Deborah number defined by Reiner [130] in 1964. Formally, it is defined as the ratio of a relaxation time, characterizing the intrinsic fluidity of a material, and the characteristic time scale of an experiment (or a computer simulation) probing the response of the material. The smaller the Deborah number, the more fluid the material appears. The Deborah number was so named because in the Bible (Judges 5:5) it is recorded that the prophetess Deborah said "The mountains flowed before the Lord", i.e. on a geological or divine timescale substantial movement (flow) of mountains would be observable but for man, in his relatively short lifetime, such movement is not detectable. The relative length of timescales is important and it is timely for the membrane community to define a modified Deborah number for colloidal stability:

$$D_m = \frac{\text{time for coagulation on the membrane}}{\text{time of observation/operation}} \tag{11}$$

For particulate systems, this number will approach infinity both in the laboratory and in practise. But for colloidal systems, the value may well change with concentration polarisation, and for a given *Pe* number, could be above one in the laboratory but below one in industrial practise [23]. Consideration of D_m values would probably help to explain the sudden rise in pressure after relatively long duration filtration that has been found in a range of systems: with protein [51], bioreactor sludge [35,80] and lactic acid fermentation broth [76].

6.3. Sustainable flux

Operation at sub-critical fluxes can be used to control membrane fouling. The original definition of the critical flux stated that operation was sub-critical if no or negligible fouling occurred. Over time there has been a relaxing of the criteria and many now consider a low rather than zero rate of fouling to be indicative of sub-critical operation especially when dealing with complex feeds. The designation "nominally sub-critical" would be more accurate. With many systems the notion of oper-
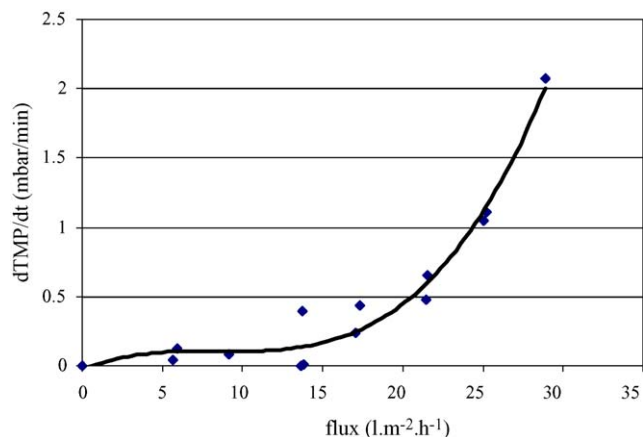
Fig. 19. Illustration of the effect of flux upon the rate of fouling. Data is taken from an updated cone-and-plate rig similar to that described elsewhere [131]. Trendline add to emphasise that the distinction to be considered is between a low fouling rate and a higher fouling rate and is *not* between no fouling and fouling.

ating at a zero fouling condition is simply not feasible but the rate of fouling (which is the rate of TMP rise if operating at constant flux) is very dependent on the flux. As mentioned in Section 3.4, useful results can be found by examining the *rate* of fouling. Significant differences above and below clearly defined fluxes have been found. These points of change are significant and relate to the operational and economic sustainability of a membrane process but they are not critical fluxes as defined above. It is appropriate that a new term has emerged, namely the sustainable flux J_{sus}. As this seeks to distinguish between low and higher fouling rates, its value is somewhat subjective. Just as it is more accurate to speak of *apparent* yield stresses, it might be more accurate to speak of *apparent sustainable flux*, J_{susA}, especially if such values are extracted from laboratory data as shown in Fig. 19 (Hughes and Field [131]).

It has to be noted that the criteria for a sustainable fouling rate is also dependent on the application field in which the filtration is performed. Thus, the criteria must be adapted to the duration of filtration, which differ greatly according to the application. A small fouling rate can be tolerated or even non-detectable when operating at a small time scale whereas it becomes unacceptable (and therefore unsustainable) for long filtration times. When the time for colloidal stability as a function of *Pe* number (and hence flux) can be defined (and if the deposition of the colloidal matter is the limiting factor), then we have a clear scientific definition of the sustainable flux *given a time of operation*. The *sustainable flux based on colloidal stability*, J_{susD}, is that which equates to a modified Deborah number (Eq. (11)) of one. The use of steady state data at constant TMP may not be the best approach for scaling up if one follows the critical flux/sustainable flux philosophy. In this case, one operates at an acceptable fouling rate between cleans. This allows a higher permeability to be used throughout the run. Operation of most large plants is controlled by the required flux and limited by the available pressure. Data, such as that in Fig. 19 can indicate a likely upper limit for a sustainable flux. However, the ideal would be to assess colloidal stability, if colloids are the limiting factor.

Howell [2] has noted that it is sometimes not appropriate to operate below the critical flux of substance A (e.g. yeast) because there could still be deposition of substance B (e.g. molasses particles), which has a much higher fouling effect. The yeast when they are deposited act as a filter aid. This example illustrates that the sustainable flux for a system can be at a higher flux than the critical flux of one of the components. In a recent paper, Hughes and Field [131] have drawn a distinction between the *filter-aid* situation, where cells can act as a secondary membrane (and are beneficial to filtration performance by screening out material that would otherwise have a high fouling impact at the membrane surface) and the *over-clogging* situation. In the second situation, the interstices of the cake of cells become clogged with either fine particles or soluble components and this detrimental effect on performance, as measured by rate of TMP rise, is more severe than that which would occur if the components had unhindered access to the membrane. In the latter case, the sustainable flux for the system is very likely to be below the critical flux of the cells.

6.4. Development of sustainable membrane technology

With regard to industrial processes the development of sub-critical membrane processes has lead to a reduction in energy consumption but there is a need for larger membrane surface area. So the decrease in running costs is partially off-set by increased investment cost. Ideally, there is the opportunity for "sub-critical" operation. Achieving or approaching such conditions has good prospects because of three advantages. Firstly, it is environmentally beneficial; there is lower energy consumption and less usage of chemical agents and therefore the operation is more environmentally friendly. Secondly, it is technically sound; sub-critical conditions yield a clean way of operation that can be more easily controlled. Ideally, it allows one to work with a membrane that is not covered by fouling multi-layers, which drastically change the selectivity efficiency. Lastly, it is economically attractive; with membrane costs decreasing sub-critical membrane operation or near sub-critical operation will be attractive to both operators of membrane processes and suppliers who will increase sales volume (Fane et al. [132]). A paper on water treatment presented at ICOM 2005 indicated that the option that had least environmental impact operated at very low fluxes; significantly lower than current industrial practise. Thus, the pressure from society will be in this direction.

6.5. Development of high separation membrane technology

The critical flux concept is of importance when a high degree of separation is required. Below the critical flux, no multi-layer deposit cover the membrane surface and then the selectivity of the process is always control by the membrane. Above the critical flux, a deposit can act as a new separator leading to a change in selectivity (Section 3.5). High separation membrane technology shows interesting perspectives in biotechnology and biogenetics applications. Such processes will have to run under critical filtration conditions in order to keep the original separative quality of the membrane.

7. Conclusions

The critical flux concept has evolved in its first 10 years of existence.

1. Critical flux definitions have been refined and there is now a family of critical fluxes. To the original forms, defined herein as J_{cs} and J_{cw}, one should add J_{ci}, the critical flux for irreversibility. The latter has a clear link, for colloidal systems, to a physical phase transition. As noted at the beginning of Section 3.1 the strong form and weak form of the critical flux, J_{cs} and J_{cw}, must be evaluated via a check on whether or not the overall resistance has remained invariant.
2. Experimental measurements of critical flux have been made with different methods and on various fluids. Numerous experimental works generally allow one to depict the effect of the three data sets that determine the efficiency of a membrane separation: membrane properties, process conditions and fluid properties. It is clear that critical flux determination can be useful when optimising operating conditions. The critical flux concept has been applied to complex fluids of relevance in numerous application domains. Examples given in Section 3 include: biotechnology—fermentation broth; waste water treatment—pulp and paper mill, bioreactors sludge; the food industry—baker's yeast, skimmed milk.
3. The critical flux concept has acquired a theoretical sound scientific basis. The physical basis for the critical flux for irreversibility is, at a fundamental level, a critical concentration that arises from a balance between convection and diffusion. On a theoretical hand, surface interaction relative to colloidal suspension has been proposed as the main factor responsible for the existence of a critical flux. Thus, at a scientific level it will be conceptually useful to address the data in terms of critical Peclet numbers. With regard to measurement, it is essential to evaluate whether there has been hysterisis and also to consider that some colloidal coagulation can be experienced at interfaces during the longer times of observation (namely during plant operation) whereas there are too slow to be observed in labs experiments.
4. The critical flux framework can guide a consideration of sustainable conditions. Critical flux filtration has given scientific arguments to process filtration at low flux "low pressure ultrafiltration and nanofiltration". For design purposes, it is useful to retain the notion of a straight forward critical flux, particularly for particulate systems, as this sets the ideal standard to be striven for where this is feasible. However, especially for complex mixtures, the concept of a sustainable flux is useful because this recognises that often only low fouling (and not "no" fouling) is achievable.

Acknowledgements

Appendix A

If one refers to (or indeed prefers) the widely used "resistance-in-series" model the various fouling situations can be described in a way that is different from that used in Section 2. Generally, a reduction in flux (or increase in pressure) for constant pressure (flux) operation is linked to a filtration law, which can be seen as an integral form of the Darcy law in which different fouling mechanisms operate.

$$J = \frac{\Delta P - \Delta \Pi}{\mu(R_m + R_{ads} + R_{rev} + R_{irrev})} \quad \text{(A.1)}$$

An osmotic pressure term, $\Delta \Pi$, reduces the efficiency of the transmembrane pressure. Furthermore, hydraulic resistances are added to the membrane resistance because of:

- Surface or pore adsorption, R_{ads} (independent of solvent transfer).
- A fouling resistance driven by the filtered volume being reversible (e.g. possibly pore blinding or cake deposit), R_{rev}, or irreversible (possibly cake deposit or gel formation), R_{irrev}.

This classification allows one to distinguish additional resistances (such as adsorption) that are independent of the pressure and permeate flux from fouling phenomena driven by the solvent transfer through the membrane. Fouling of the latter type can be reversible (R_{rev}) or irreversible (R_{irrev}) when the pressure is decreased.

When considering these fouling mechanisms, the *strong form of critical flux*, J_{cs}, has been developed to discriminate no fouling conditions (where R_m is the only resistance in Eq. (A.1)) from fouling conditions where other resistances also apply. It has been defined as the flux at which the flux–transmembrane pressure (TMP) curve starts to deviate from linearity (Fig. 4). So with the assumption that osmotic pressure effects are negligible

$$\text{for } J < J_{cs} : J = \frac{\Delta P}{\mu R_m}$$
$$\text{for } J > J_{cs} : J = \frac{\Delta P}{\mu(R_m + (R_{rev} + R_{irrev}))} \quad \text{(A.2)}$$

where at least one of R_{rev} or R_{irrev} is non-zero and when R_{ads} is considered as negligible.

The *weak form of critical flux*, J_{cw}, has been used to distinguish operation below and above the point at which the performance is influenced by fouling phenomena that are driven by the solvent transfer through the membrane. Initially, the additional term was applied only to adsorption occurring at the outset of filtration [1]. Later a distinction was made by ref. [6] between very low fouling conditions and more significant ones, with this intermediate region being between, J_{cs} and J_{cw}. However, in this review the former definition is retained.

$$\text{for } J < J_{cw} : J = \frac{\Delta P}{\mu(R_m + R_{ads})}$$
$$\text{for } J > J_{cw} : J = \frac{\Delta P}{\mu(R_m + R_{ads} + R_{rev} + R_{irrev})} \quad \text{(A.3)}$$

where at least one of R_{rev} or R_{irrev} is non-zero.

We now define a new term "*critical flux for irreversibility*", J_{ci}, to discriminate fouling with respect to its irreversibility. Above the critical flux for irreversibility, there are growing multi-layers of irreversible fouling in the boundary layer whereas below it only a concentration polarisation layer exists in all cases with an additional monolayer of adsorbed species in some cases. When filtering macromolecules or colloidal dispersion, this critical flux is related to the coagulation of the dispersed phase close to the membrane surface, followed by deposition upon it. Accumulated matter at the membrane undergoes a phase transition from a dispersed phase (concentration polarisation) to a condensed phase (multi-layer deposit).

The irreversibility form of the critical flux can be defined by:

$$\text{for } J < J_{ci} : J = \frac{\Delta P - \Delta \Pi}{\mu(R_m + R_{ads} + R_{rev})}$$
$$\text{for } J > J_{ci} : J = \frac{\Delta P - \Delta \Pi}{\mu(R_m + R_{ads} + R_{rev} + R_{irrev})} \qquad \text{(A.4)}$$

where R_{ads} might include in-pore fouling or monolayer adsorption.

There is a theoretical foundation for the critical flux for irreversibility in the work of Bacchin et al. [3] accounting for colloidal surface interaction. This approach can also be found in the experimental analysis of Defrance and Jaffrin [9,78] who defined the "critical" flux as the flux below which the TMP remains stable and fouling is reversible. These authors say that before this flux fouling is due to pore plugging and adsorption but when it was exceeded TMP increased and did not stabilise due to cake formation at the surface.

Although the concept of critical flux was originally postulated as a method of avoiding fouling it is now seen by many as a concept related to the minimisation of fouling. Thus, the useful concept of *sustainable flux* has recently evolved especially in the context of membrane engineering. Whilst having links with the concept of critical flux, a sustainable flux itself is not a critical flux. For mixtures (and this includes most industrial process streams), the concept of a sustainable flux is useful; above a certain key flux (dependent on hydrodynamics, feed conditions and process time) the *rate* of fouling is unsustainable. If there is a clear discontinuity in the rate of fouling as a function of flux then this point is very important from a practical point of view.

Three different definitions of critical flux were used above and these are summarised in Table 3. They relate to different patterns of flux–TMP-fouling behaviour. Various inter-relationships exist between the terms. For example, when adsorption and osmotic pressure phenomena are insignificant and the fouling resistance is purely irreversible, then the strong form of critical flux and the critical flux for irreversibility are exactly the same (Fig. 4a). Secondly, if adsorption (or other fouling phenomena independent of pressure) occurs but there is no osmotic effect then the weak form of critical flux and the critical flux for irreversibility are exactly the same (Fig. 4b). In those cases, where osmotic pressure cannot be neglected (e.g. colloidal and macromolecular filtration, Fig. 4c) then the critical flux for irreversibility is the only definition that is theoretically sound because a deviation from linearity might be the consequence of

the osmotic pressure (which is a reversible phenomena). The irreversibility can be shown by hysteresis in the flux–pressure relationship as flux is increased and decreased [6].

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