



Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <http://oatao.univ-toulouse.fr/>
Eprints ID: 4054

To link to this article: DOI:10.1016/j.memsci.2010.05.001
URL: <http://dx.doi.org/10.1016/j.memsci.2010.05.001>

To cite this version: Aimar, Pierre and Bacchin, Patrice (2010) *Slow colloidal aggregation and membrane fouling*. Journal of Membrane Science, vol. 360 (n° 1-2). pp. 70-76. ISSN 0376-7388

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@inp-toulouse.fr

Slow colloidal aggregation and membrane fouling

Pierre Aimar^{a,b,*}, Patrice Bacchin^{a,b}

^a Université de Toulouse, INPT, UPS, Laboratoire de Génie Chimique, 118 Route de Narbonne, F-31062 Toulouse, France

^b CNRS, Laboratoire de Génie Chimique, F-31062 Toulouse, France

A B S T R A C T

We observed that the concept of critical flux, although established on physical bases, does not describe all typical fouling situations found in membrane filtration. We especially focus on the slow flux decline that is observed in many industrial membrane applications, and that has found several types of explanations that we briefly discuss. In order to get a better understanding of this situation, we have considered the orders of magnitude of the slow aggregation kinetics that are expected to happen within a boundary layer, on an ultrafiltration or microfiltration membrane in operation. The results help to understand that whereas the critical flux is limiting cross-flow filtration of stable colloids, it should be combined to kinetics aspects of slow aggregation in cases of colloids of intermediate stability (metastable). We discuss some consequences on the design and operation of processes using membrane filtration.

Keywords:

Membrane
Fouling
Critical flux
Colloids
Stability
Metastability

1. Introduction

Many models and concepts have been invoked to understand and describe fouling during membrane filtration over the last decade. In most of these models, the rate of membrane fouling is essentially assumed limited by the convective flux of solutes towards the membrane or the filter.

To explain the flux levelling off when the transmembrane pressure difference is increased, both thermodynamic arguments, such as the osmotic pressure counter effect, and those based on mass balance across a layer stagnant over the membrane, such as the gel model [1] or the critical flux model [2] are now quite well accepted by both scientists and engineers. In particular, the transition between a dispersed and a packed phase in the vicinity of the membrane, during filtration has been a subject of theoretical modelling and numerical simulations, such as those by Elimelech and Bhattachajee [3] for hard spheres, or Chen et al. [4] for interacting particles. Solute adsorption is also taken into consideration and experimental evidence of it has been given time ago by different groups [5].

Reviewing some of the very numerous articles dealing with membrane fouling, from nanofiltration to microfiltration, of “model” solutions or of industrial, much more complex fluids, one realises that if the flux decline during the first moments of cross-

flow filtration is a common feature in all situations, the next stage can be very different, depending on a lot of parameters:

- In some very specific cases, after the first flux decline period, the flux becomes absolutely constant, and this can last for hours [6]. This is in general observed with suspensions such as latex of various types, clays, silica particles, titanium oxides, and a few others.
- In other cases, and even with “model” solutions made of only one component dispersed in an appropriate buffer, the flux continuously declines, even at a low rate. For runs carried out in “unfavourable” conditions, this decline may be very rapid, and end up with a disappointing nil flux. In other cases, where the conditions have been more carefully adjusted, the flux decline is slow to very slow, but it still exists (alternatively, at constant flux mode, the transmembrane pressure steadily increases). Examples of such flux drifts are found in membrane filtration of protein solutions, beverages, dairy fluids, fermentation broths, surface waters, etc. [7,8].

Not much progress has been made in the recent years to tackle this problem, which becomes very important as long as an industrial application is concerned and some question the relevance of the concept of critical flux for particular systems [9]. Flux drift has been ascribed to adsorption [10] or to the deposition of some fine particles present in the dispersions and which plug the fouling layers already deposited [11]. Although a fair agreement could be found between phenomenological models and experimental data, fitted values for the adsorption parameters (kinetics and equilib-

* Corresponding author at: CNRS, Laboratoire de Génie Chimique, F-31062 Toulouse, France. Tel.: +33 5 61 55 83 04; fax: +33 5 61 556139.

E-mail address: aimar@chimie.ups-tlse.fr (P. Aimar).

riums) were not consistent with those otherwise experimentally determined. Proper adsorption should be ruled out to explain the long-term flux drift, if we admit that it covers the material surface by a monolayer only. Experimental studies of adsorption on membranes show that it reaches a steady state within a few hours at most. Adsorption inside the porous structure of the membrane can explain long-term fouling, as the access to the inner part of the membrane structure ought to be slower than to the membrane surface. However, this mechanism should be greatly accelerated by convection of solutes through the membrane when it exists (non-fully retentive membranes), whereas a slow flux decline is however also observed with fully retentive membranes, which leaves space for another explanation. Deposition of fine, scarce particles, plugging a cake made of larger particles and built up in the early stages of the process is also one possible explanation for such flux slow decline.

One can take the latter explanation, and it probably stands in several examples as those mentioned earlier in this paper. However, we need to consider that most of the fluids that induce such “slow fouling” are not stable in nature but “metastable”. Under some conditions (shear, T , pH, ionic strength), they may be destabilised and their components then start forming gels or aggregates and their exact properties are very conditions-sensitive. In many practical cases, operators know that processing milk, beer or water that has been stored for various durations, in stirred or unstirred, cooled or not, tanks, may lead to very different results in terms of membrane fouling and process performance [12]: this is ascribed to fluid metastability, that was shown responsible of kinetics boundaries in the composition diagram of colloidal suspensions in drying processes [13]. It is the purpose of this paper to explore the possible role of fluid slow destabilization in membrane fouling. We more particularly address the cases of submicronic particles, colloids, biocolloids and or proteins, which are identified as serious foulants in ultrafiltration and microfiltration. We have tried to understand which link can exist between the local conditions met in the neighbourhood of a membrane and the trend of fouling phenomena. In particular, because the concept of “critical flux” has been based on the colloidal stability of a fluid, we look for a possible link between the critical flux, the subcritical flux mode of operation, and a possible slow flux decline observed in long-term membrane operations. To perform this exploratory work, we used simple models of colloidal stability and membrane boundary layer phenomena (e.g. we do not consider the axial distribution of boundary layer thickness), so as to illustrate trends and orders of magnitude. The quantitative prediction of a particular membrane fouling is, therefore, out of the scope of this paper.

2. Theory

2.1. Fluid stability on a phase diagram

If we accept the idea that once adsorption on a membrane has come to a steady state, the major cause of fouling is the fluid stability in the neighbourhood, it may be useful, at least for a matter of understanding, to use a phase diagram to represent the phenomena we want to study [14]. Such phase diagrams have been drawn for some specific dispersions as in [15], with the ionic strength as an index for the stability (vertical axis in Fig. 1 [15]). Chen et al. [4] have simulated such phase transitions of interacting particles in filtration systems by using a Monte Carlo model. They extensively discussed on the importance of the model chosen to describe the particle to particle interactions. In the present study, we have used the DLVO theory for a qualitative description of the phenomena we want to discuss. We have used the height of the energy barrier as an index of the stability of a colloidal system. Fig. 1 represents some

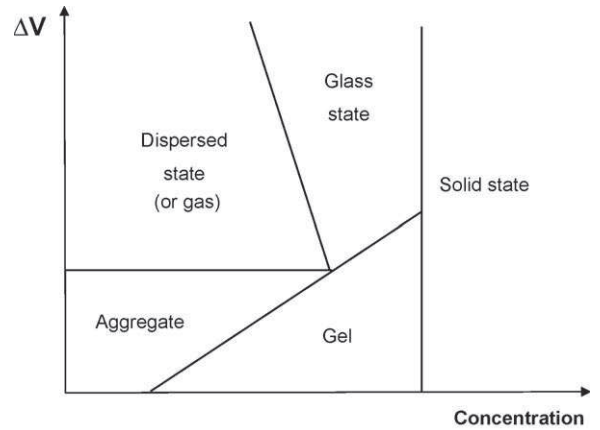


Fig. 1. Simplified phase diagram, adapted from [14]; showing some of the possible states of a colloidal suspension as a function of the stability (Arbitrary unit) and the concentration. The boundaries are as phase transitions, irreversible or very slowly reversible.

of the numerous states under which a colloidal dispersion may be found. A membrane separation operation should be represented on this graph by a line drawn between the initial and the final concentration of the fluid. Although during a membrane separation, one does not expect a phase transition to occur in the bulk solution, we shall see in this article how in some instances the stability of a colloidal dispersion may be challenged and conditions may become such that a phase transition appears, especially at the membrane surface: the solute/suspended matter then forms a new phase on the membrane surface: a “critical” or a “threshold” limit has been passed.

For this purpose, we plot in Fig. 2 the calculated interaction energies calculated using the classical DLVO relationships (detailed in [16]) between either nanoparticles (radius 10 nm) or colloids (100 nm), when dispersed at two low ionic strengths (0.1 mM or 1 mM). We have used on the X-axis the reciprocal of the concentration $1/\Phi$ instead of the normally used distance between surfaces, h , assuming the particles of diameter d are arranged on a cfc array:

$$\Phi = \left(\pi \frac{\sqrt{3}}{8} \right) \left(\frac{d}{d+h} \right)^3 \quad (1)$$

The peak characterises the stability of the suspension, and it is often considered that for peaks higher than 10–15 kT, the suspen-

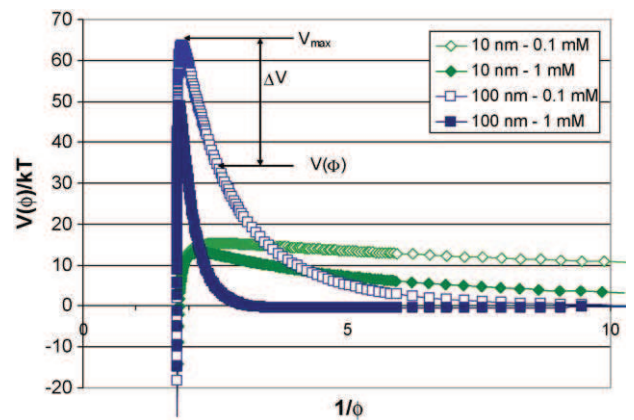


Fig. 2. Interaction energy between two charged spheres (Hamaker constant = 10^{-20} J, particles surface charge: 30 mV) calculated by the DLVO theory as a function of the separation distance here taken as the reciprocal of a volume fraction, assuming a compact hexagonal array. Squares and diamonds correspond to particles of 100 nm and 10 nm, respectively. Open symbols are for solution ionic strength of 0.1 mM in KCl and closed symbols for 1 mM.

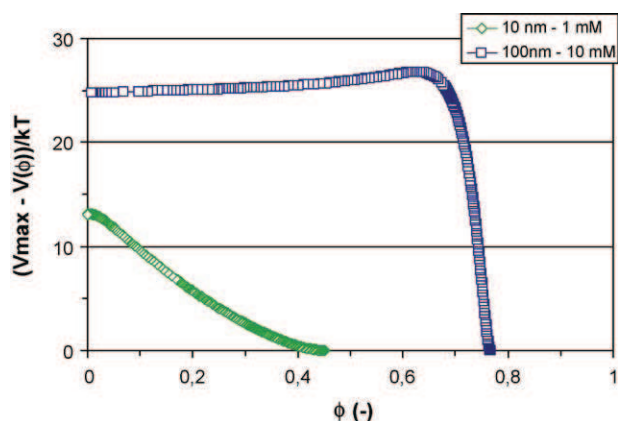


Fig. 3. Plot of the difference between the interaction energy and the maximum of interaction energy, versus the volume fraction. Same data as in Fig. 2. This graph shows that a concentration run (e.g. by ultrafiltration) would be represented in Fig. 1 as a downwards curved line. Squares and diamonds correspond to particles of 100 nm and 10 nm, respectively. Open symbols are for solution ionic strength of 0.1 mM in KCl and closed symbols for 1 mM.

sion is stable (it would not aggregate and settle within a life time), and for peaks smaller than 3 kT, the systems are not stable at all, and particles will rapidly stick to each other and settle. The rate of this latter phenomenon is limited by the diffusion of particles to each other. These classical curves show that when the particles concentration is low, there is no interaction at all, and they behave as independent particles (top left sector in Fig. 1). When the concentration increases (which costs energy) the particles start being interacting with each other. This may correspond to the gas/glass transition in the phase diagram of Fig. 1. We note that the strength of interaction at a given distance changes with the particle size and the ionic strength (and with other parameters not shown here). On each of these curves, one can measure the amount of energy, $V(\phi)$, necessary to provide the system with to concentrate it to a given concentration ϕ and the amount of energy, $V_{\max} - V(\phi)$, that would be necessary to provide to a dispersion at a concentration ϕ so as to reach the peak of energy, V_{\max} , and then aggregate particles to each other. In this paper, we assume that $V_{\max} - V(\phi)$, is a better index of the stability of the suspension than V_{\max} , as V_{\max} does not account for the suspension concentration. According to this assumption, the stability (Y-axis in Fig. 1) can be scaled as $\Delta V = V_{\max} - V(\phi)$. The volume fraction for which V_{\max} has been reached corresponds for sure to a transition. In general, as shown in Fig. 1, when the stability is decreased at constant concentration, the transition may be an aggregation, or a gelation.

In the present model, we can observe that the rate of transition to a gel or aggregates of particles, is limited by diffusion of the particles to each other. We can assume here that the aggregates become rapidly much bigger than the elementary particles, and therefore that they immediately deposit on the filter under the effect of convection (their diffusion coefficient is low) whereas the individual particles would have withstood the permeation drag forces. The conditions [flux, hydrodynamics, ionic strength, etc.] for which the transition occurs at the wall are named "critical conditions".¹

In Fig. 3 we plot the difference, ΔV , between the energy of a pair of particles at a concentration ϕ , and the energy at the critical concentration, i.e. $V_{\max} - V(\phi)$ versus the concentration. One immediately sees that colloids and nanoparticles are characterised by different shapes of curves. Colloidal suspensions seem to remain

¹ The difference between this approach and the one modelled in [2], is that in the latter, we were considering that the most important interactions were those between a single particle and a charged wall (the membrane).

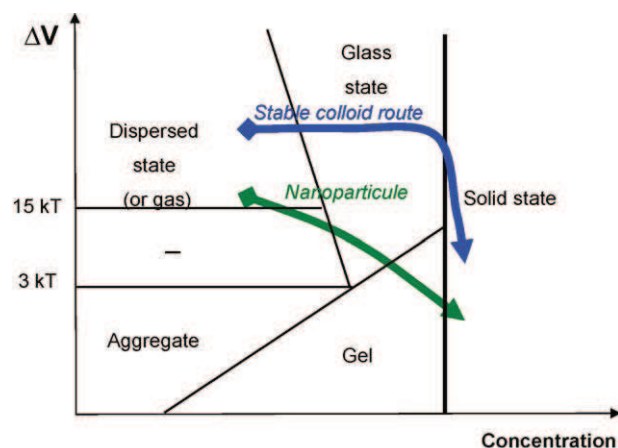


Fig. 4. Examples of routes in the phase diagram that could be taken by stable colloids (100 nm) and nanoparticles (10 nm) during a concentration process. These routes illustrate situations corresponding to interaction energies shown in Fig. 3.

stable ($\Delta V > 10$ kT) over most of the concentration range, when the smaller colloids are characterized by an energy gap smaller than 10 kT for concentrations higher than 10–20%. In a way, the curves shown in Fig. 3 represent the course of the changes in the suspension properties during a concentration process (whether in the bulk or in the boundary layer). Whether the end of these curves hits or not one of the irreversible phase sectors depends on whether we have pushed the system beyond the critical conditions. The "trajectory" of a fluid in this phase diagram will of course change according to the size, charge, initial concentration, pH and ionic strength of the suspension (examples of trajectories in Fig. 4). In Fig. 4 we have added the two stability/instability boundaries, which define a stripe within which a slow aggregation of particles is expected. The curves describing the membrane filtration in the phase diagram cross this stripe in one or another way before they meet the fast aggregation (critical) conditions.

2.2. Critical flux

As mentioned earlier, the critical flux is often defined as corresponding to the conditions for which the critical concentration has been reached in the membrane boundary layer [17]. As shown in Harmant and Aimar [18], this can be viewed as the flux for which the drag force is larger than the thermodynamic forces which keeps the particles apart. Several experimental studies support this definition. We assume that whenever the pressure is such that the flux goes beyond the critical flux, then the solutes/suspended particles form gel beads or aggregates. Such enlarged particles have a lower diffusion coefficient than the original, dispersed ones and they more easily deposit on the membrane. In existing models, this mechanism is generally assumed to be limited by the rate of convection of aggregates to the surface by the filtration flux. This approach predicts a return to a steady state after a rapid flux decline, but it does not predict any further slow flux decline.

3. Results and discussion

3.1. Kinetics of aggregation

We will consider the slow aggregation induced by the compression of particles in the boundary layer as an activated mechanism (Brownian motion helps to overcome the energy barrier). Half of

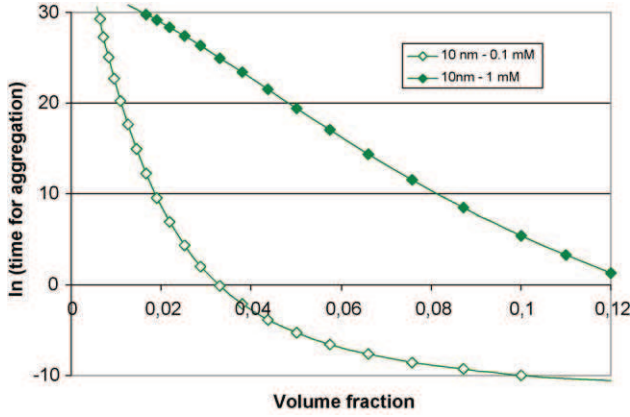


Fig. 5. Average time for aggregation calculated from Eq. (1) as a function of concentration (interaction energy calculated as for in Figs. 2 and 3). We note here that the aggregation time for concentrated suspensions is shorter for dispersions at lower ionic strength. We ascribed this unexpected (counter intuitive) result to the shape of curves in Fig. 2: although higher in potential, energy curves for low ionic strengths are flatter than at higher ionic strength: at intermediate concentration, the capacity of the suspension to resist further compression is low.

the particles have aggregated [19] at time, t_a , defined in Eq. (2):

$$t_a = t_s \exp\left(\frac{V_{\max} - V(\Phi)}{kT}\right) \quad (2)$$

where t_s is the time of aggregation in the absence of repulsion, calculated according to Schmolukovski's model. Finally we should also mention here that various driving coefficients may exist in front of the exponential term in Eq. (2), especially accounting for the relative size of the particle as compared to the width of the energy barrier. We decided to drop this coefficient in a first approximation as it does not alter the order of magnitude of the times we discuss later.

Using equation and experimental characterisation of latex stability by osmotic compression, Bonnet-Gonnet [19] found that experimental aggregation times were under estimated, and her interpretation of this discrepancy was mainly based on the fact that in aggregation by compression, the distance of attraction is found shorter than predicted by theoretical models.

Also the experimental measurement of the exact rate of gelation or aggregation remains quite difficult as mostly based on optical techniques, which are more sensitive to the large aggregates (the size and structure of which can be very much distributed), but do not allow the primary particles counting. Bremer et al. [20] suggest that measuring the critical time for orthokinetic aggregation to become preponderant (or for gelation or sedimentation) provides an interesting, relative parameter, which in turn can be calculated numerically. Similarly, they define a gelation time, as the time for which the gelled colloid occupies the whole experimental volume.

3.2. Time of aggregation

In this first approach we have only considered that the aggregation process, when it exists, is commanded by the wall concentration, although the concentration across the boundary layer is all the way higher than in the bulk, and therefore meant to promote some aggregation. In Fig. 5 we plot the expected time of aggregation computed using Eq. (2), as a function of concentration. One should here note that the DLVO model, on which our model has been based, does not account for the possible hydration of colloids. Accordingly, the actual characteristic time for aggregation or gelation must be larger than what we can calculate from our model. On the other hand, several authors mention the tremendous role of shear stress on the stability conditions of a suspension (Oles [21]).

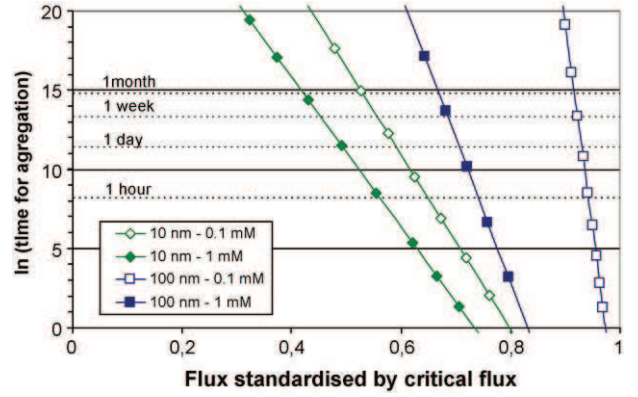


Fig. 6. Example of calculated wall concentration (in volume fraction) as a function of the flux (normalised by the critical flux). We consider here that if the time of aggregation is larger than the process time scale (time of run, time between two cleaning or back flushing procedures, etc.) then the fluid will appear stable to an operator, and fouling induced by fluid destabilization in the boundary layer will not be observed. On the opposite, if the time of aggregation is significantly shorter than the process time scale, then aggregates are expected to form, then to build up on filtration surface.

As mentioned before, the boundary layer is the most prone location for aggregation because of a higher concentration there, but, at least in cross-flow filtration, the suspension is also submitted to shear forces and this should accelerate aggregation especially for the largest particles.

Although the values of the times of aggregation are questionable, one can observe that the larger the particle and the lower the ionic strength, the narrower the range of concentrations for which a phase transition is expected in a reasonable amount of time.

3.3. Time of aggregation and critical flux measurements

This is established that a positive correlation exists between the filtration flux and the wall concentration. In Fig. 6, the time of aggregation is plotted versus the filtration flux, scaled by the corresponding critical fluxes. Calculations were made using the model developed in [16]. The Hamaker constant was taken as 1×10^{-20} J, and the particles zeta potential as -25 mV.

We observe that for a very stable suspension and for a flux smaller than (but close to) the critical flux, the time for aggregation could be extremely long. This means that if we experimentally approach the critical flux by smaller flux values, the suspension should sharply change from a well-dispersed phase into a suspension of aggregates at the wall, when the concentration there becomes very close to the critical concentration. On the other hand, the flux, that was time-independent, would become time dependant and start decreasing. The rate of flux decline then depends on aggregate size, fractal dimension and compressibility. For less stable media (e.g. higher ionic strength or smaller particle), the time of aggregation is shorter even at fluxes significantly lower than the critical flux. Although these are only simulations, this indicates that the experimental measurements of the critical flux would then be not easy if not impossible, as approaching its value would generate in a few minutes, if not less, a production of aggregates which probably would foul the filter, although the critical concentration has not been reached or even approached. The present model then predicts that we should observe membrane fouling for fluxes below the theoretical value of the critical flux for moderate stability of suspensions. In a series of experiments ran with polystyrene latex, Espinasse [22-Figs. VI-4 and VI-5] measured critical fluxes in various conditions, and computed them from the model developed in [16], but with osmotic pressure versus volume fraction curves directly fitted to experimental data of his own. In most cases, the

Table 1

Examples of the various process time scales relevant to membrane applications in various industrial or scientific applications. Figures in the right hand column to be compared to the data in Figs. 4 and 6.

Type of application	Process time scale (orders of magnitude)	Natural logarithm of process time scale in seconds
Laboratory	1 h	8.2
Dairy industry	1 day	11.3
Pharmaceutical/fine chemistry	1 week	13.3
Water production	1 month to 1 year	14.8–17.3
Life support in space shuttles	1 year	17.3
Water production with periodical back flushing/air scouring	5–30 min	5.7–7.5

experimental critical flux was always lower than the computed one. This is not a proof of evidence since other factors may have generated this difference, but the observed trend is consistent with the present model.

One of the first studies published on the dynamics of membrane fouling was the one by Michaels and his co-workers [23]. In that paper [23-Fig. 7], the authors examine the dead-end, unstirred ultrafiltration of bovine serum albumin on various types of ultrafiltration membranes. They found that for experiments run at constant transmembrane pressure, the fouling irreversibility is higher when the pressure is higher. This finding is consistent with a “gel layer” model, not so much with a standard filtration model, as reckoned by the authors. However, we should emphasize here that, as seen in Fig. 5, the higher the applied pressure (or flux) the shorter the aggregation time, and therefore we may assume that what Michaels and co-workers were observing was an increase in the kinetics of aggregation (whether they had reached or not the critical conditions, which is not clear from their paper), and therefore they can have had a larger amount of aggregated proteins at the end of test ran at higher pressure.

For nanoparticles and macromolecules, it seems that even though they are in stable conditions, a continuous aggregation is to be expected, even at fluxes lower than the critical one. This dynamic variation is difficult to account for if one wants to derive the critical flux from measurements made when such particles are present. Therefore, we have to expect some sort of a continuous but slow deposition when filtering solutions containing such small colloids. This should be clearly distinguished from adsorption, which is more dependent on membrane-particle interaction than, as here, on particle to particle interactions. Is it for this reason that the so called “gel concentrations” found from UF experiments rarely match the “solubility limits or gel concentration as determined by light scattering or similar techniques in stirred vessels?”

In the case of mixtures, whether the less stable particles infer their limitation, and in which proportion, is still unknown. A conservative approach suggests that the limitation would come from the less stable class of particles. Removing small or metastable particles is probably the right thing to aim at, but such a pretreatment must carefully avoid to produce unstable particles which would enhance membrane fouling even more than the original ones [24].

Large and medium size particles, if stable, will behave in such a way that the critical flux can be measured experimentally at lab scale, and this should match the values at the different time scales characterising the various industrial applications (Table 1). In the example taken in Fig. 6, we should not observe much flux decline during a period of time shorter than t_a , if a module is operated at a flux lower than J_s . From the point of view of an operator, J_s might be viewed as the larger flux that can be maintained during

the expected period of time between two cleaning in place or back flushing procedures, i.e. a sustainable flux.

As the process time scale changes with the type of application (Table 1) one should expect as many sustainable fluxes as applications for fluids of moderate stability. Another aspect of this observation may be discussed from an engineering point of view. We see from the trend of the curves in Fig. 5 that the “sustainable flux” increases as long as the process time scale decreases, which tends to support the idea that periodically disturbing the boundary layer is not only useful to remove the deposited matter, but also to keep the residence time below the aggregation time. Therefore, periodically backflushing or rinsing a system, pulsating the cross-flow may have this positive effect, not often discussed in the literature, to avoid irreversible deposit formation by slow kinetic processes. Of course this is not the only effect, as particle removing has a positive effect on the next initial permeability of the system. This conclusion for colloidal systems is very similar to the one shown by Gilron et al. [25] on salt precipitation in RO systems. In such systems, some of the salts may be in a supersaturation state, which is a metastable state, characterized by an induction time, which depends on the salt, temperature, presence of other electrolytes or anti scalants. These authors suggest to flush the RO or NF systems at periods shorter than the precipitation induction time, so as to avoid heavy, irreversible scaling in the modules.

3.4. Slow aggregation and shear rate

The situation in a cross-flow boundary layer is specific, since the stability is decreased because the volume fraction increases, and this happens under shear conditions. It is therefore not easy to identify which type of pure transition of the kinds depicted in Fig. 1, occurs in such conditions. One possible model, that we cannot discuss in detail here, maybe the concept of “jamming phases”, discussed for example by Farr and co-workers [26] and made popular by Trappe et al. [27], which assumes that because of lack of thermal energy, of too high concentration, or of too small shear forces to overcome the particle–particle interactions, a suspension can stop flowing and turn into a “jammed phase”. For this reason, we often write “aggregation” or “gelation” in this paper, when we think of this transition, although we know that these words have a specific meaning when in ideal conditions.

Whereas the average residence time of a rejected component in a membrane module can be calculated from the ratio of the dead volume by the cross-flow, velocities in the axial direction (parallel to the membrane) may differ and this introduces a distribution of

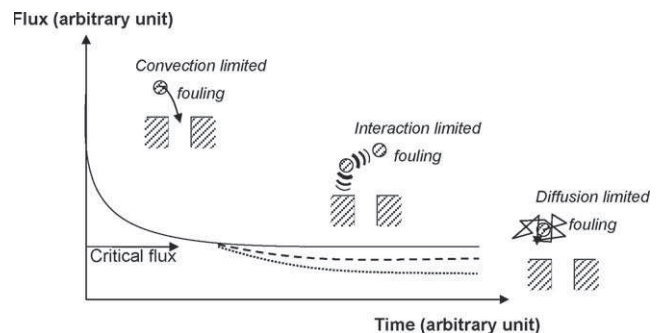


Fig. 7. Schematic representation of flux versus time curves in cases of an ideally stable situation (dotted line) and of metastable dispersions of colloids, in cross-flow suspension. In a first leg, the rate of fouling, and thus of flux decline, is controlled by convection to the membranes, whereas in a second part, the rate of material deposition is limited by the kinetics of aggregation of particles destabilised by the high concentration existing in the boundary layers. Once flux has decreased down to the critical flux value, the flux stability depends on the suspension stability within the membrane modules.

Table 2

Summary of the various fouling limiting phenomena, according to the flux regime. Fouling models here stands for classical pore plugging, cake formation, intermediate pore plugging, etc.

Flux regime	Type of suspension	Deposition rate	Model	Type of deposit
“Very low”	Any	Langmuir adsorption	Darcy	Monolayer
Subcritical	Stable (colloids, low ionic strength)	Almost nil once adsorption is at saturation	Darcy + Osmotic model	Scarce
Subcritical	Metastable (nanoparticles, proteins, low zeta potential, moderate ionic strength)	Limited by rate of aggregation in boundary layer	Slow aggregation Combined to fouling models	Loose, compressible
Critical and beyond critical (limiting flux)	Any	Limited by convection of primary particles (instantaneous aggregation of small, unstable particles or direct deposition of large particles) then limited by rate of aggregation in boundary layer (see Fig. 7)	Convection + slow aggregation combined to fouling models	Dense

residence times, which combines to the fact that the fluid is in a shear flow to create situations that enhance the slow destabilization discussed in this paper.

3.5. Fouling characterisation

The experimental determination of the critical flux has recently been addressed by several groups [28–31]. Most techniques are based on the analysis of the response of a membrane system to stepwise changes in applied transmembrane pressure or controlled flux. The determination of the exact value of the critical flux is however depending on the sensitivity of the measurement devices (flow meters, balance, pressure gauges, etc.), on the impact of such amount of matter deposited on a filter, and also on the way fouling grows along a membrane module. This helps to understand that the exact value of the critical flux may be arbitrary, such as the determination of the time for aggregation or gelation can be [20]. The situation might be summarized as sketched in Fig. 7. During the course of a membrane filtration run at constant pressure, if the initial flux is larger than the critical flux, then fouling occurs by particle deposition at a rate which is controlled by convection through the membrane. Once the critical flux has been reached, this phenomenon stops if the suspension is made of perfectly stable particles or molecules (control by particle–particle interactions). However, in case of metastability, a slow aggregation mechanism is to be expected, producing a membrane fouling limited by diffusion of particles to each other. As the flux decreases, this mechanism is meant to slow down, but this drift depends on particles stability, on residence time and shear rate in the modules: this makes the comparison of data from systems to systems very difficult, and reduces the predictive character of fouling models.

From an application point of view, if a slow aggregation may occur below the critical concentration, then membrane fouling is to be expected. In constant flux operated systems, a decrease in the membrane permeability at some places of a membrane modules has, as a consequence, an increase in flux density anywhere the membrane is still more permeable: more concentration polarisation is to be expected there, generating an acceleration in the aggregation kinetics: this divergent mechanism, mentioned by various authors [32] gives birth to a pressure swing to compensate the gradual fouling of the membrane. The fact that this phenomenon is often observed only after some time lag may be compared to this concept of characteristic time for aggregation: A simple, global way of characterising a set such as (membrane/fluid/operating conditions) might well be to determine the time lag before the pressure flies under such conditions, at each pre-set, constant global flux

value: this time is necessarily linked to the fluid stability in the process condition. Table 2 is an attempt to summarize various situations which can be encountered in practical systems.

3.6. Experimental evidence

We have based this approach on our lab and pilot scale experience, and also after reading many of the numerous papers published on membrane fouling over the recent years. Although this hypothesis of slow aggregation playing an important role in long-term membrane fouling seems very consistent with lab and industrial findings, it is still a challenge for us to design experiments that would clearly confirm or contradict this hypothesis. One possible way of experimentally checking this model was suggested by one of the reviewers of this paper. It would consist of using a field flow fractionation device as described by van de Ven et al. [33], in which suspended particles can be focused in a thin boundary layer next to a porous wall. In such a system, the residence time in the device can be adjusted by controlling the cross-flow. By particle analysis of the effluent, one should be able to measure the proportion of aggregated particles as a function of the residence time.

4. Conclusion

We conclude from this study that the experimental determination of critical flux is theoretically accessible for stable, medium size and large colloidal particles. *The critical flux represents in these conditions a well-marked transition between no fouling and fouling conditions.* Macromolecules and nanoparticles, because they probably slowly aggregate or form gels, will make the measurement of a critical flux difficult and less accurate.

One should expect that nanoparticles slowly form deposits on membrane surface that might be confused with gels, or with adsorption. However the latter is very much dependent on membrane material–solutes interactions, when the aggregation comes from the particle–particle interactions, enhanced by the concentration polarisation and shear forces at the wall. The rather unique condition existing in the boundary layer of a membrane filtration system may turn a stable colloidal dispersion into a metastable one.

Flux decline due to fouling may then successively be controlled by mass transfer through the membrane, then by repulsive interactions between particles, or diffusion to each other.

It appears from this study that the time scale at which the problem of fouling is considered should greatly influence the perception of membrane fouling: In some cases, the translation of laboratory

results to industrial or pilot scale might reveal this. On the other hand, reducing the process time scale of a process by disturbing periodically the membrane surface, by bubble flow, back flushing or any pulsatile flow device is a way to reduce the average residence time in the boundary layer, i.e. reduce the risk of slow aggregation to occur inside the equipment. Consequently this increases the sustainable flux that can be defined then as the flux for which no significant fluid destabilization is to be expected within the process time scale, which differs from one industrial application to another one.

Finally, the possible role of slow aggregation might explain why in so many instances, classical models based on convection limited deposition never properly fit the experimental data of membrane fouling. Designing experiments that would help to demonstrate if this theoretical approach is valid remains a challenge.

References

- [1] W.F. Blatt, A. Dravid, A.S. Michaels, L. Nelson, Solute polarization and cake formation in membrane ultrafiltration: causes consequences and control techniques, in: J.E. Flinn (Ed.), *Membrane Science and Technology*, Plenum Press, New York, NY, 1970, p. 47.
- [2] P. Bacchin, P. Aimar, V. Sanchez, A model for colloidal fouling of membranes, *AIChE J.* 41 (1995) 368–377.
- [3] M. Elimelech, S. Bhattacharjee, A novel approach for modelling concentration polarization in crossflow membrane filtration based on the equivalence of osmotic pressure model and filtration theory, *J. Membr. Sci.* 145 (1998) 223–241.
- [4] J.C. Chen, M. Elimelech, A.S. Kim, Monte Carlo Simulation of colloidal membrane filtration: model development with application to characterization of colloid phase transition, *J. Membr. Sci.* 255 (2005) 291–305.
- [5] P. Aimar, S. Baklouti, V. Sanchez, Membrane-solute interactions: influence on pure solvent transfer during ultrafiltration, *J. Membr. Sci.* 29 (1986) 207–224.
- [6] L. Wang, L. Song, Flux decline in crossflow microfiltration and ultrafiltration: experimental verification of fouling dynamics, *J. Membr. Sci.* 160 (1) (1999) 41–50.
- [7] J.R. Lu, Z.F. Cui, R.K. Thomas, T.J. Su, Fouling of ceramic membranes by albumins under dynamic filtration conditions, *J. Membr. Sci.* 173 (2) (2000) 167–178.
- [8] S. Metsämuuronen, J.A. Howell, M. Nyström, Critical flux in ultrafiltration of myoglobin and baker's yeast, *J. Membr. Sci.* 196 (1) (2002) 13–25.
- [9] J.S. Vrouwenvelder, J.A.M. van Paassen, J.M.C. van Agtmaal, M.C.M. van Loosdrecht, J.C.A. Kruithof, Critical flux to avoid biofouling of spiral wound nanofiltration and reverse osmosis membranes: fact or fiction? *J. Membr. Sci.* 326 (1) (2009) 36–44.
- [10] V. Gekas, P. Aimar, J.P. Lafaille, V. Sanchez, A simulation study of the adsorption-concentration polarisation interplay in protein ultrafiltration, *Chem. Eng. Sci.* 48 (15) (1993) 2753–2765.
- [11] P. Aimar, C. Taddei, J.P. Lafaille, V. Sanchez, Mass transfer limitations during ultrafiltration of cheese whey with inorganic membranes, *J. Membr. Sci.* 38 (3) (1988) 203–221.
- [12] M. Meireles, E. Lavoute, P. Bacchin, Filtration of a bacterial fermentation broth: harvest conditions effects on cake hydraulic resistance, *Bioprocess Biosyst. Eng.* 25 (2003) 309–314.
- [13] M.D. Haw, M. Gillie, W.C.K. Poon, Effects of phase behavior on the drying of colloidal suspensions, *Langmuir* 18 (2002) 1626–1633.
- [14] P. Bacchin, P. Aimar, Critical fouling conditions induced by colloidal surface interaction: from causes to consequences, *Desalination* 175 (1) (2005) 21–27.
- [15] V.L. Alexeev, P. Ilekci, J. Persello, L. Lambard, T. Gulik, B. Cabane, Dispersion of silica particles in surfactant phases, *Langmuir* 12 (10) (1996) 2392–2401.
- [16] P. Bacchin, D. Si-Hassen, V. Starov, M. Clifton, P. Aimar, A unifying model for concentration polarization, gel layer formation and particle deposition in cross flow membrane filtration of colloidal suspensions, *Chem. Eng. Sci.* 57 (2002) 77–91.
- [17] P. Bacchin, P. Aimar, R.W. Field, Critical and sustainable fluxes: theory, experiments and applications, *J. Membr. Sci.* 281 (1–2) (2006) 42–69.
- [18] P. Harmant, P. Aimar, Aggregation of colloids on a porous surface, *AIChE J.* 42 (12) (1996) 3523–3566.
- [19] C. Bonnet-Gonnet, Dégonflement et regonflement osmotiques de dispersions de latex, PhD Dissertation, University Paris VI, 1993.
- [20] L.G.M. Bremer, P. Walstra, T. van Vliet, Estimation of the aggregation time of various colloidal systems, *Colloids Surf. A* 99 (1995) 121–127.
- [21] V. Oles, Shear-induced aggregation and breakup of polystyrene latex particles, *J. Colloid Interface Sci.* 154 (2) (1992) 351–358.
- [22] B. Espinasse, Approche théorique et expérimentale de la filtration tangentielle d colloïdes: flux critique et colmatage, PhD Dissertation, 15/12/2003, Toulouse III University (France).
- [23] H. Reihanian, C.R. Robbertson, A.S. Michaels, Mechanisms of polarization and fouling of ultrafiltration membranes by proteins, *J. Membr. Sci.* 16 (1983) 237–258.
- [24] M. Stoller, A. Chianese, Influence of the adopted pretreatment process on the critical flux value of batch membrane processes, *Ind. Eng. Chem. Res.* 46 (8) (2007) 2249–2253.
- [25] J. Gilron, M. Waisman, N. Daltrophe, N. Pomerantz, M. Milman, I. Ladizhansky, E. Korin, Prevention of precipitation fouling in NF/RO by reverse flow operation, *Desalination* 199 (1–3) (2006) 29–30.
- [26] R.S. Farr, J.R. Melrose, R.C. Ball, Kinetic theory of jamming in hard-sphere startup flows, *Phys. Rev. E* 55 (1997) 7203.
- [27] V. Trappe, V. Prasad, L. Cipelletti, P.N. Segre, D.A. Weitz, Jamming phase diagram for attractive particles, *Nature* 411 (2001) 772–775.
- [28] D. Wu, J.A. Howell, R.W. Field, Critical flux measurement for model colloids, *J. Membr. Sci.* 152 (1) (1999) 89–98.
- [29] P. Le Clech, B. Jefferson, I.S. Chang, S.J. Judd, Critical flux determination by the flux-step method in a submerged membrane bioreactor, *J. Membr. Sci.* 227 (1–2) (2003) 81–93.
- [30] B. Espinasse, P. Bacchin, P. Aimar, On an experimental method to measure critical flux in ultrafiltration, *Desalination* 146 (1–3) (2002) 91–96.
- [31] P. van der Marel, A. Zwijnenburg, A. Kemperman, M. Wessling, H. Temmink, W. van der Meer, An improved flux-step method to determine the critical flux and the critical flux for irreversibility in a membrane bioreactor, *J. Membr. Sci.* 332 (1–2) (2009) 24–29.
- [32] S. Ognier, C. Wisniewski, A. Grasmick, Membrane bioreactor fouling in sub-critical filtration conditions: a local critical flux concept, *J. Membr. Sci.* 229 (1–2) (2004) 171–177.
- [33] W. van de Ven, I. Pünt, A. Kemperman, M. Wessling, Unraveling ultrafiltration of polysaccharides with flow field flow fractionation, *J. Membr. Sci.* 338 (1–2) (2009) 67–74.