Desalination and Water Treatment 8 (2009) 17–23
www.deswater.com
1944-3994/1944-3986

Characterisation of polysaccharide fouling of an ultrafiltration membrane using model solutions

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Received 28 October 2008; accepted 2 July 2009

ABSTRACT

Polysaccharides (PSs) have been identified to cause long term mechanically irreversible fouling in membrane bioreactors, although findings are still contradictory, partly due to the fact that generally lump concentrations are measured. To elucidate contributing factors to the varying fouling propensity of PSs, the influence of the characteristics of the PSs on membrane fouling was studied by comparing the filterability of different solutions of model PSs using the Berlin filtration method (BFM), which uses a novel air-sparged *in situ* filtration test cell. Critical flux measurements were performed with solutions of eight different substances: xanthan gum, alginate, carrageenan, starch, carboxymethylcellulose (CMC), pectin, agarose and heparin, in which pH and conductivity were adjusted at 7.5 and 800 μS/cm, respectively. The protocol used for the critical flux determination included relaxation and, in some cases, irreversible fouling could be detected. No relationship was found between critical flux characteristic of short term mechanically reversible fouling and the following investigated parameters: PS concentration, transparent exopolymer particles (TEP), viscosity and molecular weight (MW) of the PSs. Severe irreversible fouling was found for agarose and carrageenan. Results stress the need a) to be aware of differences in fouling propensity when model PSs are used in fouling investigations and b) not to over-interpret findings based on lump concentrations.

Keywords: Membrane filtration; Fouling; Critical flux; Model polysaccharides

1. Introduction

Fouling is an intrinsic problem associated to all membrane processes. The extent to which fouling can be controlled is proportional to the understanding of the mechanisms that govern this process and the compounds that promote it. Fouling of ultrafiltration (UF) membranes during, e.g., apple juice processing is mainly a consequence of the retention of carbohydrates, polyphenols and/or proteins [1]. In wine treatment, membrane fouling is mainly due to the accumulation of macromolecular or colloidal compounds (such as proteins and polyphenols) [2]. Fouling of UF membranes in milk industries is mostly caused by precipitation of microorganisms, proteins, fats and minerals on the membrane surfaces [3]. When studying the fouling layer built after membrane filtration of beer, Taylor et al. [4] concluded that, for all beers tested, the fouling layer consists of both protein–polyphenol complexes and carbohydrate gels. In membrane bioreactor technology, the complexity of the mixed liquor makes the fouling process still not well understood to date, despite huge R&D efforts. Some authors have pointed at polysaccharides (PS) as one of the major fouling boosters, but results are still contradictory. While Rosenberger et al. [5] found at pilot scale a linear relationship between

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Presented at the First UK–Israeli Workshop and Research Event on the Application of Membrane Technology in Water Treatment and Desalination, 15–20 June 2008, University of Oxford, UK.

daily fouling rates and PS concentration in soluble microbial products (SMP), posterior studies with different operating conditions could not support this finding [6]. ''*PS*'' is a very generic term; they show a broad diversity of nature and properties. Keeping this in mind, besides the influence of ionic strength and pH, one of the reasons for the contradictory results when trying to correlate fouling with total PS concentrations as typically analysed by the phenol-sulphuric assay could be this diversity of nature, some specific PS having greater propensity to foul the membrane than other PS groups. Therefore, a deeper study of the fouling characteristics of different PS should be performed. Some authors have recently related the concentration of a specific group of PS, the transparent exopolymer particles (TEPs) with fouling in MBR systems (as impacting on the monitored critical flux of the system) [7] and in RO systems [8,9] introducing thus novel parameter into membrane fouling investigation. TEP are mainly acid mucopolysaccharides and represent a sticky fraction of the extracellular polymeric substances (EPS). When measuring TEP, only those PSs with carboxyl or sulphated groups will be detected.

Numerous studies have been conducted for the study of PS fouling using model solutions, often using only one compound (mostly sodium alginate) as a model PS [10–13]. In addition, in most of these articles, the experiments were performed using dead-end filtration whereas membrane bioreactor processes operate under quasi cross-flow conditions due to air scouring. It is well known that the fouling mechanisms that occur in dead-end filtration are different from those encountered during cross-flow filtration.

Another important property of the PSs is the gelling capacity, and its relationship with fouling was recently discussed by Wang and Waite [14], who found more severe fouling when filtering the gelling Ca-alginate than when filtering the non-gelling Na-alginate at constant flux. However, the influence of calcium can be positive to a certain extent in the sludge matrix as it was demonstrated by Kim and Jang [15], who operated an MBR under both low and optimum calcium concentrations and found higher filtration resistance when the calcium concentration was low, because of a beneficial influence of the cation on the hydrophobicity of the EPS and an increased flocculation by means calcium bridges. The influence of divalent cations is therefore a complicated issue which goes beyond the scope of this study.

In this study, cross-flow filtration experiments of model solutions of eight different PSs were performed using the Berlin filtration method (BFM). This method uses a flat-sheet filtration test cell which operates under similar hydrodynamic conditions as encountered in a real MBR in order to obtain representative fouling data. The concentrations of PSs as well as transparent TEPs were measured in the eight solutions. These and other properties like gelling properties, viscosity, charge density and molecular weight (MW) were studied in the model solutions in order to find any possible relationship of these parameters and the fouling occurrence in terms of critical flux (J_c).

2. Experimental

2.1. BFM test cell

A scheme of the apparatus and set-up can be seen in Fig. 1. The Berlin filtration method (BFN) uses a UF flat-sheet made of PES (BIO-CEL® by Microdyn-Nadir, Germany, 9 cm × 13 cm, filtration surface 0.025 m^2) with an MWCO of 150 kDa. The whole equipment is designed to be transported to the MBR units to perform *in-situ* measurements. The frame of the membrane module is perforated at the bottom, which provides the module with an integrated aeration via a blower. The permeate side is connected to a pressure transducer so that the evolution of the pressure is monitored continuously during the measurement. The superficial gas velocity applied to the test cell was 0.036 m/s. The spacing between plates was fixed at 7 mm, a common value of spacing between plates in flat sheet MBR modules. In this study, the test cell was introduced into a tank filled with 10 L of PS solution.

2.2. Model solutions

About 10 L solution of 20 mg/L were prepared for every PS, in which the conductivity was adjusted by addition of NaCl at 800 μS/cm, and the pH at 7.5 by adding NaOH or HCl.

All PSs were obtained in powder form. Sodium carboxymethylcellulose, sodium alginate, sodium heparin and agarose were purchased from Carl Roth (Germany). Xanthan gum was obtained from Rodhia (Germany). The other PS tested were Iota carrageenan (Sigma–Aldrich, Germany), pectin (Natura, Germany) and starch (Merck, Germany). The solutions were prepared by stirring in deonized water at room temperature. Agarose and starch had to be dissolved in boiling water and cooled down before use. A brief description of the tested PSs is given in Table 1. As the MW was not measured, the values of the MWs presented in the table are only approximate values. These values and the information about the gelling properties from the table were obtained from manufacturers and general resources.

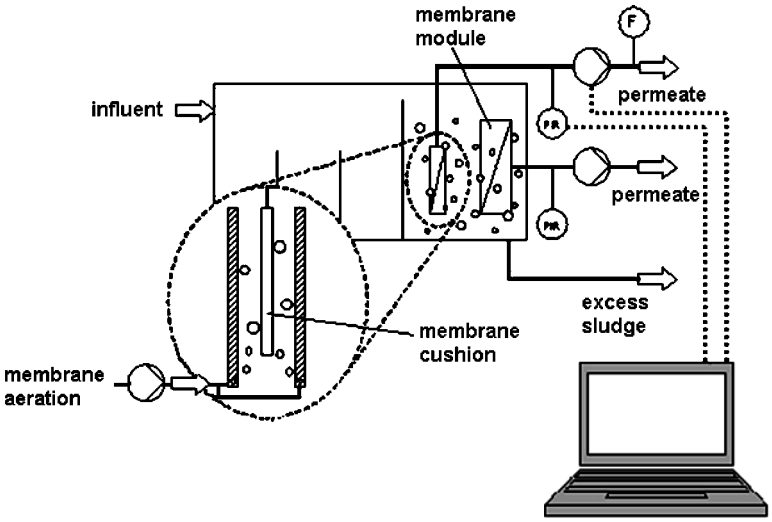

Fig. 1. Scheme of the *in situ* BFM test cell.

2.3. Analysis methods

PS analysis was performed following the phenol–sulfuric method by Dubois et al. [16]. In this method, the reaction of carbohydrate with phenol and sulphuric acid yields a brown colour which can be used for the quantitative photometrical determination of

Table 1
Basic properties of the investigated polysaccharides

Polysaccharide	Supplier	Functional group	Medium MW polymer* [kDa]	MW unit [g/mol]	Gelling properties	Others
Xanthan	Rhodia	$-COOH^-$	500–500,000	934	Mainly considered as non-gelling	Natural thickener
Alginate	Carl Roth		1–154	175	Forms gels with Ca^{2+}	–
CMC	Carl Roth		250–50,000	189	Non-gelling at the studied conditions	Degree of substitution 0.6–0.95
Pectin	Natura		30–100	158	Gel with high concentrations of cosolutes (e.g. sugar) and pH < 3.4	Pectin from apples. Degree of substitution 0.75
Heparin	Carl Roth	$-OSO^{3-}$, $-NHSO^{3-}$ and $-COOH^-$	3–50	195	Non-gelling	Highly negative charged polymer. Anticoagulant
Carrageenan	Sigma–aldrich	$-OSO^{3-}$	20–1000	Not applicable	It forms gels with Ca^{2+}. Without Ca^{2+}, considerable thickening occurs	Gelling Agent
Agarose	Carl Roth	–	170	Not applicable	It forms gels after cooling	Low degree of chemical complexity. Neutral PS
Starch	Merck	–	130	162	It forms cohesive and clear gels	Soluble potato starch for analysis. Neutral PS. 20–25% amylose, 75–80% amylopectin

* Values obtained as a mean value from several literature sources or manufacturer information.

monosaccharides and their polymerization products. TEPs were analysed with alcian blue (Clin-Tech, Germany) using the method from Arruda et al. [17] modified by de la Torre et al. [18]. Viscosity was measured with a Rotational Rheometer Haake (Germany). Duplicates of all parameters (PS concentration, TEP concentration and viscosity) were obtained.

2.4. Critical flux measurement

The protocol followed for the determination of the filterability consisted of a modified flux-stepping method for the determination of the critical flux. This protocol was based on [19] and included relaxation between every filtration step, so that the filtration conditions are similar to the plant operation conditions. The flux was varied between 2 and 22 L/(m^{2}h), with a step height of approximately 3 L/(m^{2}h). Filtration time was 5 min and relaxation time 2 min. Membrane permeability was regularly checked by filtering deionised water. Chemical cleaning was performed by filtering during 2 h at a flux of 10 L/(m^{2}h) a chlorine solution (4500 ppm) when the permeability loss with deionised water was greater than 10%. This happened only after filtering the agarose solution. Critical flux in the BFM test cell was defined as the maximum flux at which dTMP/dt was lower than 0.1 mbar/min. At least two duplicates were performed for every PS. The recovery factor was quantified for a fixed flux of 10 L/(m^{2}h) for all substances. This corresponds to the difference between the TMP values (the average TMP during the filtration step) at the same flux during the descending and the ascending phases of each hysteresis loop [20].

3. Results and discussion

3.1. Critical flux experiments

The results from the flux stepping experiments are summarized in Table 2 as a mean value from the duplicates. The reproducibility of the experiments was satisfactory as the J_c values generally did not vary more than one flux step (3 L/(m^{2}h)) when the experiment was repeated. The critical flux values obtained differ significantly for each PS, varying from 3 for agarose to more than 21 L/(m^{2}h) for heparin. Fig. 2 shows an example of determination of critical flux for a pectin solution.

The recovery factor values presented in Table 2 were obtained using Figs. 3 and 4. In these figures, the average TMP in every filtration step is represented against the flux during the experiments for all PSs tested. In most curves, the expected convex trend typical for critical flux measurements is not observed. This can be attributed to the relaxation breaks, which avoid the accumulation of the cake layer on the membrane surface along the experiment. The filtration resistance for carrageenan and agarose is significantly higher than for the other PSs.

Table 2
Results from the critical flux experiments and other measured parameters

Polysaccharide	J_c [L/(m^{2}h)]	μ [mPa s]	Recovery factor at 11 L/(m^{2}h) [mbar]
Xanthan	7	1.3	0.5
Alginate	16	0.8	0.2
CMC	15	2.0	0.1
Pectin	17	1.4	0.3
Heparin	21	1.1	0.9
Carrageenan	5	1.3	1.4
Agarose	3	2.0	7.4
Starch	19	2.4	0.5

3.2. Reversible and irreversible fouling

As no significant fouling was detected by filtering the pectin solution, the evolution of the TMP with the flux presented the same pattern by both increasing and decreasing the flux (Fig. 5a). The severe fouling produced by agarose did not allow the TMP to recover by reducing the flux, as can be seen from Fig. 5b. This is related to the phenomenon of mechanically irreversible fouling (which cannot be removed by mechanical means like aeration or backwash), although adsorption effects can additionally take place. As can be observed in Fig. 3, this hysteresis phenomenon can be observed especially in those experiments which were run much beyond the critical flux values (those with low J_c: carrageenan, agarose), and demonstrates the fact that for these substances, the 2 min relaxation steps do not allow, under the conditions of the trials, to recover the loss of permeability due to cake building during the filtration.

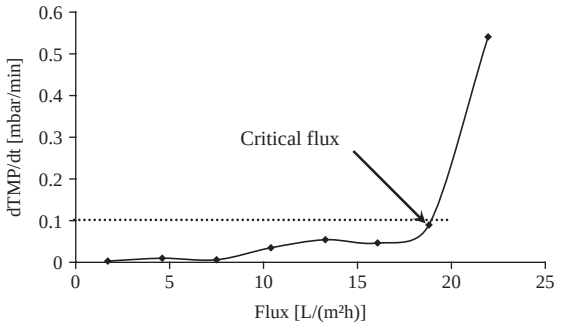

Fig 2. Determination of critical flux of a pectin solution.

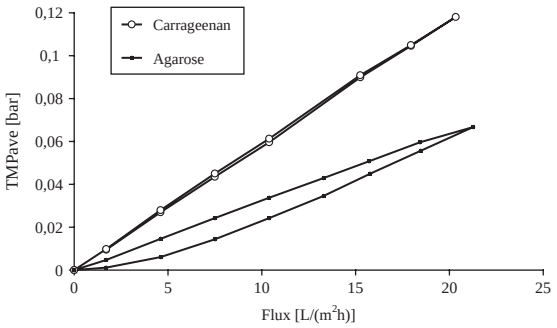

Fig. 3. TMP average and flux for the solutions of carrageenan and agarose.

3.3. PSs and TEP concentration

By looking at the studied properties of the PSs (Fig. 6), no direct relationship could be observed between these and the filterability behaviour in terms of critical flux values or recovery factors. A different filtration behaviour was found for the different PSs (critical fluxes varied between 3 and 21 L/(m^{2}h)), but that could not be strictly related neither to the measured amount of PS following the conventional method (phenol–sulphuric method) nor to the TEP concentrations of the solutions. TEP concentrations of 0 mg/L were found for agarose and starch as expected, being neutral PSs not detected by the analysis with alcian blue. This fact questioned the relevance of the concentration of TEP as a fouling indicator because, as it was seen with agarose, neutral sugars can also contribute significantly to the fouling phenomenon with the investigated membranes (very low J_c).

Although the model solutions were all prepared with 20 mg/L polymer mass, the global PS method resulted in very different concentrations. The reason for this discrepancy is that, using the phenol-sulphuric method, each PS yields a different absorbance after reacting with the sulphuric acid for the same concentration of 20 mg/L. When these absorbance values are then referred to the calibration curve of glucose, values from 8 to 22 mg/L are obtained. This is illustrated in Fig. 7 and it can be seen that measuring a solution of 20 mg/L of xanthan gum with the phenol–sulphuric method results in 15 mg/L glucose equivalent. This is an inherent consequence of the calibration with a standard, as it reflects the problem of measuring total concentrations of sugar with this method, which was developed only for pure sugar solutions calibrated with the same sugar which is being measured. The same situation occurs with the TEP concentrations. Therefore, it seems reasonable that in Fig. 6, no relationship between filterability and these concentrations can be found.

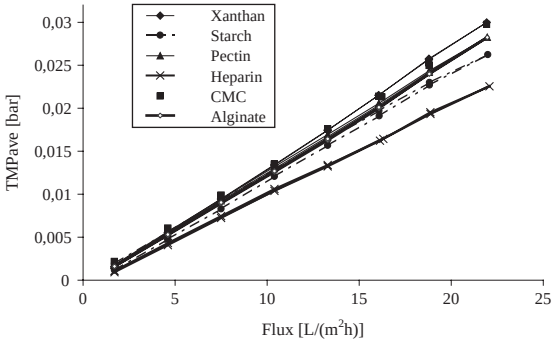

Fig. 4. TMP average and flux for the solutions of xanthan, starch, pectin, heparin, CMC and alginate.

3.4. Viscosity

The viscosity of the model solutions is presented in Table 2 and no further information could be obtained from this parameter in relationship with the filtration behaviour. A higher concentration of PSs would have been necessary in order to have a wider range of viscosities that would allow a comparison.

3.4. Molecular size

In Fig. 8, the MW of the different PS is represented against the critical flux values obtained. The average, maximum and minimum MW values were taken from diverse literature sources and, as this parameter varies considerably depending on manufacturing procedure, supplier, raw material, etc. in biopolymers, the range is considerably wide. However, it can be appreciated that the MW of the polymers does not explain the critical flux values measured. A possible relationship between the critical flux value and the MW of heparin may exist because this PS showed a very high filterability, and it has the smallest molecular size with approximately 15 kDa, which is much lower than the MW found in the literature for the other PSs. This low value for the MW is also much lower than the MWCO of the membrane (150 kDa), which probably permitted the PS molecules to pass through the membrane. Analysis of permeate concentrations should have been performed in order to check this issue, for this and the other substances.

3.5. Charge density

The charge density was estimated by calculating the number of electric charges in the monomers divided by the MW of the monomers. As this was represented against critical flux, a clear trend indicating higher critical flux at higher charge density of the polymers was found, especially by the PS containing carboxylic

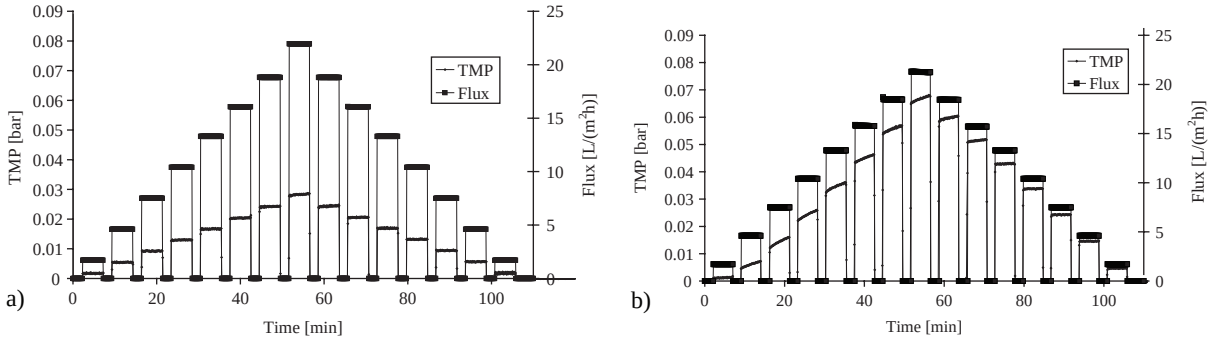

Fig. 5. Critical flux measurement of a 20 mg/L pectin solution (a) and a 20 mg/L agarose solution (b). TMP and flux evolution.

groups. Sulphated groups seem not to influence filterability as much as carboxylic groups, as can be seen in the Fig. 9. This suggests a charge repulsion effect between the hydrophilic PES membrane and the negatively charged PSs, leading to higher rejection and less interaction between molecules and less adsorption. Lower flux decline and adsorption in filtration of NOM with hydrophilic PES membranes at higher negative charge due to carboxylic groups (higher pH) was already reported in the literature [22].

4. Discussion

The objective of distinguishing one PS property as relevant for fouling has failed for the eight PSs tested in this study, although interesting information has been obtained. By looking at the different substances tested, each of them may have a different reason for their J_c value so that no linear correlation can be found against parameters like viscosity, MW, charge density, PS or TEP concentration. The gelling capacity of the substances did not seem to be the most significant characteristic for fouling, showing starch and agarose (those substances which form gels at the studied conditions) the highest and the lowest critical flux values, respectively. This might be attributed to a different gel structure which consequently caused different fouling. The high filterability of heparin was explained by its low MW, being the PS able to pass the membrane without affecting TMP value. The medium fouling propensity of compounds like CMC, xanthan gum and alginate can be related to their already known ''stickiness'' and their acidic nature, which makes them more likely to interact with the hydrophilic membrane than a neutral PS like starch, which showed the highest J_c value together with heparin. The severe fouling encountered by filtering the carrageenan solution could not be explained by looking at any of the studied parameters.

An interesting relationship between charge density (calculated as number of charged groups per monomer divided by its MW) and the critical flux was found. Especially for those PS containing carboxylic groups, higher J_c values were found at higher charge densities, probably due to a repulsion effect with the membrane.

The significant differences encountered in the fouling propensities of the PSs and the lack of a relationship with the measured parameters question the usefulness of the employed analysis methods and confirm that the quality of the PSs can be more important than quantity when dealing with fouling issues. Even

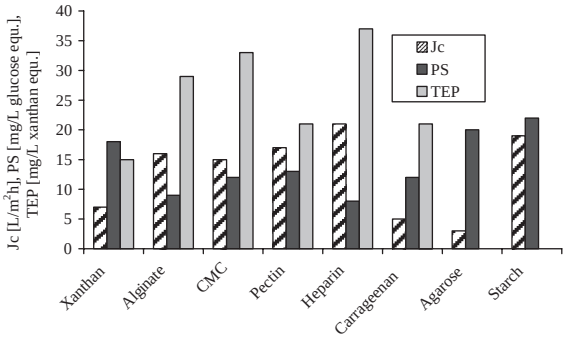

Fig. 6. J_c, TEP concentrations and polysaccharide concentrations measured for the different PS.

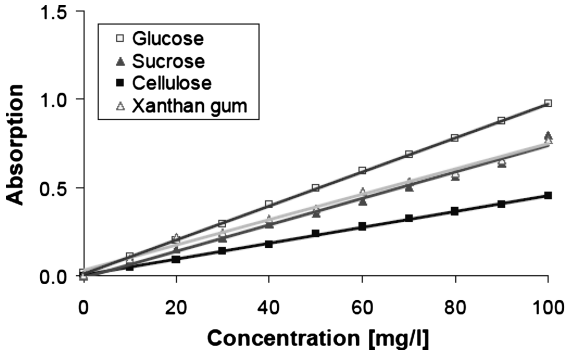

Fig. 7. Calibration curves for different sugars using the phenol–sulphuric method [21].

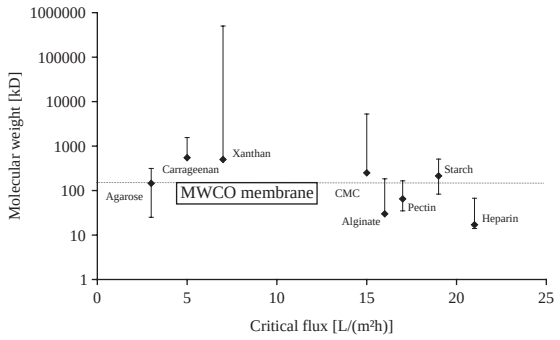

Fig. 8. MW and critical flux values. Error bars indicate max. and min. values, symbols average.

the same PS can behave differently depending on the source and/or the industrial process used to extract and purify them [23] because the chemical structure of these PSs varies. It can be concluded that, when working with model PS, the selection of the PS must be very carefully done and the representativeness of a model solution is questionable. In the last years, articles investigating the filterability of different mixtures of PSs and calcium ions as well as humic substances in different pH conditions have multiplied, which shows that it has been noticed that we are dealing with a complex phenomenon which cannot be simplified with the use of a model solution of a single compound. Also the membrane material plays also an important role, as well as the pore size and hydrophobic/hydrophilic character; so that the conclusions obtained for one membrane material cannot be extrapolated for the rest of them.

5. Conclusion

The different PSs tested showed very different fouling propensities, which could not be related to any of the studied properties of the PS. The problematic use of the phenol–sulphuric method when quantifying PS mixtures revealed that findings based on this lump parameter are questionable. The results stress the difficulty of finding a global fouling indicator for PSs and a representative model PS for fouling investigations. In fact, it might be impossible to find a model substance that simulates all filtration properties of real feeds. More investigations are needed with other membrane materials, mixtures of PS, in combination with humic substances, divalent ions and maybe with a different matrix (i.e. permeate instead of deionised water) and pH.

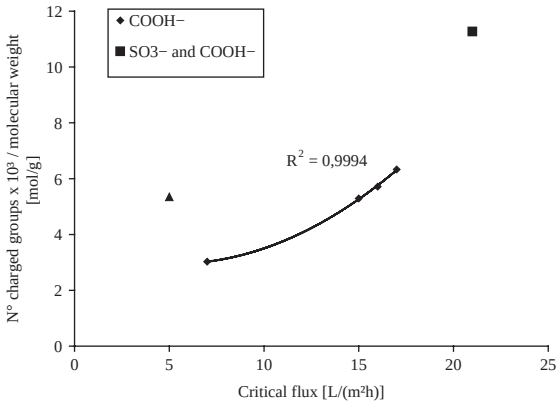

Fig. 9. Influence of the number of charged groups per monomer divided by MW in the critical flux values.

Acknowledgement

This project is supported by the European Commission under the 6th FP Project MBR-TRAIN (MEST-CT-2005-021050), ''Marie Curie'' Host Fellowship for EST. The authors want to thank Microdyn-Nadir for the membrane material supply.

References

[1] J. De Bruijn and R. Bórquez, LWT Food Sci. Technol., 39 (2006) 861-871.
[2] F. Salazar, J. De Bruijn, L. Seminario, C. Güell and F. López, J. Food Eng., 79 (2007) 1329-1336.
[3] T. Mohammadi, S.S. Madaeni and M.K. Moghadam, Desalination, 153(1-3) (2003) 155-160.
[4] M. Taylor, D.B.F. Faraday, C.L. O'Shaughnessy, B.O. Underwood and R.J.R. Reed, Sep. Purif. Technol., 22-23 (2001) 133-142.
[5] S. Rosenberger, C. Laabs, B. Lesjean, R. Gnirss, G. Amy, M. Jekel and J.-C. Schrotter, Water Res., 40(4) (2006) 710-720.
[6] A. Drews, M. Vocks, U. Bracklow, V. Iversen and M. Kraume, Desalination, 231(1-3) (2008) 141-149.
[7] T. de la Torre, B. Lesjean, A. Drews and M. Kraume, Water Sci. Technol., 58(10) (2008) 1903-1909.
[8] T. Berman and M. Holenberg, Filtr. Sep., 42(4) (2005) 30-32.
[9] M.D. Kennedy, F. Munoz, G. Amy and J. Schippers, Proceedings of the MIDW08 20–22 October 2008, Toulouse, France.
[10] Y. Ye, V. Chen and A.G. Fane, Desalination, 191 (2006) 318-327.
[11] P. Le-Clech, Y. Marselina, Y. Ye, R. Stuetz and V. Chen, J. Membr. Sci., 290 (2007) 36-45.
[12] K. Katsoufidou, S.G. Yiantsios and A.J. Karabelas, Desalination, 220 (2008) 214-227.
[13] D. Jermann, W. Pronk, S. Meylan and M. Boller, Water Res., 41 (2007) 1713-1722.
[14] X. Wang and T. Waite, J. Membr. Sci., 325 (2008) 486-494.
[15] I.S. Kim and N. Jang, Water Res., 40(14) (2006) 2756-2764.
[16] M. Dubois, K. Gilles, J.K. Hamilton, P.A. Rebers and F. Smith, Anal. Chem., 28 (1956) 350-356.
[17] S.H.S. Arruda, A.A. Henriques and O.F. Fatibello-Filho, Talanta, 62 (2004) 81-85.
[18] T. de la Torre, B. Lesjean, A. Drews and M. Kraume, Environ. Sci. Technol., in preparation.
[19] P. Le-Clech, B. Jefferson, I.S. Chang and S. Judd, J. Membr. Sci., 227 (2003) 81-93.
[20] G. Guglielmi, D. Chiarani, S. Judd and G. Andreottola, J. Membr. Sci., 289 (2007) 241-248.
[21] R. Mehrez, M. Ernst and M. Jekel, Water Sci. Technol., 56(6) (2007) 163-171.
[22] G.L. Amy and J. Cho, AWWA Research Foundation and American Waterworks Association, Denver, 2001.
[23] M. Rinaudo, Biomacromolecules, 4 (2004) 1155-1165.