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Title

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Quality Assurance

Boris Lesjean, KWB

Deliverable number

D 2.5.7.

This report is:

PP = Restricted to other programme participants (including the Commission Services).

Summary

Access to microbiologically and chemically safe water is limited not only in developing countries, but also in transition countries and even in remote areas of developed countries. For these cases, decentralized water supply concepts such as point-of-use (POU), point-of-entry (POE) or small-scale system (SSS) technologies can be promising alternatives to centralized treatment concepts. Membrane-based treatment systems have gained importance for drinking water treatment in the developed countries. In principle, application of membrane technology is attractive also for the transition and developing countries, because it provides absolute barriers for control of hygienic hazards (Ultrafiltration (UF)) and because the modular construction enables implementation on each possible scale size. However membrane technology is still not affordable for the poorest part of the world population.

The sustainable application of POU membrane system presumes that system should be operated without or with limited addition of chemicals, with limited possibility of regular backflushing and with low pressure, presumably hydrostatic. On the other hand, while the water needs for drinking and cooking for a family of four people constitute approx. 20 l/day, operation of POU UF system under low flux conditions is possible.

One of the most important limitations for application of ultrafiltration in simple household devices, is membrane fouling. In order to overcome the reasons of the limited application of UF in POU systems, the better understanding of the UF process in these specific conditions and specially membrane fouling is needed.

Recent studies have shown that dissolved or colloidal polysaccharides and proteins and their interactions with the membrane and between macromolecules might have more severe impact. During long term dead-end filtration, accumulation of the macromolecules on the membrane surface and increase of their concentration is severe. The interactions between those macromolecules in the conditions of high concentrations in the boundary layer affect the structure of the layer and its permeability. However, in most of the studies, only the foulant-membrane interactions are considered like relevant for reversibility of fouling. The foulant-foulant interactions in the boundary layer have been studied only superficially.

Therefore, we systematically investigated the impact of polysaccharide and solution properties on UF membrane fouling in conditions of low flux and limited backflushing, under constant TMP conditions (hydrostatic pressure of 120 mbar - 150 mbar).

Our experimental results lead us to the following conclusions:

Regarding the initial stage of flux decline (0-80 ml permeate/cm²) the polysaccharide structure, and particularly availability of carboxyl groups, has a major impact on the membrane fouling, while the molecular weights of polysaccharides does not play a significant role (in the studied range of Mw 5-250 kDa). Such solution conditions as presence of metal ions and ionic

strength are also detrimental for the fouling, while both metal ions and ionic strength have impact on the gel structure and properties, generally stabilizing it, and increasing the possibility of water trapping by hydrogen bonding, which leads to the higher permeability. However, independently of the initial solution conditions, after approx. 80 ml has been filtered through 1 cm² of the membrane, flux becomes stable on the level of approx. 10 L/(h·m²) over the whole period of operation (several weeks in some cases). We suppose that the gel layer formed by polysaccharides play a role of a "second" membrane on the surface of the PES UF membrane, keeping remaining permeability on the certain level, determined by the water retention properties of the gel structure.

Regarding practical application, the obtained results open a new direction for the ultrafiltration in specific conditions of household systems. The long term ultrafiltration should be studied on natural waters to prove the flux stabilization phenomenon. This phenomenon may give a possibility to produce up to 10 L/h of water from 1 m² of the membrane applying only 120 mbar of hydrostatic pressure (1.2 m water level difference) without backflushing or crossflow, which may simplify the design and maintenance of the system and significantly reduce its costs.

Next activities in Techneau project will include the further evaluation of the long term ultrafiltration on natural waters; characterization of the impact of biofouling on the flux decline; and evaluation of the operational parameters of the Point-of-use system, based on the proposed above concept to treat at least 20 L/day.

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1 Introduction

1.1 General background

Access to microbiologically and chemically safe water is limited not only in developing countries, but also in transition countries and even in remote areas of developed countries. For these cases, decentralized water supply concepts such as point-of-use (POU), point-of-entry (POE) or small-scale system (SSS) technologies can be promising alternatives to centralized treatment concepts. Membrane-based treatment systems have gained importance for drinking water treatment in the developed countries and can be considered as the dominant technology for new applications at present. In principle, application of membrane technology is attractive also for the transition and developing countries, because it provides absolute barriers for control of hygienic hazards and because the modular construction enables implementation on each possible scale size. While in most cases the major problems are related to microbiological aspects, ultrafiltration (UF) should fulfill the needs of water treatment and may present an optimal solution. During the last decade UF technology has become more efficient and the costs of membranes have decreased significantly (Churchhouse, 2000). Nevertheless membrane technology is still not affordable for the poorest part of the world population. Research and development of membrane systems specific for the developing and transition countries remains limited to isolated cases which are often not published in the open literature. In an extensive literature and state-of-the art review the research and development needs of membrane-based POU systems in developing and transition countries were evaluated (Varbanets and Pronk, 2006). From this report it was concluded that prerequisites for application of membrane-based POU systems include low available maintenance and control, as well as operation without additional energy supply. This presumes that POU UF systems should be operated without or with limited addition of chemicals, with limited possibility of regular backflushing and with low pressure, presumably hydrostatic. Also, the water demand in POU systems is not constant, and in order to avoid large storage vessels (hygiene), intermittent operation is required. On the other hand, while the water needs for drinking and cooking for a family of four people constitute approx. 20 l/day, operation of POU UF system under low flux conditions is possible.

One of the most important limitations for application of ultrafiltration in simple household devices, is membrane fouling. Due to operational and maintenance problems, as well as low raw water quality, traditional ways of operation and fouling prevention in UF membrane systems cannot be used in specific conditions of developing and transition countries. This dramatically limits their application.

The fouling of membranes by natural organic matter is well documented, however the fouling process is much less well understood. In order to overcome the reasons of the limited application of UF in simple household

system, the better understanding of the UF process and specially membrane fouling is needed.

1.2 Membrane fouling

Natural organic matter is generally recognized as a main foulant in water treatment. Many researchers have suggested that humic substances are the most detrimental NOM-foulants causing fouling by membrane adsorption and pore blocking (Clark and Lucas, 1998; Jucker and Clarck, 1994).

However, recent studies have shown that hydrophilic, non humic, dissolved or colloidal NOM might be a more significant foulant for UF membranes, namely polysaccharides and proteins. It has been suggested that the polysaccharides foul the membrane mainly by pore blockage and gel layer formation (Kimura et al., 2004).

When regarded mechanistically, it has been observed in many studies that fouling is caused not only by size exclusion of solutes but also by adsorption and chemical or electrical attraction/repulsion between them and the membrane (Amy and Cho, 1999).

The influence of such interactions between NOM molecules have been studied, but in spite of the complex nature of natural waters, almost all those studies have focused only on one foulant for the purpose of simplicity. In case of polysaccharide fouling studies, dextran and alginate are dominant compounds of the synthetic media chosen to model impact of polysaccharides on fouling.

However, it is known from the macromolecular science, that behavior of polysaccharides in the solution is dependent from the chemical structure of the single units, conformation, availability of the other ions and solution matrix (ionic strength, pH). Presence of some specific functional groups in the polysaccharides can intensify or prevent gelation, some metal ions can form metal bridges between macromolecules to initiate aggregation of them, possibility to form intermolecular hydrogen bonds that can stabilize conformation, and therefore affect the hydrodynamic radius of the molecule in the system. During long term dead-end filtration, accumulation of the macromolecules on the membrane surface and increase of their concentration is severe. The interactions between those molecules in the conditions of high concentrations in the boundary layer affect the structure of the layer and its permeability. However, in most of the studies, only the foulant-membrane interactions are considered like relevant for fouling and its reversibility (Amy and Cho, 1999). The foulant-foulant interactions in the boundary layer have been studied only superficially.

1.3 Operation under low filtration flux

To avoid large membrane surface the main precondition of operation of large scale ultrafiltration is to assure high flux, which necessitates high transmembrane pressure. High reversible and irreversible fouling rates observed result in application of such control measures as backflushing and chemical cleaning, which have severe impact on the properties of the fouling layer. Most of the mentioned in Section 1.2 membrane fouling studies have been conducted under usual for large scale operation conditions.

NOM fouling of ultrafiltration membranes operated in conditions of low flux and limited backflushing has not been systematically investigated before. However these conditions are most relevant for decentralized applications, while the required capacity of the systems are low (20-50 L/day for POU system).

1.4 Goals and objectives of the study

Therefore, the objectives of this study were to systematically investigate the impact of polysaccharide structure, availability of functional groups and molecular weight on membrane fouling under low trans-membrane pressure (TMP) conditions (hydrostatic pressure of 1.2-1.5 m). While it is generally accepted that polysaccharides cause fouling by pore blocking due to gel layer formation (Ye et al., 2005), the ability of different polysaccharides to form gels under certain conditions have been considered and the membrane fouling in these conditions has been studied.

2 Materials and methods

2.1 Characteristics of the polysaccharides

Several polysaccharides have been chosen for the study. Their main properties are shown in the table 1. Our choice was based on the molecular structure of the polysaccharide, availability of the specific functional groups and the molecular weights.

Table 1 Characteristics of the polysaccharides

Polysaccharide	Specific groups	Molecular weights of polymer, kDa	Molecular weight of single unit (approx.)
Alginate	-COONa	12-80	175
Hyaluronate	-COONa	68-340	189
Pectin	-NH-CO-CH ₃	30-100	158.5
	-COONa		
Heparin	-COOCH ₃	4-6	195
	-NH-SO ₃ Na		
	-O-SO ₃ Na		
N-acetylated-de-O-sulphated heparin	-NH-CO-CH ₃	12-15	184
	-NH-SO ₃ Na		
Carboxymethylcellulose	-O-CH ₂ -COONa	250	189
Dextran	-	5	162
		50	
		670	
Starch	-		162

All reagents were obtained from Sigma-Aldrich and were of following characteristics:

- Carboxymethylcellulose sodium salt, medium viscosity, degree of substitution 0.6-0.95.
- Alginic acid, Sodium Salt, produced by brown algae in natural water
- Dextran Standard, 5000, 50000, 630000, certified according to DIN for GPC
- Hyaluronic acid, sodium salt, from human umbilical cords,
- Pectin from apples, degree of esterification 0.7-0.75
- Heparin sodium salt, from porcine intestinal mucosa
- Starch soluble

2.2 Composition of the synthetic media

For the fouling experiments with polysaccharides, solutions of 0.002 mM polysaccharide were used. The molar concentration was determined on the basis of the molar mass of the single polysaccharide unit. We use this approach and not DOC like in all previous studies (Jermann, 2007), in order to be able to compare the impact of differences in structure of polysaccharides

on membrane fouling they cause. The molar concentration of the metal ions were determined in molar ratios to the polysaccharide concentrations and later plotted in the same way.

The background solution for all experiments consisted of deionized water, NaCl (0.5 mM), NaHCO₃ (0.125 mM) and the buffer solution MOPS (0.5 mM). The pH was adjusted by addition of HCl (0.1M) or NaOH (0.1M) and was kept constant at pH 7.6 - 7.8. The ionic strength was controlled by conductivity measurements and when necessary adjusted with NaCl.

2.3 UF membranes

We used a fresh flat sheet 100 kDa polyethersulfone membrane (Biomax, Millipore) for each experiment. Beforehand the membranes were stored for min. 24 h in deionized water, which has been changed three times, and then filtered with 5 L of deionized water under 150 mbar pressure. This membrane pretreatment procedure was preliminary developed to remove conservation substances from the membrane. The efficiency of this procedure was assessed by DOC measurements of the deionized water permeate in the LC-OCD. The cleaning procedure was considered as prerequisite to avoid contamination of subsequent samples by membrane leaching and to perform reliable experiments with low NOM concentrations similar to natural water.

2.4 Membrane test units

The membrane test unit was a 400 ml stirring cell with removed stirrer (Amicon). The level in the stirring cell was maintained constant on 250 ml by a feed gear pump connected to a glass reservoir (10 L). The pressure in the cell was kept constant at 150±5 mbar by a pressure control device, which steered the feed pump. The permeate flowed into glassware on a scale, which was connected to a PC. Data were logged every 2 min.

2.5 Fouling experiments

We performed all experiments at room temperature and constant transmembrane pressure (0.15 bar). Previous to every experiment the flux of the clean membrane was measured. The short term experiments consisted of three cycles. One cycle included filtration of 1L of synthetic solution, backwash with 50 mL deionized water, filtration of 100 mL deionized water (used to determine the reversibility).

The long-term experiments consisted of one cycle. Min. 2L of solution has been filtered through the membrane and the flux was controlled on-line.

3 Results and Discussion

3.1 Impact of different polysaccharides on the membrane fouling

The flux values of experiments with alginate, hyaluronate, carboxymethylcellulose and dextran of different molecular weights in the solutions of similar matrix on membrane fouling are depicted on the Fig.1. As shown in Fig.1 (a) the flux decreased much more severely during filtration of Alginate, Hyaluronate (HA) and Carboxymethylcellulose (CMC) in comparison to Dextran independently of its Mw. The difference between flux decline for different Mw Dextrans was not severe. This result was not expected, considering the fact that membrane cut-off is equal to 100 kDa. Dextrans of 5 and 50 kDa were expected to pass through the membrane and lead to less fouling than the 630kDa Dextran, which is completely retained. In case of Alginate, HA and CMC the flux decreased similarly. Also the reversibility of fouling for these polymers was lower, than in case of Dextran. The similarity of the flux decline should indicate the similarity of fouling mechanisms, and its difference to the case of Dextran. As we can see from the table 1, Alginate, HA and CMC are independently of their structure negatively charged polysaccharides, while Dextran is neutral. This indicates the importance of electrostatic interactions in the membrane fouling mechanism.

However, as shown in Fig. 1 (b) the flux decreased for the same polysaccharides differently in the presence of Ca cations. While in case of Dextran, the difference is negligible, the charged polysaccharides react differently on the presence of Ca. In Fig. 1 (c), the influence of Pectin, Heparin, N-acetylated heparin and Starch in Ca containing solutions on flux is shown. Behavior of non charged starch is similar to one of dextran and pectin causes the similar fouling as alginate, however both Heparins have different impact. This difference may be caused by two factors - the lower molecular weights of both substances (12-15 kDa), and absence of the carboxyl functional group, which is present in all other charged polysaccharides considered in this study.

While the impact of the molecular weights on the fouling in case of Dextran has proven to be insignificant, we can assume that the presence of charged carboxyl group plays a significant role in fouling. The fact that alginate causes more severe flux decline than pectin, which has similar structure, but partially methylated carboxyl groups, also supports this assumption.

Summarizing the results and discussion above, we can conclude that the presence and availability of charged carboxyl groups and presence of Ca ions have a severe impact on the flux decline, while the molecular weights of the polysaccharides does not play a significant role in the conditions studied.

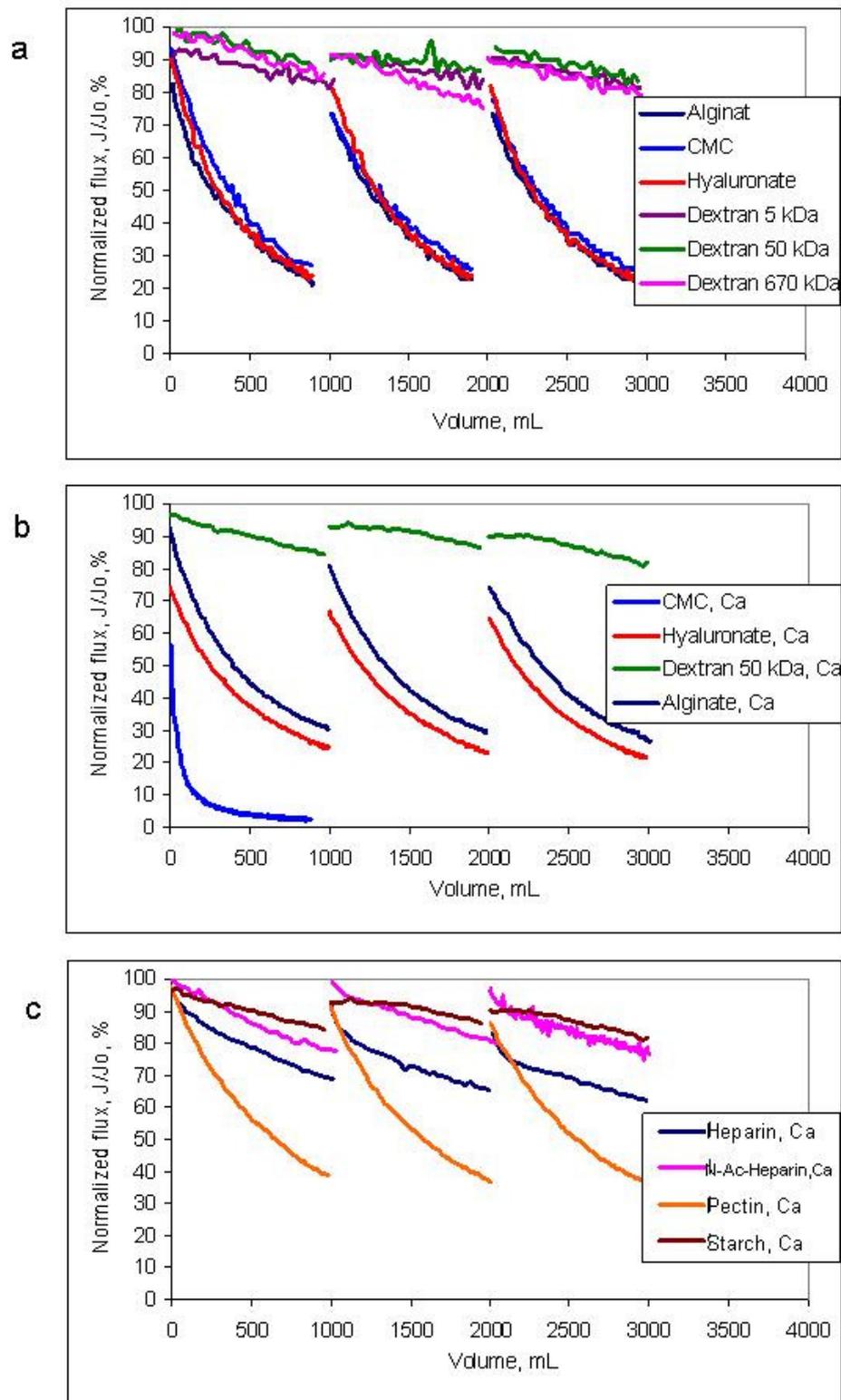


Fig.1 Impact of different polysaccharides on the flux decline: (a) polysaccharides in solutions without Ca, (b, c) in solutions with Ca, Polysaccharide/Ca = 1/1.

3.2 The role of metal ions

As we can see from the Fig. 1 (b, c) Ca also plays an important role, but the character of the flux curves differs for different polysaccharides.

It is generally accepted that metal ions are able to form networks with polysaccharides containing carboxyl groups through metal bridge formation and interlinking of polymers between each other, therefore obtaining organized structure. This structure is able to form a gel with the increase of polysaccharide and metal concentrations in the solution.

For example alginate shows specific ion binding characteristics and the affinity for alkaline earth metals increases in the order $Mg \ll Ca < Sr < Ba$. Thibault (Thibault and Rinaudo., 1985) found that under Na and Mg salt forms, the general behavior of single chain polyelectrolytes is confirmed, while with Ca, Sr and Ba a double chain structure is stabilized, also known as an egg-box model (Bryce et al., 1975).

It was found by these authors that with Na and Mg the polymers are water soluble while Ca, Ba and Sr are known to induce the gelation with an ionic selectivity corresponding to $Ba > Sr > Ca$ for the ability to form a gel (Rinaudo, 2006).

In natural systems gel formation is considered as one of the mechanisms of the membrane fouling. Also in studies of membrane fouling by alginate, the gel formation on the membrane surface has been considered as the main reason of flux decline (Jermann et al., 2007). However, the effect of gels on the fouling has never been studied before.

The Fig. 2 indicates that fouling is more severe in case of the system with Na and Mg ions, than the system with Ca and Ba in the same concentrations.

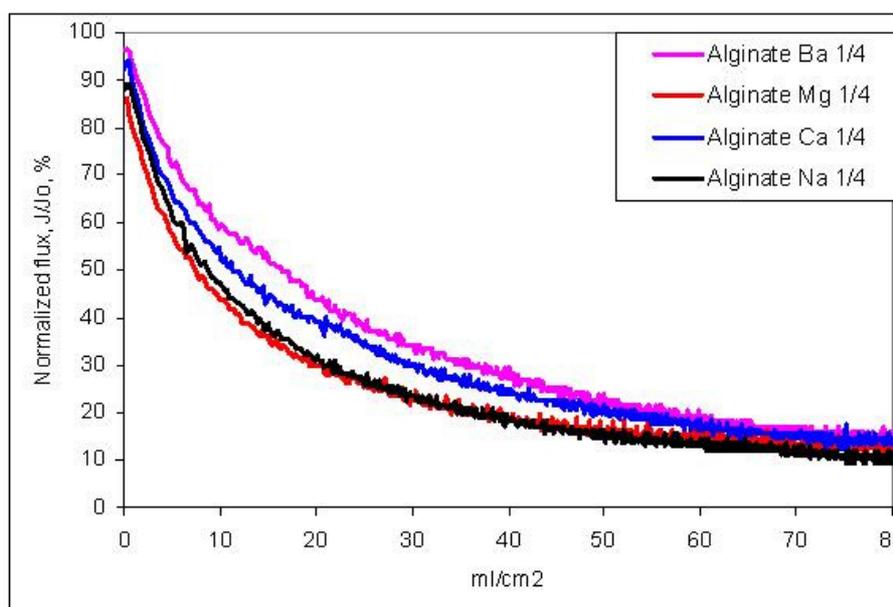


Fig. 2 Impact of Ca, Mg, Ba and Na on flux

It was mentioned above, that alginate in the presence of Mg and Na has the behavior of a single chain polysaccharide and therefore is not able to form organized networks and gels. This leads us to the conclusion, that fouling is

more severe in the systems where organized network cannot be formed under other similar conditions. It means that formation of the gel layer on the membrane has a positive effect on the membrane fouling in certain conditions. This fact is with agreement with the evidence that Ca containing gel layers are more hydrated than the gels adsorbed without Ca, with water molecules trapped by hydrogen bonding in the gel matrix (de Kerchove and Elimelech, 2006). The higher rate of hydration leads to the higher permeability of the gel layer, and therefore to the higher flux.

3.3 Iron containing systems

Iron is often present in natural waters. The property of Fe(II) and Fe(III) ions to form complex substances with NOM and its fractions are well known. Also polysaccharides containing carboxyl functional groups, are able to interact with Fe (III). Many studies have shown (Xia et al., 2004; Choo et al., 2005) that Iron is one of the ions which is partly retained by the UF membranes and is often detected in the matrix of fouling layers. Therefore, it is necessary to consider the role of Fe ions in membrane fouling by polysaccharides. We studied the impact of Fe (III) on the flux decline in Alginate containing systems. While Fe(III) at the pH conditions of the experiments may form colloidal solution and therefore is retained by the membrane, we considered also the impact of Fe(III) alone. Besides of this, the solutions were prepared in two different ways: using Fe(III) acidic solution as stock solution, and by slow oxidation of Fe(II) by increasing the pH in a system already containing Alginate. The reason for that was to insure the complete reaction of Fe (III) with Alginate. In the case, where Fe (III) has been directly added to the system containing Alginate, fast increase of pH may lead to formation of colloidal $\text{Fe}(\text{OH})_3$ rather than to formation of Fe-Alginate complex, while the reactions with macromolecules are known to be slow. Therefore, slow oxidation of Fe(II), which does not react with Alginate, to Fe(III) by air and slow pH increase ensures complete reaction and formation of the complex. However, in both cases we used the excess of Fe, and, therefore, except of the Fe-Alginate compound, colloidal iron hydroxides were also formed in the system.

Fig. 3 represents the flux values of the experiments with Fe (III), with and without alginate.

As shown in the Fig. 3, in both experiments without Alginate under studied conditions (Fe concentration - 0.008 mM, pH 7.7) the flux is not influenced by the filtered solution. However, there was no iron detected in the permeate in both cases, which meant that all Fe(III) has been retained by the membrane, independently from the way the Fe(III) colloids have been obtained. However, both Alginate containing systems show significant flux decline, comparable to the Ca containing systems but lower than with Alginate alone. This indicates the similar mechanisms of fouling with Fe as with other metals ions considered in paragraph 3.3, independently from the presence of colloidal particles in Fe containing systems.

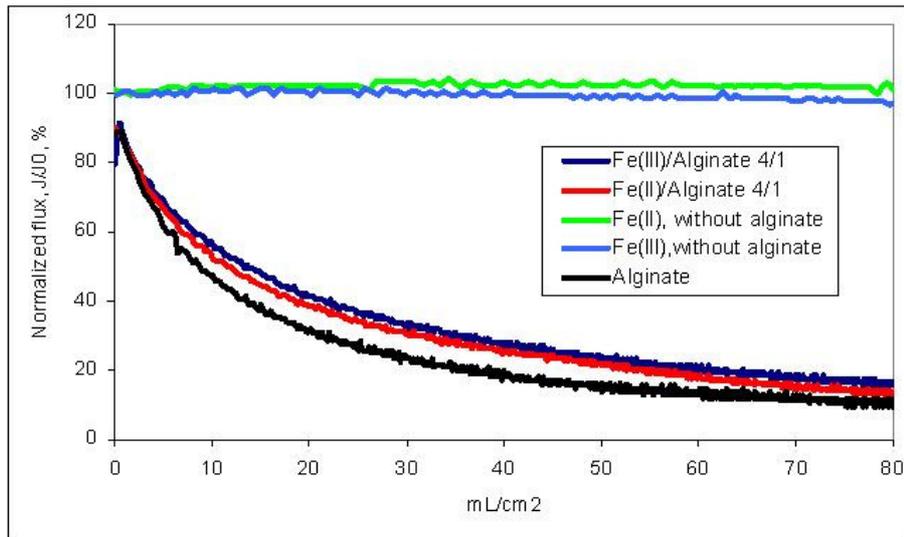


Fig. 3 Impact of Fe(III) on flux in systems with and without Alginate. As Fe(III) are marked the systems where Fe(III) was directly added to Alginate solutions, while Fe(II) corresponds to the system where, initially, Fe(II) has been added, and then slowly oxidized to Fe(III)

Besides of this, not only the presence of particles in the system did not make any difference to the flux decline, also the structure of particles did not influence the flux significantly. As we can see on the Fig.4, the Fe(III) crystals obtained through oxidation of Fe(II) have crystalline structure, while in the other case, Fe(III) is amorphous.

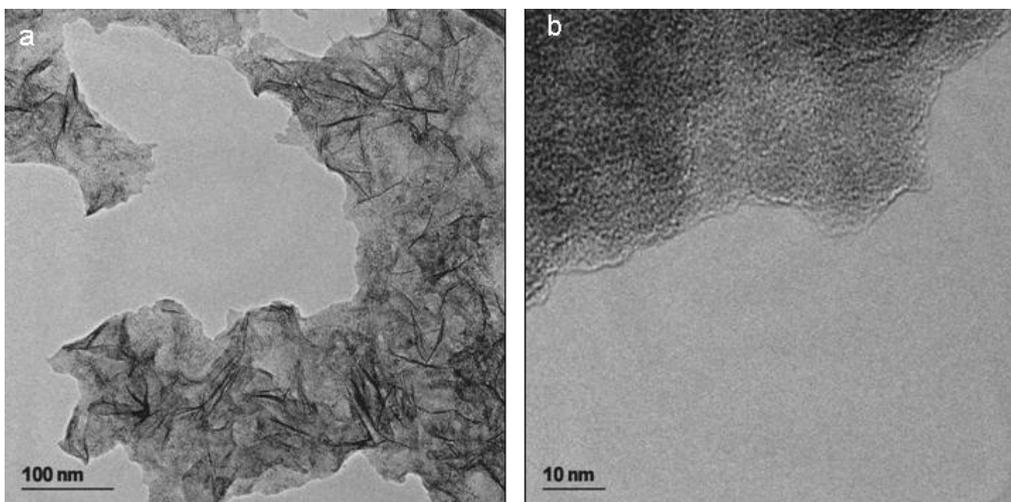


Fig. 4 - TEM pictures of particles obtained from Fe-Alginate solution, where (a) $Fe(OH)_3$ was made by oxidation of Fe(II)-Alginate solution with air and pH increase, (b) - $Fe(OH)_3$ was obtained by precipitation from Fe(III)-Alginate solution

3.4 The role of ionic strength

The impact of the ionic strength on the polysaccharide behavior in solution and on the surface of the membrane is an important factor reflecting the role of electrostatic interactions in the fouling process. Impact of the ionic strength on the fouling by NOM has been considered in some studies before (Frank

and Belfort, 2003). It is generally known that NOM molecules change from linear to spherical conformation on increasing ionic strength. This is due to neutralization of anionic carboxylic acid and phenolic groups by the cation of the added salt, which is known also as a shielding effect. Besides of this, size of the macromolecules also depends on the ionic strength - the higher the ionic strength, the smaller the molecule (Schaefer, 2001). Both facts are also true for the negatively charged polysaccharides (Berriaud et al., 1998). However it also means that except of conformational and size changes, anionic polysaccharides should behave like nonionic ones with the addition of simple salts due to the shielding effect (Ise and Sogami, 2005). Considering our assumption that negatively charged polysaccharides decrease flux severely, the increase of the ionic strength should have positive impact on fouling.

In Fig.5, the impact of ionic strength on the flux decline caused by Hyaluronate is shown. As we can see from the character of flux decrease in Fig. 5, increase of the ionic strength to a certain salt concentration in the solution leads to increase of the flux.

However, from a theoretical point of view, the increase of the ionic strength should result in compaction of the adsorbed layer and increase of the polysaccharide adsorption (de Kerchove and Elimelech, 2006) leading to lower permeability.

A possible explanation for the opposite effect may be that the increase of the ionic strength leads to electrostatic destabilization of the charged polysaccharide molecules due to charge shielding. This induces van der Waals interactions and formation of inter- and intra-molecular hydrogen bonds, which can contribute to the swelling of polysaccharides in the solution and on the surface. If the formation of a gel in these conditions is still possible, it should act as looser and more fluid structure.

The presence of the threshold NaCl concentration (0.1M) after which the further increase of the ionic strength does not result in the increase of the flux also supports the assumption above. Once the intra and intermolecular hydrogen bonds are formed stabilizing certain structure, further increase of the concentration of simple salt should not have an impact on the structure anymore.

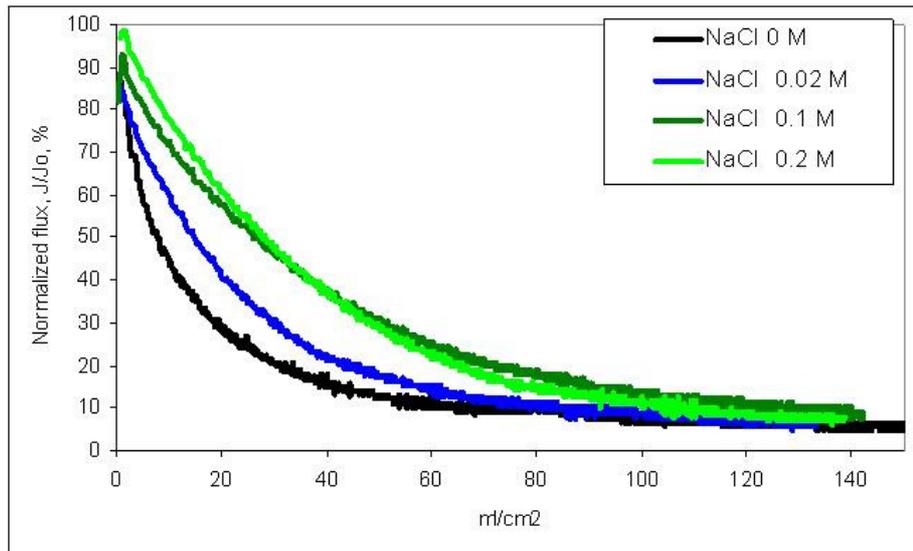


Fig. 5. Impact of the ionic strength on the flux decline caused by hyaluronic acid.

3.5 Long term experiments and flux stabilization

Fig. 5 (and also Fig. 2, 3) shows the flux behaviour during the long time filtration without backflushing. In spite of the significant differences observed in the initial part of the flux curves (volume of the polysaccharide solution filtered through the membrane up to 80 mL/cm²), with the increase of the volume of the filtered solution, the flux stabilized and the impact of different factors on fouling became negligible. The differences observed for polysaccharides and impacts of solution conditions cannot be noticed anymore on this stage of ultrafiltration.

These flux decline pattern indicate that mechanism of fouling layer formation differs at the beginning of the cycle, from the situation when substantial fouling layer should already have been formed.

The impact of different parameters on the first part of the cycle has been discussed in paragraphs 3.1-3.4, in this paragraph we will focus on phenomena of flux stabilization.

As mentioned above, the stabilization of the flux curve is being observed after approx. 80 mL of solution passed through 1 cm² of the membrane. This corresponds to the accumulation about 0.03 mg of Alginate over 1 cm² of the membrane. Assuming that polysaccharide is accumulated in a layer of 100 μm, the concentration of alginate in the layer should reach approx. 2.92 g/L. This concentration corresponds to the concentration in a gel structure (Rolin et al., 1998), which being a network of randomly distributed chains, should act as a filter for transport of other macromolecules (Laurent, 1995). This network, as any filter, can be characterized by certain porosity and water permeability through it (Beeriaud et al., 1998; Cavalieri, 2006; Rolin, 1998). Therefore we can consider the fouling layer formed on the membrane surface as a semi permeable membrane itself. This assumption may be supported by figures 6a-b. Fig. 6a shows the AFM pictures of Alginate gel obtained from Alginate solution of 0.365 μg/L by centrifugation. Comparing these pictures to the AFM pictures of the membrane 6b we could see similar, but looser porous structures for the case of alginate as for the PES membrane. It is not

surprising, while Alginate has been used in different fields of separation for production of membranes (LaFrance et al., 1981; Patil et al., 2007). In case of more complex systems with some different polymers participating in the formation of the fouling layer we may expect similar behavior. It is a general phenomenon that two or more polymers with different properties may have limited miscibility in aqueous solutions. This behavior is characteristics of macromolecules because the entropy of mixing which strives at making molecules distribute evenly within the entire available space is much weaker for large molecules than for small once (the entropy of mixing is related to number of molecules rather than to their mass). In turn, the entropic strive against uniformity may be overcome even by relatively weak intermolecular forces (Morris, 1990; Berg, et al., 2007). Therefore, in case of mixed polymer systems, like for example Polysaccharides in the presence of humics, we could also expect the formation of the permeable gel layer of the polysaccharides with inhomogenously incorporated in it humics aggregates.

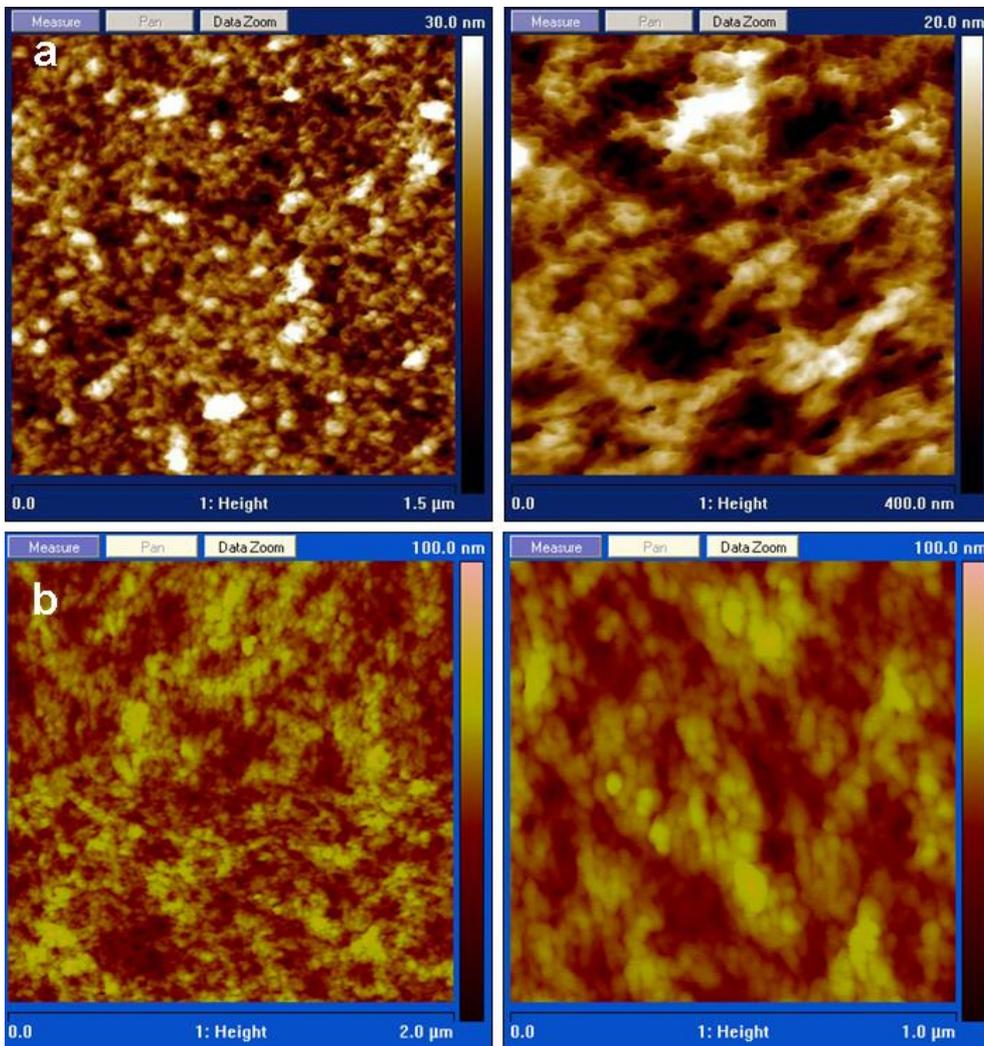


Fig.6 AFM Pictures of a - Alginate, b - clean PES membrane

3.6 Relevance to practice

Stabilization of the flux on a level of 10 L/hm² in model systems with polysaccharides under conditions of the long term filtration without backflushing has been observed and partly explained in paragraph 3.5.

If it is possible to observe the flux stabilization without backflushing also in systems working on natural water, it means it should be possible to produce up to 10 L/h of purified water from 1 m² of the membrane applying only 120 mbar of hydrostatic pressure (1.2 m water level difference). Such capacity exceeds the required capacity of the Point-of-use system (20-50 L/day).

Therefore, the smaller membrane surface can be used for the system, or/and system can be operated intermittently.

Besides of this, the results (fig. 2, 5) showed that flux stabilizes on the same level independently from the polysaccharides used or solution conditions, even if the initial flux pattern differs severely. Such independence of solution conditions may also be related with independence of flux after it is stabilized from the natural water matrix. This hypothesis should be studied in detail on different natural waters.

4 Conclusions

We have systematically investigated the impact of polysaccharide structure, availability of functional groups and molecular weight on membrane fouling in conditions suitable for POU systems: hydrostatic pressure of 120-150 mbar and limited or no backflushing. Our experimental results lead us to the following conclusions:

- Regarding the initial stage of flux decline (0-80 ml/cm²) the polysaccharide structure, and particularly availability of carboxyl groups, has a major impact on the membrane fouling, while the molecular weights of polysaccharides does not play a significant role (in the studied range of Mw 5-250 kDa).
- Presence of metal ions is also detrimental for the fouling: in general Ca, Fe and Ba are found to stabilize a gel structure of the fouling layer. The metal containing gel layers are in general more hydrated than the gels without metals, with water molecules trapped by hydrogen bonding in the gel matrix. The higher rate of hydration results in the higher permeability of the metal containing gels.
- In case of the impact of the ionic strength, an increase of permeability may be explained through the formation of hydrogen bonds. Hydrogen bonds can contribute to the swelling of polysaccharides in the solution and on the surface results that formed gel acts as a looser and more fluid structure.
- However, independently of the initial solution conditions, after approx. 80 ml has been filtered through 1 cm² of the membrane, flux becomes stable on the level of approx. 10 L/(hm²). The reasons of the long term flux stabilization are still not completely understood. However, we suppose that the gel layer formed by polysaccharides play a role of a “second” membrane on the surface of the PES UF membrane, keeping remaining permeability on the certain level, determined by the water retention properties of the gel structure.

In regard to practical application, obtained results open a new direction for the ultrafiltration in specific conditions of household systems. The long term ultrafiltration should be studied on natural waters to prove the flux stabilization phenomenon. This phenomenon may give a possibility to produce up to 10 L/h of water from 1 m² of the membrane applying only 120 mbar of hydrostatic pressure (1.2 m water level difference) without backflushing or crossflow, which may simplify the maintenance of the system and significantly reduce its costs. The required capacity of the Point-of-use system is 20-50 L/day. Therefore, the smaller membrane surface can be used for the system, or/and system can be operated intermittently.

Next activities in Techneau project will include the further evaluation of the long term ultrafiltration on natural waters; characterization of the impact of biofouling on the flux decline; and evaluation of the operational parameters of the Point-of-use system, based on the proposed above concept to treat at least 20 L/day.

5 Literature

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