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ULTRA-LOW PRESSURE ULTRAFILTRATION FOR DECENTRALIZED DRINKING WATER TREATMENT

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MARYNA PETER

M.S. Chem. Technol. and Eng.
National Technical University of Ukraine “KPI”

born 15.12.1981

citizen of Ukraine

accepted on the recommendation of
Prof. Dr. Willi Gujer
Dr. Wouter Pronk
Prof. Dr. TorOve Leiknes

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Abstract

Inadequate access to microbiologically safe drinking water continuously threatens the health and well-being of about a billion people, primarily in developing countries. Effective, low-cost and robust technologies are needed to redress this situation and meet the Millennium Development Goals for drinking water. Although ultrafiltration technology has become affordable for decentralized water treatment in developing countries, its widespread application is limited by membrane fouling and biofouling. Conventionally, regular backflushing, disinfection and chemical cleaning are applied in order to limit fouling, resulting in complex, expensive and maintenance intensive systems not suitable for application in developing countries. The goal of this thesis was to investigate a new approach to ultrafiltration and fouling control in order to develop a low-cost membrane-based decentralized system and reduce energy and chemical demand in membrane systems in general.

The stabilization of flux during dead-end ultrafiltration without backflushing, cross-flow or chemical cleaning under ultra-low pressure has not been observed before. This phenomenon allows gravity-driven ultrafiltration of surface water without any maintenance and pre-treatment at stable flux values of 4-10 $L \cdot h^{-1} \cdot m^{-2}$ for at least 6 months of operation at a hydrostatic pressure of 40-150 mbar, which corresponds to a height difference of about 0.4 - 1.5 m.

In this thesis, the phenomenon of flux stabilization is documented and evidence is provided that flux stabilization is related to biological processes leading to structural changes in the fouling layer. The development of cavities, channel networks and heterogeneous structures causes the decrease in resistance of the fouling layer. These processes counteract the increase of resistance of the fouling layer due to deposition, physico-chemical interactions and pore constriction due to irremovable fouling. The concentrations of biopolymers and low molecular weight compounds, the dissolved oxygen concentration and the concentration of colloidal humic acids are the major factors affecting flux stabilization. It is concluded that biofouling, always considered to be the major limitation of membrane processes and associated with reduced performance, actually causes stabilization of flux.

The phenomenon of flux stabilization can be implemented in simple low cost gravity-driven ultrafiltration systems for decentralized drinking water treatment. The stable flux value of 4-10 $L \cdot h^{-1} \cdot m^{-2}$ is sufficient to cover daily needs of water for drinking and cooking for a family of five people using less than 0.5 m^2 of membrane. While no pretreatment, pumps, chemicals or process control is required, the system costs could be kept low, especially when such systems can be produced or assembled locally. Furthermore, possibilities exist to further increase the capacity of the system. It is shown that the flux can be enhanced by intermittent operation as well as manual forward flushing of the membrane.

There is a great potential for application, but also a need for further investigation and system development of the ultra-low pressure ultrafiltration technology. Further investigation of the mechanisms of flux stabilization should enable prediction of the impact of feed water quality and operational parameters on the stable flux, and could lead to new strategies to improve the performance. Decentralized systems based on this concept should be further evaluated in field studies in order to assess maintenance requirements, financing schemes, system lifetime and socio-economic aspects. Furthermore, the phenomenon of flux stabilization can be explored in membrane bioreactors for wastewater treatment and re-use as well as in nanofiltration.

Zusammenfassung

Momentan haben weltweit ungefähr eine Milliarde Menschen kein Zugang zu keimfreien Trinkwasser. Ihre Gesundheit und ihr Wohlergehen sind dadurch gefährdet, wobei besonders Menschen in Entwicklungsländer davon betroffen sind. Einfache, effektive und kostengünstige Technologien werden benötigt um dem entgegenzuwirken und schließlich somit auch die Millenium Development Goals für Trinkwasser zu erreichen. Ultrafiltrationstechnologien in der dezentralen Wasseraufbereitung sind bereits in den Industrieländern zu erschwinglichen Preisen auf dem Markt. Probleme durch das auftretende Fouling und Biofouling der Membranen verhindern jedoch eine breite Anwendung. So müssen gängige Methoden wie Rückspülung, Desinfektion und chemische Reinigung eingesetzt werden, um dieses Fouling zu verringern oder weitestgehend zu vermeiden. Dies führt allerdings zu komplexen, teuren und auch wartungsintensiven Systemen, die so nicht in Entwicklungsländern eingesetzt werden können.

Ziel der vorliegenden Dissertation war es, einen neuen Ansatz zu erforschen, wie man mittels Ultrafiltration und einer möglichen Kontrolle des Foulings ein günstiges und einfaches dezentrales Membransystem, welches einen geringeren Energie- und Chemikalenverbrauch hat, entwickeln kann.

Die Stabilisierung des Durchflusses während einer Ultrafiltration im Dead-End Betrieb, ohne jegliche Rückspülung oder chemische Reinigung wurde bisher noch nicht entdeckt. Gerade aber dieses Phänomen ermöglicht eine schwerkraftgetriebene Ultrafiltration von Oberflächenwasser ohne große Wartung und Vorbehandlung. So sind Durchflussraten von 4-10 $L.h^{-1}m^{-2}$ während mindestens sechse Monaten Betrieb und einem hydrostatischem Druck von 40-150 mbar möglich. Dies würde einer Höhendifferenz von ca. 0.4- 1.5 m entsprechen.
Das Phänomen der Stabilisierung des Durchflusses wird in dieser Dissertation beschrieben und es wird gezeigt, dass die Stabilisierung mit biologischen Prozessen zusammenhängt, welche Veränderungen in der Struktur der Foulingschicht bewirken. So bewirkt die Entstehung von Hohlräumen, kanälchenartigen Netzwerken und verschiedenartiger Strukturen eine Abnahme der Widerstandsfähigkeit der Faulschicht. Dem wiederum stehen Prozesse gegenüber, welche eine Zunahme der Widerstandsfähigkeit, durch Sedimentation, physikalisch-chemische Einwirkungen und irreversible Porenverblockung, verursachen. Haupsächlich beeinflussen folgende Faktoren die Durchflussstabilierung: die Konzentration von Bipolymeren und leichten, niedermolekularen Stoffen, sowie die Konzentration von gelöstem Sauerstoff und kolloidaler Huminsäuren. So scheint das Biofouling, welches allgemein als grösste Einrschränkung bei Membranprozessen gilt, hier für die Stabilisierung des Durchflusses verantwortlich zu sein.

Dieses Phänomen der Durchflussstabilisierung kann für einfache, kostengünstige, schwerkraftgetrieben Ultrafiltrationssysteme für die dezentrale Trinkwasseraufbereitung verwendet werden. Die dauerhafte Durchflussrate von 4-10 $L.h^{-1}m^{-2}$ genügt bei der Verwendung von 0.5 m^2 Membranfläche, um den Wasserbedarf für Trinken und Kochen einer fünfköpfigen Familie zu decken. Da keine Vorbehandlung, Pumpen, Chemikalien oder Steuerungseinheiten benötigt werden, können die Systemkosten gering gehalten werden und ermöglichen besonders eine Produktion vor Ort. Zudem kann die Kapazität des Systems noch weiter gesteigert werden: bei periodischem Betrieb und bei manueller Spülung der Membrane kann der Durchfluss vergrössert werden.

Neben dem hohen Potential für die Anwendung, besteht aber auch noch Bedarf an weiteren Untersuchungen und der Entwicklung eines Systems für die Ultrafiltrationstechnologie unter

ultra tiefen Druckverhältnissen. Weitere Untersuchungen zum Mechanismus der Durchflussstabilisierung sind nötig, um z.B. den Einfluss der Rohwasserqualität zu quantifizieren und Möglichkeiten für Optimierung zu finden. Dezentrale Systeme welche auf dem hier geschilderten Ansatz basieren, sollten in Feldstudien weiter bewertet werden um Wartungsaufwand, Finanzierungsmodelle, Lebensdauer des Systems und sozio-ökonomische Aspekte abzuschätzen und zu betrachten. Zudem kann das Phänomen der Durchflussstabilisierung in Membran Bioreaktoren von Abwasserreinigungsanlagen und Brauchwasser-recycling und in der Nanofiltration weiter erforscht werden.

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Introduction

Introduction

Presently, about 900 million people lack access to improved drinking water sources (MDG, 2008). The worldwide-accepted Millennium Development Goals aim at reducing this number by 50% by the year 2015 (MDG, 2008). The main drinking-water risks in developing and transition countries are associated with microbial pollution (Montgomery and Elimelech, 2007). About two dozen infectious diseases are related to water quality and can be caused by bacteria, viruses, protozoa or larvae (Gadgil, 1998; Helmer, 1999). These water-borne diseases are predominantly due to fecal contamination of the water source and are thus strongly linked to the poor hygiene and sanitation conditions (Montgomery and Elimelech, 2007).

Most problems occur in developing and transition countries, where centralized water treatment systems often malfunction or do not exist at all. Implementation of large scale centralized systems requires considerable investments, infrastructure and engineering expertise which may not be available in these countries (Shannon et al., 2008). Based on conventional methods of water disinfection, centralized systems rely on chemically, energetically and operationally intensive treatment technologies that cannot be afforded or maintained on a long term (Shannon et al., 2008; Montgomery and Elimelech, 2007).

Even those who do have access to centralized drinking water treatment and distribution systems or other improved drinking water sources may still be exposed to health risks due to microbial contamination of drinking water, for two reasons. At first, “improved sources” are not necessarily safe: in a survey of six developing countries conducted by WHO and UNICEF it was found that only 69% of boreholes, and 43% of protected dug wells (both “improved sources” according to MDGs) met WHO guideline values for thermotolerant coliforms (JMP, 2010). Secondly, even if water is safe at the source, leaky distribution systems, unclean containers and poor hygiene practices such as dipping cups into a reservoir introduce pathogenic microorganisms to drinking water before consumption (Wright et al., 2004).

In response to these concerns, there is an increasing interest in Household Water Treatment and Safe Storage (HWTS), which has been associated with considerable reductions in disease, when applied in developing countries (Fewtrell et al., 2005). At present there are about 20 million users of household water treatment systems worldwide (WHO, HWTS). Furthermore, most of the rural communities in developing countries and many in industrialized countries rely on small community water treatment systems (WHO, SCWS).

Application of household water treatment is currently restricted by high costs, time-consuming daily operation and/or maintenance difficulties (Montgomery and Elimelech, 2007), aesthetic concerns (e.g. aversion of the taste of chlorine) and lack of consideration of consumer desires (WHO, 2009). In addition, efficiency of community systems is often limited by unqualified operation, lack of maintenance and high investment and operational costs. Therefore, a challenge exists to develop effective, low-cost, robust, user-friendly and less chemical- and energy-intensive technologies to disinfect water (Shannon et al., 2008) on household and community scale.

At the outset of this thesis the available technologies for decentralized drinking water treatment are reviewed and the potential of the membrane based systems for drinking water treatment is analyzed. It is shown that in principle, membrane technology is also attractive for the transition and developing countries because it provides absolute barriers for controlling hygiene hazards, and its modular construction allows implementation on all possible scales. Although this technology has become more efficient and the costs of membranes have decreased significantly (Churchhouse, 2000), it remains unaffordable and too complex for

decentralized applications in developing and transition countries. Research and development of membrane systems specifically for the developing countries is limited to isolated cases (e.g. Pillay and Buckley, 2003; Modise and Krieg, 2004, Arnal et al., 2007) and is often not published in the open literature. The overview of the available systems (Peter-Varbenates et al., 2009) has shown that only few membrane based systems designed for applications in developing countries exist, namely Skyjuice (SkyJuice, 2009) and Life Straw Family (Clasen et al., 2009)). However, the exiting systems do not fully comply with all of the performance criteria developed to evaluate the efficiency and potential for dissemination of the systems. Thus, the research and development needs for the membrane systems are indentified in order to develop a membrane system which would correspond to all of the performance criteria.

The focus of this thesis is on ultrafiltration (UF), while it provides an effective barrier for pathogenic microorganisms and can in principle be operated by gravity. However, membrane fouling and biofouling are considered to be the major limitation for the widespread application of UF (Shannon et al., 2008; Flemming et al., 1997). Polysaccharide and humic acids are well-known membrane foulants occurring in natural waters, leading to pore blocking, gel layer formation and adsorption (Jermann et al., 2007). If no anti-fouling measures are applied during ultrafiltration of surface waters, the foulants are retained on and in the membrane causing reduction of flux. Furthermore, microorganisms retained by the membrane tend to adhere to the membrane surface, excreting extracellular polymeric substances and leading to severe flux reduction due to biofouling (Meng, et al., 2009). Current approaches to prevent biofouling and fouling by natural organic matter (NOM-fouling) are energy intensive (e.g., backflushing, cross-flow) and chemical intensive (e.g., regular chemical cleaning) and therefore are not suitable in decentralized UF systems for developing countries. Thus, a new approach to control fouling and reduce the operation and maintenance requirements of UF based decentralized systems is needed.

The stabilization of flux during dead-end ultrafiltration without backflushing, cross-flow or chemical cleaning has not been observed before and is first documented in this study. This phenomenon allows operation of UF without any maintenance and pre-treatment at stable flux values of 4-10 $L \cdot h^{-1} \cdot m^{-2}$. These values are low compared to the flux typically used to operate the conventional UF systems (50-100 $L.h^{-1}m^{-2}$) but relevant for operation of UF on household and community scale. Thus, the phenomenon of flux stabilization is a focal point of the thesis, which focuses on the understanding of the mechanisms of this phenomenon and development of an UF technology based on it.

Goals and general research questions

Therefore, the **goals** of the thesis were:

- Assess the potential of membrane-based decentralized systems for applications in developing and transition countries and identify the research and development needs;
- Develop a new approach to membrane filtration processes and fouling control in order to develop a membrane-based system suitable for decentralized applications in developing or/and transition countries;
- Investigate the mechanisms of the phenomenon of flux stabilization in order to develop a technology based on this phenomenon;
- Investiagte the influence of operation parameters (e.g. transmembrane pressure, intermittent operation) on ultra-low pressure ultrafiltration in order to identify optimum conditions;
- Assess the limitations of ultra-low pressure ultrafiltration.

General research questions were identified as follows:

- What are the major limitations of membrane filtration and the available membrane based decentralized systems? *(Chapter 1)*

- What approaches can be used to allow implementation of ultrafiltration on decentralized scale in developing or/and transition countries? *(Chapters 1, 2)*

- What is the mechanism of the phenomenon of flux stabilization? *(Chapters 2, 3)*

- What factors affect the resistance of the fouling layer and irremovable fouling during UF under ultra-low pressure conditions? *(Chapters 2, 3)*

- Are there simple approaches to enhance flux and extend the service life of the system? *(Chapter 4)*

- What are further research and development needs to allow successful implementation of decentralized UF systems based on the phenomenon of flux stabilization? *(Outlook)*

The outline of the thesis

Chapter 1 "**Review: Decentralized Systems for Potable Water and the Potential of Membrane Technology"** discusses available decentralized systems that treat the potable water (drinking and cooking) of a single household (point-of-use systems) or a community (small scale systems). The review evaluates existing decentralized systems according to the performance criteria and assesses the potential for applying membrane-based decentralized systems. Moreover, the relevant research and development needs are identified in order to make the benefits of the membrane technology available to a larger part of the world population. The focus of this review is on disinfection (removal of pathogens), because microbial contamination remains one of the major threats to human health in developing and transition countries.

Chapter 2 "Stabilization of flux during ultra-low pressure ultrafiltration" shows that gravity-driven ultrafiltration of several types of surface waters under ultra-low pressure conditions, without flushing or cleaning, results in the formation of a biologically active fouling layer with a heterogeneous structure. Contrary to conventional membrane filtration theory, the hydraulic resistance of the fouling layer and water flux stabilize after about 1 week of operation. Evidence is provided that stabilization of the flux and resistance is caused by biologically-induced development of cavities and channels in the fouling layer. It is concluded that biofouilng, always considered to be "the Achilles heel of membrane processes" (Flemming et al., 1997) and associated with reduced performance, actually causes stabilization of flux. The phenomenon of flux stabilization can be implemented in simple low cost gravity-driven ultrafiltration systems for decentralized drinking water treatment and has a potential to reduce energy and chemical demand in membrane systems in general.

The focus of **Chapter 3 "Mechanisms of membrane fouling during ultra-low pressure ultrafiltration"** is on the role of different fractions of natural organic matter, particulate matter and dissolved oxygen conditions in the membrane fouling in ultra-low pressure ultrafiltration. The impact of the water quality parameters on the structure and resistance of the fouling layer and the role of irremovable fouling in the decline and stabilization of flux are

investigated using 7 types of water (14 water qualities). It is shown that the major stages of the fouling layer development and flux stabilization include deposition of the foulants in the fouling layer and structural changes within the layer, caused by biological growth and degradation. Irremovable fouling in ULP-UF contributes to 40-60% of the flux decline. Under conditions of a stable flux, the increase of resistance of the fouling layer due to deposition, physico-chemical interactions and resistance due to irremovable fouling counteracts the decline of resistance due to structural changes in the fouling layer.

In **Chapter 4 "Intermittent operation of ultra-low pressure ultrafiltration for decentralized drinking water treatment"** the impact of intermittent operation on stabilization of flux during ultra-low pressure ultrafiltration is investigated. The standstill periods of 3-19 h are studied during at least 3 month of dead-end operation without cleaning or backflushing under ultra-low pressure conditions. The impact of regular forward flushing of the membrane during continuous operation and after a standstill period is investigated in regard to the impact on stabilized flux and composition of the fouling layer. The mechanisms of flux recovery during a standstill period are discussed and a model to estimate the average stable flux and production capacity of the system depending on the duration of a standstill period is proposed for the river water studied.

In the **"General conclusions and outlook"** the major findings of the thesis are summarized and a potential for further development of ultra-low pressure ultrafiltration is assessed. 4 major directions for further development are identified, namely (1) understanding of the mechanisms of flux stabilization; (2) optimization of the process to enhance flux and increase removal efficiency; (3) development and implementation of decentralized membrane systems based on the phenomenon of flux stabilization; (4) exploration of this phenomenon in other membrane processes, such as NF and MBRs for wastewater treatment and water re-use.

In the **Appendix A**, a conference paper "**Operation and maintenance of decentralized drinking water treatment systems based on ultra-low pressure ultrafiltration**" discusses the results relevant for the implementation of the decentralized systems based on the phenomenon of flux stabilization. Choice and necessity of the pre-treatment and post-treatment are evaluated in regards to the capacity of the system. The efficiency of biological sand filtration as pre-treatment is discussed.

In the **Appendix B**, a conference paper "Low-pressure ultrafiltration and membrane fouling by polysaccharides" shows systematical investigation of the impact of polysaccharide and solution properties on UF membrane fouling in low-pressure membrane systems. The focus of this paper is on the impact of polysaccharide structure, composition and properties on the membrane fouling.

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Chapter 1

Review: Decentralized Systems for Potable Water and the Potential of Membrane Technology

Maryna Peter-Varbanets, Chris Zurbrügg, Chris Swartz, Wouter Pronk

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Review: Decentralized Systems for Potable Water and the Potential of Membrane Technology

Maryna Peter-Varbanets[1], Chris Zurbrügg[1], Chris Swartz[2], Wouter Pronk[1]
1: Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, CH-8600 Dübendorf, Switzerland.
2: Chris Swartz Water Utilization Engineers, PO Box 745, Mossel Bay, 6500, South Africa.

Abstract
Decentralized drinking-water systems are an important element in the process of reaching the Millennium Development Goals, as centralized systems are often deficient or non-existent in developing and transition countries (DC and TC). Most water-quality problems are due to hygiene factors and pathogens. A range of decentralized systems is available to counter these problems, including thermal and/or UV methods, physical removal and chemical treatment.
This review focuses on decentralized systems that treat the potable water (drinking and cooking) of a single household (point-of-use systems) or a community (small scale systems). For application in DC and TC, important boundary conditions for decentralized systems include low costs, ease of use, sustainability, low maintenance and independence of utilities (energy sources). Although some low-cost systems are available, their application is limited by time-consuming daily operation and maintenance. Other systems are too expensive for the poor populations of DC and TC and in most cases do not fulfill the system requirements described above. Point-of-use systems based on membranes are commercially available and are designed to operate on tap pressure or gravity.
Membrane systems are attractive since they provide an absolute barrier for pathogens and remove turbidity, thus increasing the palatability of the water. The costs of membrane have decreased rapidly during the last decades and therefore membrane systems also become in reach for application for low-cost applications in DC and TC. Some membrane systems rely on gravity as a driving force, thereby avoiding the use of pumps and electricity. On basis of the present literature data, no small scale systems could be identified which meet all the requirements for successful implementation. Furthermore, in the available literature the performance of highly fouling water types has not been reported. For such cases, more extensive studies are required and it a need for suitable pretreatment was identified.
It can be concluded that there are good perspectives for decentralized systems based on membranes, but that a need exists for research and development of systems with low costs and low maintenance, specifically designed for DC and TC.

1 Introduction
Global assessments by the WHO and UNICEF show that a large proportion of the world's population does not have access to adequate or microbiologically safe sources of water for drinking and other essential purposes: at the beginning of 2000, one-sixth of the world's population (1.1 billion people) were without access to adequate water supplies (Mara, 2003). Insufficient water supplies, sanitation, and hygiene contribute to 3.7% of globally quantified DALYs (indicator for the overall burden of disease) (WHO 2002). Target 10, described in the seventh millennium development goal (MDG), states that by 2015 the proportion of people without sustainable access to safe drinking water and sanitation should be halved as compared

to 1990 (UN, 2006). Considerable progress has been achieved in reaching these goals. According to the most recent sources, the percentage of people using drinking water from adequate sources increased from 71% in 1990 to 80% in 2004 (UN, 2006; WHO, 2004a). However, a large effort is still necessary to reach this goal by 2015. For example, the growing populations of Asia and Africa pose a major challenge, and there are wide disparities among countries and between rural and urban areas. It is foreseen that sub-Saharan Africa in particular will be unable to meet these goals by the year 2015 (WHO, 2004a). Moreover, even if this goal is reached by then, some 11-15% of the world's population will still remain without access to safe drinking water, and solutions are also needed as soon as possible for this large group of people. Evidently, most problems occur in the developing countries ("DC") as well as in the transition and rapidly industrializing countries (summarized by the abbreviation "TC"). This overview will focus on the problems occurring in DC and TC. The problems in developed/industrialized countries ("IC") will not be addressed explicitly unless related to the situation in DC/TC.

Problems with drinking water in the developing and transition countries often concern microbial pollutants, although organic and inorganic chemical pollutants can also play a role (Ashbolt, 2004). Infectious diarrhea is claimed to be responsible for most of the 1.7 million deaths per year (3.1% of all annual deaths) caused by poor water quality, sanitation and hygiene, and 9 of 10 of these deaths are children, virtually all in developing countries. Furthermore, 3.7% of the annual health burden worldwide (54.2 million disability adjusted life years (DALY)) is attributed to unsafe water, sanitation and hygiene (Ashbolt, 2004).

In urban and densely populated areas, the principle of "economy of scale" generally favors central solutions for the supply, distribution and treatment of water. However, many existing cases and examples show that such solutions often fail to achieve the desired results in DC and TC, mostly due to political or socio-economic factors (Zerah, 2000, Kyessi, 2005; Gadgil, 1998; Basu and Main, 2001). The outcome is an unreliable water service in terms of quantity and/or quality. It is clear that improving the water quality in an existing water supply system (including the raw water supply, water treatment plant and water distribution network) may be prohibitively costly and time-consuming, whereas only 2.5-5% of tap water is used for domestic consumption (drinking and cooking). Proposed solutions consequently revolve around setting up alternatives such as a separate dual-water supply system or ensuring point-of use treatment for drinking water. Nevertheless, in only a few cases has a dual water supply been officially recognized by the local authorities, notably in China (Daquing, China (Ma *et al.*, 1998)) and in Odessa, Ukraine (Strikalenko *et al.*, 1999). In many cases, the user reaction to the unreliable quality of water is widespread and heterogeneous installation of decentralized point-of-use treatment solutions, especially by the richer part of the population.

In rural areas of DC and TC, centralized drinking water treatment is in general prohibitively expensive, leading to the frequent use of untreated natural water sources (rivers, lakes, groundwater or rain). These sources are generally not well protected and may contain chemical or microbial pollutants, mostly derived from a lack of adequate sanitation and thus contaminated by human and animal excreta which are either active cases or carriers of disease (Gadgil, 1998). In rural or informal urban or peri-urban communities of DC, where a centralized water supply is lacking, decentralized systems are consequently often the only means to improve the quality of water obtained from contaminated sources.

When the necessary investments for the installation and operation of centralized or even small-scale water treatment plants are unavailable to the local authorities or community, it

remains up to the households to find their own solutions for water treatment or else bear the health consequences. Moreover, the economic viability of centralized systems is crucial in the sparsely populated rural areas of all countries (including industrialized countries), and a trend towards decentralized drinking water systems can also be observed in these cases.

The use of membrane systems has increased significantly, especially for water and wastewater treatment (Anon., 2006). While membrane sales were US$ 900 million in 1997 (Anon., 1999), the global market in cross-flow membrane systems for water and wastewater applications is expected to grow from US$ 6.7 billion in 2006 to US$ 10 billion in 2010 (Anon., 2006). Most large-scale applications of membrane technology are naturally found in the IC, but a large increase is expected in strongly growing economies like China (Anon., 2006). In principle, membrane technology is also attractive for the TC and DC because it provides absolute barriers for controlling hygiene hazards and its modular construction allows implementation on all possible scales. Although this technology has become more efficient and the costs of membranes have decreased significantly (Churchhouse, 2000), it remains unaffordable for the poorest part of the world population. Research and development of membrane systems aimed specifically for the DC remains limited to isolated cases (Wessels, 2000; Pillay and Buckley, 2003; Goldie *et al*, 2004; Modise and Krieg, 2004) and is often not published in the available literature (Pillay, 2006).

In the present review, an overview of available POU systems is given and the potential for applying membrane-based POU systems is assessed. Moreover, the relevant research and development needs are identified in order to make the benefits of this technology available to a larger part of the world population. The focus of this review is on disinfection (removal of pathogens), because microbial contamination remains one of the major threats to human health in DC and TC.

2 Problems of the water supply situation in developing and transition countries

2.1 Water quality and health

The main drinking-water risks in developing countries are associated with microbial pollution. About two dozen infectious diseases are related to water quality (Arnal *et al.*, 2001). Water-borne diseases are spread by the water acting as a passive carrier for the infecting pathogens. These diseases are predominantly due to fecal contamination of the water source and are thus strongly linked to the sanitation conditions. Use of such water for drinking and cooking, as well as contact with it and its ingestion during bathing and washing, or even inhalation of small droplets in the form of aerosols, may result in infection (Gadgil, 1998). These illnesses can be caused by viruses, bacteria, protozoa or larvae (e.g. cholera, typhoid, bacillary dysentry, infectious hepatitis, leptospirosis, giardiasis and gastroenteritis). Other microorganisms present in water are fungi, algae, rotifers and crustaceans (Arnal *et al.*, 2001). This is the most relevant category of water-supply diseases when discussing the issues surrounding drinking-water treatment. Other categories are water-based diseases caused by water supporting an essential part of the life cycle of infecting agents (e.g. aquatic snails and diseases such as schistosomiasis, dracunculosis, bilharziosis, philariosis and oncholersosis, as well as threadworm and other helminths). Water-related diseases are spread by vectors and insects that live in or close to water (e.g. mosquitoes, flies and insects) and include yellow fever, dengue fever, encephalitis, malaria, filariasis, sleeping sickness and onchocerciasis. Finally, washing-water diseases are caused by a lack of adequate quantities of water for the proper

maintenance of personal hygiene (e.g. scabies, trachoma (an eye-infection), leprosy, conjunctivitis, salmonellosis, ascariasis, trichuriasis and hookworm) (Ashbolt, 2004). A total of about 1400 species of infectious organisms known to be human pathogens have been recorded (Ashbolt, 2004). The minimum infectious dose for the average healthy adult varies widely for different microorganisms. It ranges from just a few organisms for *Salmonella typhi* (typhoid causing bacteria), to several hundred organisms for *Shigella flexneri* (dysentery-causing bacteria), and to several million cells of *Vibrio cholerae* (cholera-inducing cells). These doses are significantly lower for infants and small children than for the general adult population (Gadgil, 1998).
In DC and in some cases also in TC, water disinfection methods are generally not applied and cannot guarantee effectiveness even where they are applied. Currently, the most frequently used disinfection method in these countries consists of boiling the water. Given the high energy requirement for boiling and the often limited availability or affordability of energy sources, thermal treatment is frequently omitted. Besides, using wood as an energy source for boiling water results in deforestation (Sobsey, 2002). Consumption of untreated water causes a high rate of infections that, although not severe in most cases, have sometimes been the cause of major epidemics (Arnal *et al.*, 2001). Even if a disinfection agent – mostly chlorine gas or hypochlorite – is used, the presence of suspended matter and colloidal turbidity in the water can protect micro-organisms from effective disinfection and stimulate bacterial growth (Pryor *et al.*, 1998). Coliform organisms are generally accepted by the WHO as indicator organisms for fecal contamination of water and the possible presence of pathogens. Although other bacterial pathogens are less or comparably resistant to disinfection than the coliform organisms, enteroviruses and the cysts of some parasites are more resistant. Therefore, the absence of coliforms from disinfected water does not necessarily indicate the absence of enteroviruses and the cysts of *Cryptosporidium, Giardia*, amoebae and other parasites (Gadgil, 1998).

Arsenides and fluoride are among the best-known, widespread and significant naturally occurring waterborne chemical pollutants (Meenakshi and Majeshwari, 2006): guidelines define their maximum acceptable concentrations as 10 µg/l and 1.5 mg/l respectively. In severe problem areas, increased concentrations in drinking water can lead to skin diseases (e.g. hyperkeratosis), cancer (by arsenic poisoning) or crippling diseases (skeletal fluorosis) (Meenakshi and Majeshwari, 2006). These two chemicals alone affect something like a hundred million people in the developing countries (Gadgil, 1998). Besides these chemical pollutants, the WHO has set guidelines in the form of TDI (tolerable daily intake) values for the following elements: antimony, barium, boron, cadmium, chromium, copper, lead, manganese, mercury, molybdenum, nickel, selenium and uranium (WHO, 2004b). Guideline TDI values are also set for compounds and ionic groups such as cyanide, nitrate and nitrite. Health risks due to toxic chemical compounds can therefore originate from natural sources (e.g. fluorine, arsenic), industrial sources (e.g. heavy metals), and agricultural sources (e.g. pesticides) (Helmer, 1999). In addition to excessive concentrations, risks may also be due to deficiencies of chemical elements, such as iodine or fluoride (Helmer, 1999). The class of contaminants relating to agricultural sources is often neglected, but is of equally great importance considering that some 3 million people suffer from pesticide poisoning in the developing countries, resulting in a total of 220,000 deaths p.a. (WHO, 1992). Among the organic contaminants, the WHO guidelines address several toxic substances that increasingly find their way into drinking water supplies in the developing countries, where agricultural chemicals are commonly used without appropriate regulation and the chemical, dyestuff and process industries are spreading. This list contains chlorinated alkanes, chlorinated ethenes, aromatic hydrocarbons, chlorinated benzenes and 36 pesticides (Gadgil, 1998).

Typically the type of water pollution differs in developing, industrialized and transition countries. WHO statistics confirm that with regard to water quality, microbial contamination of the water supply is the major health risk in developing countries, while in industrialized countries the anthropogenic chemical contamination of drinking water is considered a more significant threat to human health, although the actual risks are low (Helmer, 1999). The urban populations of rapidly industrializing and transition countries of Asia and Eastern Europe are also increasingly facing health risks due to chemical hazards in drinking water. Gadgil states that there is evidence suggesting that the concentrations of anthropogenic chemical pollutants in the drinking water supplies of Eastern Europe and the former Soviet republics are much higher than in the rural areas of most developing countries (Gadgil, 1998). However, the traditional microbial contamination problem in these areas still has not been solved and remains the major threat to human health in some areas (Helmer, 1999; WHO, 2002).

People lacking access to adequate and safe water supplies are most at risk from water-borne diseases. In view of the importance of the water-supply service for health and wellbeing, it is crucial to have reliable knowledge about the status of this service as well as to understand the reasons for the increasing interest in household solutions.

2.2 The present situation in developing and transition countries

2.2.1 Rural communities

Rural communities are situated further away from the major centers. This often leads to reduced management and supervision capacities for water-supply infrastructures and services (Pryor, *et al*., 1998). Typically, centrally organized infrastructures and services are seldom available, and water is obtained individually from surface or underground water sources. The quality of the surface water is often critical and its quantity may also be limited in arid areas. Where an improved water-supply infrastructure is installed – typically with shared facilities such as bore wells with hand pumps – access is often a limiting factor, as either water availability is critical, the infrastructure has to be shared by many users or the facilities have fallen into disrepair (Lenton, 2004). Rural communities are generally unable to exploit economies of scale for such community-level water supply solutions. As a result, per-capita improvement costs are generally high, while the potential for cash contributions from households tends to be low. Where water supply infrastructures are already installed, inadequate financial resources for their operation and maintenance, the unavailability of spare parts or technical skills and/or weak institutional arrangements may negatively affect their sustainability (Lenton, 2004; Swartz, 2000; Momba et al., 2005).
If water treatment technology is used, it is often limited to removing suspended materials by means of media filters with or without coagulation. In such cases, operation and maintenance are essential and loss of filter media or infrequent washing can result in greatly reduced treatment efficiency. Slow sand filtration is also used in some cases, usually at smaller waterworks facilities. Although this achieves some natural disinfection, excessive raw water turbidities during seasons of high rainfall, inadequate operation of the filters with inappropriate flow rates or lack of flow control can result in an inefficient treatment process (Pryor, *et al*., 1998). Besides the technical and financial problems typical of rural communities, there is often also a lack of health-risk perception and related hygiene practice or any information on treatment products (Sobsey, 2002).

2.2.2 Urban and peri-urban areas

The concentration of large numbers of people created by rapid urbanization in the second half of the 20th century has produced a potential for distribution efficiencies unavailable to dispersed rural populations. Nevertheless, urban water management has often failed to benefit from this advantage to adequately supply rapidly growing urban populations with water (Basu and Main, 2001). In fact, the dynamics of these rapidly changing situations present a challenge to the provision of water infrastructure and services. Rapid urban population growth – consisting mostly of the poorest households – gives rise to massive shanty towns/slums where the establishment of a centralized infrastructure may be neither economically nor technically feasible (Basu and Main, 2001; Thomas and Ford, 2005).

The estimates of the populations in urban areas with access to a reliable water supply given by the WHO may be set too high (Sobsey, 2002): in some cities, water systems draw unsafe water from unprotected or contaminated sources and deliver it to consumers with no or inadequate treatment, despite being classified as improved and safe. This would imply that the number of people without direct access to safe drinking water may be very much higher than the 1.1 billion mentioned in the introduction.

Another problem contributing to the underestimation of the population served by unsafe water is the contamination of water during its distribution to homes via pipes or carriers. Many cities have protected or improved water supplies and treated water that is microbiologically safe when collected or when it leaves a treatment plant. However, the urban infrastructure for water distribution to consumers is sometimes so inadequate that infiltration of contaminated water can occur due to pressure drops and other intermittent pressure changes, or to deteriorating, open or leaking conveyances, illegal connections and other distribution system deficiencies, which leads to an increased risk of water-borne diseases (Sobsey, 2002). Moreover, in many large cities, including some of the world's megacities, peri-urban settlements are not served by the centralized water system for socio-cultural, economic, political, technological and other reasons. These urban dwellers are forced to make their own informal arrangements (Basu and Main, 2001). For example, in the city of Dhaka, Bangladesh, the number of informal settlements reached 3007 with a total population of 4 million in 1996. The formal system provided only 1643 street hydrants, forcing people to use hand pumps or obtain water from water vendors, unprotected dug-wells, ponds, rivers, canals and swamps (Akbar *et al.*, 2007).

Small towns and former villages that have expanded without their infrastructure systems evolving to a level comparable with large cities are normally excluded from both national water-supply programs targeting rural areas and those focused on cities. They are generally large enough to exploit some economies of scale for the water supply, but are too small and/or dispersed for traditional urban utility management models to operate effectively. These types of communities often have the economic capacity to make considerable improvements in their water supply, but the absence of a supportive institutional framework results in a variety of household-level solutions. As a result, some wealthier households install private wells while other users obtain water from vendors and/or surface water sources (Lenton, 2004).

2.3 Problems of the centralized water supply

The improvement and extension of water treatment remains an important and necessary objective of governments in many countries, and many development agencies assist in this endeavor (Mintz, 2001). Centralized water treatment and distribution may be feasible for densely populated settlements of DC given their economies of scale, and already exists in most cities and towns of TC. Where centralized water supplies exist, the renovation of water treatment technologies and distribution networks will improve the water supply situation.

However, this demands financial resources and as well as positive changes in water management operation and maintenance. Thus in the case of Targoviste, Romania, it was possible to reduce the cost of a water unit as well as water loss in the network (from 14 million m^3 in 1997 to less than 4.5 million m^3 in 1999) within two years by installing new pressure valves in the pumping system, making minor technical modifications backed up by strong media support and running information campaigns together with the installation of water meters in the apartments of private households (Mocanu, 2000).

In rural areas of DC and TC, investments for centralized systems are often unaffordable given the remote locations and lack of financial resources (see also § 2.2.1). In the rare cases where centralized systems are installed, the system often fails due to unprofessional maintenance and management (Lenton, 2004). Tap water from a supply network and a central water treatment facility is therefore generally unavailable in rural areas. Typically, water is accessed individually from surface water, groundwater or rainwater, with no source protection or water disinfection before consumption.

A further problem is that the traditional approach to making water/source infrastructure improvements has been influenced by the view that "contamination of water in the home is relatively unimportant". "What matters is whether the water coming out of the tap or pump is contaminated". However, this view is no longer valid (Moyo *et al.*, 2004): hygiene risks arise not only from the source water – contamination can also take place between source and point-of-use by several mechanisms (Wright *et al.* 2004; Clasen and Bastable, 2003). Thus recontamination was observed during the storage and handling of clean water due to unhygienic practices in the household in case studies in Zimbabwe (Moyo *et al.* 2004) and Honduras (Trevett *et al.* 2005). Contamination can also occur during storage in the household (Brick *et al.* 2004). In this case, promoting alternative water treatment options such as treatment at the POU is often the most feasible way of improving the water supply situation of the households.

In urban areas of developing countries, the inequality of water access and availability, i.e. where services are provided only to the richer part of the population through a central supply and distribution network, is due to political, institutional and economic reasons. Research undertaken by Akbar (Akbar *et al.*, 2007) shows that the employees of some public water providers prefer not to provide water to informal settlements because this would reduce extra income through bribes. In addition, informal dwellers are continually afraid of eviction, which discourages them from spending money on reliable water supplies (Akbar *et al.*, 2007). International assistance for water supplies through local or national government departments often does not reach the poor either (Islam 1997 in Akbar 2007). But it is a mistake to believe that the urban poor are unable or unwilling to pay for water. Some studies (Akbar 2005; Daniere and Takahashi, 1999) have shown that most of the poor are already paying higher rates than high-income communities.
It can be concluded from these arguments that approaches relying solely on centralized solutions may work in some regions of DC/TC, whereas in many cases structural problems which are unlikely to be resolved in the foreseeable future lead to malfunctions. Where governments are unable or unwilling to improve the water supply service, the concept of self-help or the involvement of the private sector in local water management often leads to the appearance and introduction of decentralized solutions. Nevertheless, the authorities still maintain the theoretical principle of centralized treatment while neglecting the support in terms of informational, political and economic factors required by decentralized approaches to treatment.

3 Decentralized solutions

Decentralized approaches to supplying water are already applied in many parts of the developing and transition countries. These decentralized solutions cover both quality and quantity problems and include the direct use of alternative water sources (ground or rain water), household water treatment systems, dual tap water treatment and distribution as well as delivery and sales of treated water. Despite their popularity in some cases, these installations often have an informal character and are rarely accepted or supported by local governments. Regional differences occur in their implementation due to the local socio-cultural, economic and political situation. However, some general situations can be identified in which these technologies are being or may be applied.

3.1 Solutions practiced in cases of limited water quantity

Groundwater wells

When a centralized water supply is not available or the quantity is limited, poor households have to rely on water obtained from rivers or shallow wells. Wells are often the preferred solution, as the distance to them may be shorter, access easier and the water considered to be less polluted. In many cases (Basu and Main, 2001; Palamuleni 2002; Moyo 2004), households build private shallow wells at their own cost, obtaining water for their family needs or sharing it with neighbors. Wells operated by hand pumps and tube wells with motor pumps are also common. They may be used by local water vendors or the local authorities to provide a community supply (Kyessi 2005), or by businesses, high-rise apartment blocks, hotels and restaurants in the cities (Basu and Main, 2001). However, there are several constraints on the construction and use of groundwater wells. If hydrogeological data are not available, an efficient planning of groundwater wells is challenging (Charalambous, 1982). Contaminations can occur if the wells are placed too close to sources of contamination or if the wells are too shallow. Furthermore, depletion can occur due to overdraft and salinization can occur in case of inadequate drainage (Schmoll *et al*., 2006; Konikow and Kendy, 2005).
For example, in Yemen the groundwater abstraction in the highland plains exceeds recharge by 400% (Shah *et al*., 2000). In the Fuyang river basin of North China, the water table of lower aquifiers decreased from 8 to 50 m within 30 years, while the industries polluted the upper once (Shah *et al*., 2000). Besides industrial, agricultural and domestic pollution, the groundwater contamination may be caused also by natural occurrence of Arsenic and Fluoride in some countries (As in Bangladesh, Nepal, Taiwan, etc.; Fluoride in Tanzania, South Africa, etc.) (Smedley and Kinniburgh, 2002; Schoeman and Steyn, 2000). If groundwater quality is unsatisfactory, additional treatment is necessary.

Rainwater harvesting

In some semi-arid areas of the world, a knowledge of rainwater harvesting technology has existed and been further developed for centuries. For example, in 50% of the area of Tanzania, people rely completely on rainwater for their survival (Mbilinyi *et al*., 2005). Rainwater harvesting provides water at the point of use and family members have full control of their own systems, which greatly reduces operation and maintenance problems. There are also examples of community rainwater harvesting systems, when water is collected from roads or fields (Gould and Nissen-Petersen, 1999). The disadvantages of rainwater harvesting are the seasonal variability in supply, the uncertainty of rainfall and often also the unreliable water quality due to infection and regrowth during storage. Harvesting water from roads, fields or even roofs after dry periods may also lead to contamination (Zhu *et al*., 2004). Other

non-conventional modes of access and use of water resources are outside the scope of this review and are described elsewhere (Qadir *et al.* 2007).

3.2 Solutions practiced for water quality problems

3.2.1 Point-of-use, point-of-entry and small-scale systems

If a centralized supply exists but distribution or treatment does not function, people have to resort to using ground water wells or carrying water home from rivers or ponds and/or have to put up with untreated river water or microbiologically contaminated water, and thus an increased risk of water-borne disease. The main precondition for the application of decentralized technologies to improve the water quality is active concern by households, community leaders or local NGOs. When the connection between water and disease is understood, the choice of solution depends on local customs, the availability of information and resources as well as the market and the required scale.

Because different definitions for decentralized systems exist, the following definitions will be used in the present paper: point-of-use (POU) systems treat only the part of water used for drinking. The minimum requirement for drinking water amounts to about 2 liters per person and day, while the maximum for drinking and cooking is 8 liters per day (DeZuane, 1997), which implies that the requirement for a four-member family amounts to 8-32 L/day. Point-of-entry (POE) systems refer to the treatment of all the water supplied to a household (Craun and Goodrich, 1999). The treatment capacity is therefore much higher than for POU systems (in the order of 100-150 L per person and day). Small-scale systems (SSS) usually refer to a system of larger scale than POU or POE, but with a distinctly smaller capacity than centralized systems. Typically, SSS treat the water consumed by several families or a small village. The capacity of SSS cannot be unequivocally defined, but usually varies between 1,000 – 10,000 L/day. The term "household systems" can refer both to POU and POE systems. The term "decentralized systems" can refer to POU, POE and SSS.

3.2.2 Available POU Technologies

In principle, all decentralized technologies can be applied in the same way as the centralized treatment of drinking water. For the smallest scale of systems, the POU systems, some specific technologies and systems have been developed, described and evaluated for household use on the basis of several performance criteria. Besides efficiency in improving the microbiological quality of the water and the system costs, these performance criteria include the ease of use of the system or technology, its environmental sustainability, socio-cultural acceptability and potential for dissemination (which includes also availability of skilled personal able to provide repairs, availability of spare parts, or required maintenance in general). A number of studies and considerable field experience have shown that the introduction of any POU water treatment technology without consideration of these criteria is unlikely to be either successful or sustainable (Sobsey, 2002). Moreover, systems for decentralized applications should preferably be independent of utilities such as electricity or tap pressure. Some of the POU systems will be discussed in the following part of this section on the basis of their performance criteria.

Most of these methods are already being explored or used in the DC/TC to some extent (see also Sobsey, 2002).

- Heat and UV-based systems:
    - Boiling with fuel
    - Solar radiation
    - SODIS (combined action of heat and solar UV)
    - UV lamps

- Chemical treatment methods
    - Coagulation, flocculation and precipitation
    - Adsorption
    - Ion exchange
    - Chemical disinfection
- Physical removal processes:
    - Sedimentation or settling
    - Filtration, including membranes, ceramic and fiber filters
    - Granular media filters, including sand filters
    - Aeration

Some of these methods, such as boiling with fuel, are traditionally and widely used, although they may not always be the optimal solution. Other methods (such as SODIS) have a high potential for application. Several of the methods listed will be discussed in more detail below.

3.2.2.1 Heat, UV and chemical disinfection

Boiling with fuel effectively destroys all classes of water-borne pathogens (Sobsey, 1989). However, a major disadvantage of boiling is its consumption of energy in relation to the availability, cost and sustainability of fuel. In areas of the world where wood, other biomass fuels or fossil fuels are in limited supply and must be purchased, the costs of boiling water are prohibitive. Therefore, boiling household water is considered unrealistic and inaccessible to many of the world's poorest people due to the scarcity and high cost of fuels and the lack of sustainability of biomass or fossil fuels in the community or region (Sobsey, 1989; Sobsey, 2002). Another problem of boiling is that it provides no residual protection: water can easily be recontaminated after cooling and is also associated with the risk of scalding, especially among infants (Mintz *et al.* 2001).

Solar Water Disinfection (SODIS) is a simple technology for improving the microbiological quality of drinking water by using solar radiation to destroy pathogenic microorganisms (Mintz *et al*., 2001).
The SODIS system consists of four basic steps: removing solids from highly turbid (>30 NTU) water by settling or filtration; placing low-turbidity water in clear PET bottles of 1-2 liter volume; aerating the water by shaking it in contact with air and exposing the filled, aerated bottles to full sunlight for about 5 hours (Mintz *et al.*, 2001; Reed *et al.*, 2000; Wegelin *et al.*, 1994, 2001). The system is suitable for treating small volumes of water (<10 l), especially if it is of relatively low turbidity (<30 NTU).
A potential limitation of SODIS besides its dependence on sunlight for disinfection is that the process is rather laborious. In order to ensure its daily supply, a family of four or more people would need upwards of 17 two-liter bottles. In some cases (Murcott, 2005), the drinking-water bottles discouraged people from using the clean water for anything besides drinking directly from the bottles.
Pasteurization without UV can also be carried out using solar energy. If the exterior of the vessel is completely black or similarly capable of absorbing heat (such as most metal containers), only thermal effects occur and temperatures can reach >60 ºC. Most enteric viruses, bacteria and parasites are rapidly inactivated at these temperatures (Ciochetti and Metcalf, 1984).

UV irradiation with lamps has received renewed interest in recent years because of its well-documented ability to extensively (>99.9%) inactivate two waterborne, chlorine-resistant

protozoans, *Cryptosporidium* parvum oocysts and *Giardia* lamblia cysts, at relatively low doses.
However, UV lamp disinfection has some disadvantages for use as a drinking water disinfectant at household level. Particulates, turbidity and certain dissolved constituents can interfere with or reduce the efficiency of microbial inactivation. A reliable and affordable source of electricity is required to power the UV lamps. These lamps require periodic cleaning, especially in the case of submerged lamps, they have a finite lifespan and must be periodically replaced (Gadgil, 1998). To make the cleaning and replacement possible, an efficient infrastructure is needed, which may not always be possible. This increases the operational costs of UV-based systems and impacts their environmental sustainability.

Chemical treatment is widely used for disinfection purposes. Of the drinking-water disinfectants, free chlorine is the simplest, most widely used and the most affordable. It is highly effective against nearly all water-borne pathogens, with the notable exception of *Cryptosporidium parvum* oocysts and the *Mycobacteria* species (Sobsey, 2002; Mintz *et al*., 2001; Clasen and Edmondson, 2006). Tablets or powders that combine a coagulant-flocculant and a chemical disinfectant have been described for POU treatment at household level (Rodda *et al*., 1993; Kfir *et al*., 1989). Extensive reductions of bacteria, viruses and parasites were reported, and the costs of treatment were estimated to be relatively low (US$ 0.01 per liter). However, the socio-cultural acceptance of disinfection with chlorine-containing reagents tended to be low in some cases, due to taste and odor problems (Murcott, 2005). Moreover, if insufficient time intervals are applied for reaction and sedimentation, the effectiveness of these methods is low.

3.2.2.2 Physical removal processes

Several types of media can be used, including granular media of various grain sizes. Such mechanical filters may be an attractive option for household treatment because they can be produced on the spot with locally available materials; they are mostly simple, easy to use and potentially long-lived (Wegelin *et al.*, 1991; Galvan and Victorica, 1997; Lantagne *et al.*, 2007).
However, regular cleaning is required to maintain flow rates at acceptable levels, so that some skills and knowledge are required to operate and maintain these filters, unless they are fully automated (Burch and Thomas, 1998).

Slow sand filtration has been adapted for use in the home and is known as Biosand filtration (BSF). Biosand filters are containers filled with sand in which a bioactive layer is allowed to grow as a means of eliminating disease-causing organisms. Laboratory and field tests showed that BSF removes bacteria consistently if not completely, on average by 81-100%, and protozoa by 99.98-100%. However, these filters have limited virus-removal efficiency (Lantagne *et al.*, 2007; Kaiser, et al., 2002).
Furthermore, paper, fiber or fabric filters may be applied at household level. They can be effective in the removal of larger water-borne pathogens such as free-swimming larval forms (cercariae) of schistosomes and *Faciola* species, guinea worm larvae within their intermediate crustacean host (*Cyclops*), and bacterial pathogens associated with relatively large copepods and other zooplankton in water, such as the bacterium *Vibrio cholerae* (Sobsey, 2002; Huq *et al*., 1996). However, these filters are not recommended for the general treatment of household water because their pores are too large to significantly retain viruses, bacteria and smaller protozoan parasites (Sobsey, 2002; Sobsey *et al*., 2008).

Activated carbon filters, often in the form of pressed blocks, followed by UV disinfection or silver (Ag) pre-coating, are being used as table-top units for additional tap water treatment in TC (Ecosoft, 2007) and IC (Abbaszadegan *et al.*, 1996). However, they have only a limited operating life (six months in the case of Ecosoft) and relatively high costs, making them unaffordable to most of the population in DC.
Membrane processes, including ceramic membranes, can also be considered as filtration processes. They will be discussed in more detail later (Section 0).

3.2.3 Available small scale systems (SSS)

Small-scale systems (SSS) are defined as systems of larger capacity than POU or POE systems, but smaller than centralized systems Typically, SSS treat the water consumed by several families or a small village (around 1,000 – 10,000 L/day).

In principle, most of the POU methods described above can also be applied for SSS. Also technologies usually applied on a large scale may be adapted for decentralized or emergency use. For example, liquid chlorine or chlorine oxide dosage may be replaced by chlorine tablets or coagulant/flocculant mixing is conducted in pipes (Oxfam, 2001). Slow sand filtration is often used for community water treatment in DC often in combination with roughing filter, when maintenance or transport of chemicals is limited or not possible (Wagner and Lanoix, 1959; UNHCR, 1992; LeChavallier and Au, 2004). For example, the ICRC applied roughing and slow sand filters in Iraq as emergency systems (ICRC News, 2003).

3.2.4 Areas of application of POU, POE and SSS

The main reasons for and objectives of their applications, the types of water treated and the main initial requirements for successful installation and operation differ for POU, POE and SSS.
POU systems are represented by a variety of technologies for treating surface, ground or rain-water, as well as poorly treated or stored tap water. Whether used in a traditional way (boiling), introduced by NGOs or the market, they are currently applied widely by households with different financial resources in DC, TC and sometimes even IC (Sobsey, 2002).
The necessary requirements for the successful application of POU treatment methods are the awareness of the population, the availability of information, low initial costs (for the local households) as well as low operational costs, simple maintenance and ability to control the efficiency of treatment.
POE systems are mostly used in IC; their application in TC and DC is limited to the supplementary treatment of tap or good quality well-water for the homes of rich people and hotels as well as childcare and medical institutions (Tsvetkova and Grinkevich, 2004). As they are often built on the basis of multi-stage treatment technology, qualified periodical control and maintenance are needed for their stable operation (Craun and Goodrich, 1999).
The most typical application of SSS in DC is for the community water supply (Pryor *et al.*, 1998; Arnal *et al.*, 2001; Burch and Thomas, 1998). However, in some cases SSS are used in the private sector of TC and DC for the production of bottled and treated water intended for water kiosks and private deliveries (Strikalenko *et al.*, 1999). The availability of financial resources and organizational support are the critical factors for the construction and operation of SSS for the community supply, which also requires the involvement of NGOs, government or local community leaders. In both cases, qualified operation and maintenance are required to assure stable operation (Burch and Thomas, 1998).

In case of emergency, special SSS are already in use (Arnal *et al.*, 2007). However, one of the main problems here is the response time of international organizations to deliver and install water-treatment material, which is normally around 10 days (Arnal *et al.*, 2001). Container-based systems which do not require any on-site installation are consequently needed in these cases. POU systems are rarely applied in such cases, as the time and infrastructure needed for people to learn and adopt these methods are currently not available. However, some examples of successful applications exist, including distribution of hydration bags based on the forward osmosis principle (Cath et al., 2006).

3.2.5 Dual water systems

Although a centralized water supply system exists in many urban situations, the water quality may not be reliable for the reasons discussed in Chapter 2. A dual water supply system can make good sense in such cases.

In principle, two types of dual water systems exist:

Type I: Dual central treatment, dual distribution system: water of two different qualities is produced and distributed, one for drinking and one for general use.

Type II: Central treatment for household purposes, decentralized treatment for drinking water quality

As an example, the first concept (dual distribution systems) is used for the IJburg district of the city of Amsterdam in the Netherlands (van der Hoek *et al*., 1999) and in Hong Kong (Tang *et al*., 2007). In the case of Rousehill (Sydney, Australia), recycled water from waste-water effluent is used for non-potable domestic sources (Law, 1996).

The second concept (central supply, decentralized treatment) was proposed for city of Daquing, China (Ma *et al*., 1998), with a population of 1 million. In this city, the costs and time frame required to improve the whole water supply system were considered to be unacceptably high, and a Type II dual water supply system was therefore proposed as an alternative. Decentralized "polishing" water-treatment plants (based on ozonation & membrane technology) fed with tap water were set up in seven of the city's districts for treating and distributing this 2.5-5% of the water. The distribution of treated potable water was organized separately with an independent network or with bottles (Ma *et al*., 1998).

Although a distribution system exists in Odessa, Ukraine, the water is not of drinking quality. The government has recognized that it is not feasible to improve the situation centrally and supports water kiosks instead. A large number of POU/POE systems are also applied (Strikalenko *et al.*, 1999).

4 Membrane-based decentralized systems

4.1 Membrane technology

In general, membrane processes are characterized by the use of a semi-permeable film (membrane) and a driving force (Mulder, 2000). The driving force can be a difference in pressure, concentration, temperature or electric potential. Most membrane processes are pressure-driven and are commonly referred to as membrane filtration processes. In water treatment, however, electrically driven (electrodialysis) and thermally driven processes (e.g. membrane distillation) are also used. For POU systems, only membrane filtration processes are currently considered. The separation range of membrane processes is shown in Fig. 1.

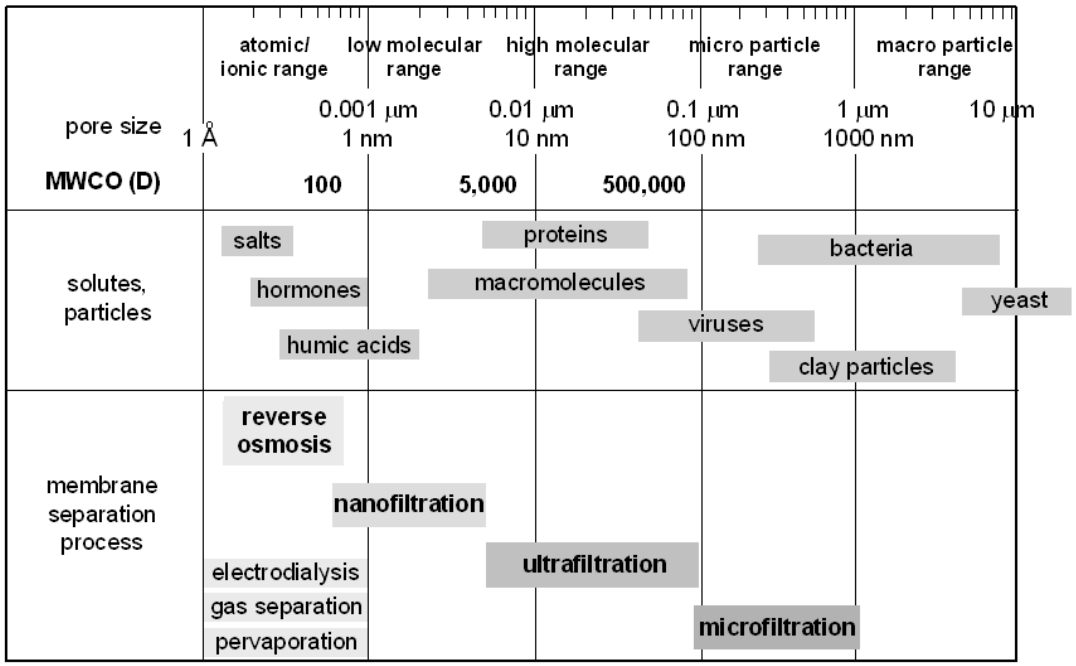


Fig. 1 - Membrane separation processes, pore sizes, molecular weight cut-off (MWCO) and examples of sizes of solutes and particles.

As regards the production of drinking water, it is important to assess membrane technologies in relation to water-borne contaminants. The pore size of ultrafiltration (UF) membranes is small enough to ensure high log-removal of all kinds of microbiological hazards such as *Cryptosporidia*, *Giardia* and total bacterial counts (Hagen, 1998). Microfiltration (MF) is also claimed to have these properties, but some doubts have recently arisen with respect to bacterial retention by these membranes (Wang *et al.*, 2007). Substantial virus removal can be attained with UF membranes since the size of viruses is in the range of 30-300 nm.
Nanofiltration (NF) and reverse osmosis (RO) can be used to remove inorganic contaminants from water. Most NF membranes are effective in removing bivalent ions (typical retention >90%), but RO membranes are required for monovalent ions. For example, desalination of seawater or brackish water is currently performed with RO membranes.

In comparison to conventional water treatment, the main advantages of membrane processes are that in principle water can be treated in one stage without chemicals or utilities, while the treatment footprint is relatively small. The developments in the membrane technology field during the last decades resulted in a significant decrease of membrane costs and energy requirements (Churchhouse, 2000). In addition, membrane systems are built in a modular form which enables easy adaptation of process scale.
However, the main limitation of membrane systems is membrane fouling. Fouling prevention measures for MF and UF usually include regular backflushing (approximately every 30 min in large scale applications) and chemical cleaning. In case of NF and RO, pre-treatment is usually used, and the systems are being operated in a cross-flow mode. Such fouling prevention measures require automated process control and regulation, resulting in increased investment costs.

4.2 Decentralized membrane systems available

The same industrial-grade membranes used in large-scale water treatment plants around the globe have been incorporated into POU/POE water purifiers. They were developed for residential and small commercial/industrial applications. Initially developed in IC and for IC, these systems are being increasingly used in TC to improve quality of available tap or groundwater.

The global directory for environmental technology (GreenPages, 2007) presents 531 companies (governmental and nongovernmental organizations, utility companies, importers, engineering consultants etc.) working on the market or in membrane technology mostly in IC and TC. At least a quarter of them produce, import or provide services involving POU/POE membrane-based systems. Small scale systems also employ similar membrane processes as for large scale applications. Many of these systems were initially developed for emergency water supply, but also systems are available which are specifically designed for remote areas in DC and TC (Hoa *et al*., 2008). As the literature presents only limited systematic data on these kinds of systems, the overview presented below is based mainly on market information and reports of NGOs.

4.2.1 RO-based systems

Most commercially available POU systems in IC use reverse osmosis membranes as a key element of water treatment. In general, RO-based POU water treatment is a multi-stage process that includes pretreatment and post treatment stages in addition to an RO spiral-wound membrane module (AMI, 2007; AMPAC, 2007; APEC, 2007; FountainSofteners, 2007; Novatec, 2007; WESE, 2007; WGSI, 2007).

Typical pretreatment stages include sediment filters or microfilters and activated carbon. Post-treatment stages used in the system also include activated carbon filters. Such systems are normally installed to purify tap water from a centralized supply in IC, and can be placed under a sink in a kitchen. They work without an electricity supply, the necessary pressure being provided by the feed tap water in the system. The maintenance of the system in most cases requires the replacement of pre- and post- filters once in 6-18 month, while membrane lifetime is 2-3 years. The price of the system varies according to the flow rate in the range from US$ 200 to 700 (APEC, NOVATEC, AMI membranes, etc.). Their annual operation costs are approx. US$ 85-135.

Being designed to treat tap water in IC, most systems also have limitations with respect to the allowable feed water quality. In general, these kinds of multiple-stage RO systems are complex and relatively expensive installations that require service and replacement of parts and a defined source-water quality. So their application in DC is not realistic even if they are widely used and accepted in IC. However, these systems can be increasingly found on the market in TC for secondary treatment of tap water.

An RO-based system designed to be used independently of energy sources was developed by Schafer *et al.* (2005). This "ROSI" system is designed to treat water from a variety of sources, ranging from highly turbid surface waters to highly saline brackish waters. The filtration process consists of two stages - the pretreatment stage using an ultrafiltration membrane is followed by the desalination stage using an RO or NF membrane. The UF membrane removes most pathogens such as bacteria as well as particles and some colloidal material, thus protecting the RO/NF membrane from excessive fouling, in particular bio-fouling, and reducing the cleaning frequency of the modules (Schafer *et al.,* 2005). Being equipped with photovoltaic or solar modules, the ROSI system is may be used independently of any energy sources in regions with a high sunshine intensity. The ROSI system was tested in remote rural areas in Australia. There are no published data on costs of this system. The equipment is

relatively complex, including UF, RO and photovoltaic modules. Therefore, the investment costs are expected to be high, and maintenance is required by qualified personnel.

Reverse Osmosis technology has been also used for brackish or sea water desalination in emergency situations. There are few systems available from different producers (Emergency Seawater 800, (Big brand water filter, 2008); MORO AQUAMOVE (Elaga-Berkefeld); GE Emergency RO (GE, 2008), etc.). Generally, these systems are driven by electicity or gasoline engines, and are equipped with several pre-treatment stages (Sediment filtration, MF, UF). The systems require relatively good raw water, are relatively expensive (approx. US$ 10,000) and require maintenance, which considerable limits their application.

An example of application of forward osmosis for POU water treatment in emergency situations is a hydration bag (Hydration technologies, 2008). In the hydration bags, a consumable draw solution (e.g. sugar or beverage powder) is packed in a sealed bag made of semi-permeable forward osmosis membrane. Upon immersion of the bag, water diffuses through the membrane due to the osmotic pressure difference and dilutes the initial solution. At the end of the process, the diluted draw solution may be consumed as a sweet drink containing nutrients and minerals (Cath et al., 2006).

4.2.2 UF-based systems

As pointed out above (Chapter 2.1), most water-quality problems are due to pathogens, which are completely retained by ultrafiltration membranes (see Figure 1). Moreover, these membranes require significantly lower pressures than RO membranes, due to the latter's higher resistance and because RO generates an osmotic pressure which counteracts the water transport through the membrane. Nevertheless, POU systems based on ultrafiltration technology are not used widely for treating household drinking water. Some POE technologies are available on the market, and some of them also have a pretreatment stage and hollow-fiber membrane modules.
One of the few UF-based POU systems existing is LifeStraw Family from Vestergaard Frandsen (LifeStraw, 2008). The system consists of a UF module (20 nm pore size), a pre-filter for reducing turbidity and a chlorine chamber. A feed water tank, connected to the module by a flexible hose, is placed elevated to create a pressure of 100-150 mbar. The module has to be manually backwashed once in 1-2 days. A first assessment of LifeStraw Family by the University of Arizona showed stable operation and high efficiency of bacteria and virus reduction during filtration of 18,000 L of water (Turbidity 100 NTU, TOC 10 mg/L) with a final flowrate of 6-8 L/h. The system is being currently tested in Congo and China.

One of the most widely used in IC and TC home tap water-treatment systems based on ultrafiltration POE and suitable for a wide range of feed water qualities is Homespring® developed by Zenon (Homespring, 2007). This kind of system is supposed to provide good quality water to the whole home (POE). It also includes a pretreatment stage with an activated carbon filter. The hollow-fiber ultrafiltration membrane is a key part of the system, supposed to remove bacteria, cysts and viruses. The system is designed to treat surface, well or tap water without any other pretreatment. Homespring is intended to be used with existing pressures (e.g. from the tap water) and requires annual maintenance. The carbon filter capacity is the limiting parameter of the process capacity and the filter needs to be replaced once a year. These systems are designed to provide a continuous flow of 14-17 L/min, or approx. 840-1020 L/h (20,160 - 24,480 L/day).

Another domestic POE UF system, manufactured by MEMFIL, is available on the market in Malaysia, China and Singapore. According to the information given by the manufacturer (MEMFIL, 2007), this system is also based on a hollow-fiber module but is designed for higher flows from 1500 to 3000 L/h (36,000-72,000 L/day). Its operating pressure varies from 1.5 to 3.5 bar and either tap pressure or a pump should be used. The peculiarity of this system is that it normally needs back-flushing only once a week, which should be done manually by the household through closing and opening some valves (in large scale application UF membranes are usually backflushed every 30 min). It also has a limitation on raw water quality: the source water turbidity should not exceed 20 NTU. It is normally used for the additional treatment of tap water or for deep ground-water wells.
From the limited information available, the module available from Malaysian company Hezong Trading Sdn Bhd (Hezong Trading Sdn Bhd, 2007) appears to be very close to the MEMFIL® system. However, it has a flow rate of 2200 L/h (52,800 L/day) and operates only on tap water.

Three low-pressure ultrafiltration membrane systems have been tested in South Africa for community water supply (Pryor et al., 1998, Jacobs et al, 2000; Jacobs et al, 2004). They were tested on surface waters containing high levels of suspended matter and occasional occurrences of algal blooms and diffuse pollution caused by surface runoff into the rivers. The plants were designed to supply 10,000 L/day of treated water in cross-flow mode and required regular cleaning. Detergent and complexing agents were used to clean the system when operating on waters with a high organic load, whereas sodium hypochlorite was used when the plant operated in conditions of lower organic pollution. The low plant operating pressure of 100 - 150 kPa enabled the process to be applied to rural and peri-urban applications by utilizing the head of water without a need for a feed pump. A recycle pump was used in these pilot plants, so that an energy source (electricity) is required (Pryor *et al.*, 1998; Jacobs *et al*, 2000; Jacobs *et al*, 2004).

Arnal (Arnal *et al.* 2001) proposed an ultrafiltration module also suitable for application to urban supply systems in developing countries. The proposed membrane module has a treatment capacity of 1000 L/day when operating at maximum efficiency and the number of modules can be extended, with a consequent increase in the treated product flow, adapted to the specific case and demand. The module is equipped with a polysulfone spiral-wound membrane with a molecular weight cut-off of 100 kDa. Before the feed water enters the feed tank of the UF facility, it is firstly pretreated in a series of different filtration units:

- coarse filter
- microfilter (500 μm)
- security filter (5 μm)

The equipment was modified to supply water directly from a source to small geographically isolated communities with no water or electricity supply. The module was equipped with a manually operated wheel whose rotation produces energy for the pump. This manual ultrafiltration plant can provide water for direct consumption of up to 300 persons when working at top efficiency (Arnal *et al.* 2001; Arnal *et al.* 2002; Arnal *et al.* 2004). The projected manual plant does not require any fuel or additional power source, thus facilitating its application, and has a compact design to assure easy handling and transport (Arnal *et al.* 2001).
A similar UF small scale plant has been installed in Ecuador for supplying the local community with water. Its production capacity is 480,000 L/day and it was designed to work only on hydrostatic pressure. A sand filter and a 50 μm pre-filter are used for the pre-

treatment. The water from this plant is also used for the production of milk and meat-based products by a local agro-company (Arnal *et al.*, 2007).

Skid-mounted or container-based systems are available for the continuous production of drinking water or as an emergency solution (e.g. floods, hurricanes). These small-scale systems, available from producers such as Opalium (France) (Opalium, 2007), can be equipped with MF or UF membranes, depending on the application, and are adapted to a wide range of source-water qualities, including surface waters with high NOM concentrations. The UF membrane modules of the OPAMEM type (Opalium, 2007), developed by Opalium (France), are hollow-fiber modules with a nominal pore size of 0.01 µm, made from chlorine-resistant polyethersulphone. The unit operates in dead-end or cross-flow inside-outside mode with backwashing for cleaning and has a capacity of up to 5,760,000 L/day per unit.
The Perfector-E® water purification system from X-Flow (NORIT, the Netherlands) was specially designed for supplying water to the tsunami victims in Asia by treating heavily polluted surface water. According to their information (X-Flow, 2007), it uses a two-stage pre-treatment process consisting of a coarse filter and two parallel micro-strainers. The main treatment stage consists of two UF dead-end modules operated with backflushing as well as an optional UV disinfection barrier. The system may be operated by unskilled personal but is rather expensive (approx. US$ 26,000).
There are also examples of using UF units as a pretreatment stage for NF or RO treatment. The ROSI system, developed by (Schafer, 2005), is described above (4.2.1).

4.2.3 MF-based systems

Ceramic microfiltration is among the few membrane technologies applied in DC and recommended by the WHO (Sobsey, 2002). Most ceramic MF membranes are available in the form of monoliths or hollow cylindrical tubes and have a nominal pore size of around 0.2 µm (Clasen *et al.*, 2004). Due to its pore size, such filters provide a complete protection to bacteria, but only a partial protection to viruses (size range of 30-300 nm). Filters produced and distributed in DC are normally in the form of pots (e.g. clay pots) and their pore size is larger, normally reaching 0.6-3.0 µm (Lantange *et al.,* 2007). As filterable bacteria range well below 0.6 µm (Wang *et al.,* 2007), size exclusion alone in principle cannot provide a complete disinfection with this kind of filters. Many commercially produced ceramic filters are impregnated with colloidal silver to act as an additional disinfection step and prevent biofilm formation on the filter (Sobsey, 2002). Pore constriction or cake layer formation can be an additional mechanism of removal. Thus, the efficiency of removing bacteria depends on the filter configuration and the mode of production. Filters produced in IC generally show superior performance in removing bacteria and viruses than those produced in DC (Sobsey, 2002). The rate of bacteria removal by the ceramic filters distributed widely by "Potters for Peace" reaches 99.99 % in laboratory tests, for example. However, their effectiveness in inactivating and removing viruses is unknown and their performance in field applications has not been evaluated (Lantange *et al.*, 2007).
Microfiltration is being increasingly used in POU systems developed in IC for travelers from the IC. One of the best known systems is produced by Katadyn, Switzerland. The filters consist of ceramic 0.2 µm membrane, and are operated by gravity or a handpump. These portable systems may be used also on turbid and polluted with organic matter water, but their lifetime is limited to 20,000 - 100,000 L of filtered water depending on raw water quality and type, and the costs are relatively high (US$ 250-600)
A new application of microfiltration is the "FilterPen" from the FilterPen Co of New Zealand and Filtrix Co of The Netherlands (Filtrix, 2007). The concept of "point-of-use" is applied

here in its most decentralized form, whereby the source water is sucked through a straw-like device which is actually a microfiltration membrane. The membrane has an average pore size of 0.15 μm and a surface area of 0.02 m^2. Initial (clean water) flow rates are about 0.1 L/min at a pressure difference of 0.1 bar. According to the manufacturer data, depending on the feed water quality, the service life is approximately 4 weeks or 100 L of treated water (which corresponds to a water production of about 3.5 L/day). The membrane material is a blend of different polymers (PES, PVP and PP). Filtrix has been developed for travelers from IC going to DC, and now is also used by the German Military based in DC.
LifeStraw Personal is a similar product by Vestergaard Frandsen developed for personal use for people in DC traveling away from home for long periods of time (e.g. shepherds). Original purpose of this membrane filter was to protect people from Guinea Worm Disease, however, filter showed also Log 6 efficiency in removal of waterborne bacteria and Log 2 efficiency against viruses. The life time of the LifeStraw is limited to the filtration of approx. 700 L of water.
SkyHydrant unit (SMF-1) developed by SkyJuice Foundation (Australia) is intended for community water supply in DC and disaster relief applications. This process combines MF (membrane pore size of 0.1 μm) with chlorine disinfection, and may be operated on hydrostatic pressure of at least 30 mbar. The membrane has to be backflushed manually every 1 to 12 hours depending on the water quality, and regularly washed with 10% Hypochlorite solution. Thus, the system requires a more or less skilled operator. SMF-1 is adapted to highly turbid waters (max 500 NTU) and has been implemented in approx. 10 countries in South East and Central Asia and South America (SkyJuice, 2008).

Microfiltration was combined with biological degradation in a membrane bioreactor for producing drinking water from contaminated surface water sources by Li and Chu (2003). Membrane bioreactors are normally applied for waste-water treatment, but in this case a drinking water application was investigated. The process was found to increase the biological stability of the water as well as to reduce the trihalomethane formation potential. The process was operated for 500 days with three chemical cleaning steps and weekly physical washing (Li and Chu, 2003). However, the process has not been tested in the DC yet.
Woven filters based on fine polyamide fibers were developed by Pillay (2006). Because the spaces between the fibers are in the range of micrometers, this material could be considered as a microfiltration membrane. The materials and production costs are relatively low, which in principle makes their application suitable for the poor. Cleaning can be carried out mechanically or by drying combined with mechanical cleaning, as the sheets are resistant to wear and insensitive to drying. Development and characterization of these sheets is currently in progress, but their ability to retain bacteria has not yet been confirmed (Pillay, 2006).
A fast response emergency water treatment unit has been developed also at the University of Kassel (Frechen, 2007). The MF membrane module is driven by gravity, is chemical free, may be carried by one person (<25 kg dry weight) and operated by non-trained persons. It is intended to treat highly polluted water for 200-500 people during first 5-10 days after a disaster. The main idea behind this system is to provide simple water treatment to cover the time gap until disaster relief teams are able to deliver, install or repair long term drinking water supply systems (Frechen, 2007).

5 Suitability of decentralized systems for developing and transition countries

5.1 Evaluation of decentralized systems

In section 3.2.2, the performance criteria for decentralized systems (including POU, POE and SSS) were discussed. In Table 1, the available decentralized systems are evaluated against these criteria. The upper part of the Table 1 summarizes systems for DC, while the lower part represents systems mainly developed and used in IC and TC (including membrane systems). The meaning of the symbols in Table 1 is explained below.

Performance: "++": the produced water is microbiologically safe according to WHO standards if the treatment is performed correctly; "+": water produced by the system is safe only under certain conditions (e.g. if raw water is not turbid) or the system is efficient against most of the pathogenic microorganisms with few exceptions.

Ease of use: "++": daily operation is limited to filling in of raw water and collection of treated water; "+": require additional (time consuming) operations which, however, may be performed by unskilled person with no or little training.

Sustainability: "+": system may be produced locally from locally available materials, with limited use of chemicals and non renewable energy; "-": system requires chemicals or non renewable energy sources for daily operation; "--": system widespread application causes or may cause in future significant environmental damage (e.g. deforestation due to boiling)

Social acceptability: "++": application is based on tradition or it is already in use; "+": available studies showed good social acceptance; "+/-": available studies are contradictory, or results depend on the region studied.

The investment costs listed in this table generally include the costs needed to buy, deliver and install the system. The operational costs include the costs of reagents, energy and servicing if needed, as well as maintenance and replacement of parts of the system. The World Health Organization (WHO) categorizes costs for POU systems as low, medium and high on a worldwide basis that includes the poorest people. The categories for annual household cost estimates in US dollars are less than US$ 10 for low, US$ 10-100 for moderate and >US$ 100 for high. These cost categories will clearly be different for different economic situations in various regions and countries of the world (WHO, 2002). Nevertheless, we will use them further to compare the various systems.

Only few of the available POU technologies (SODIS, biosand filters and free chlorine) can fulfill the low-cost requirements for DC and provide an acceptable water quality if operated correctly. The costs of most of the POU technologies are in the moderate range and may be affordable to households in TC and some households in DC.

Some of the available systems are widely used, although they may not always be the optimal solution. For example, boiling with fuel is widespread but is not very sustainable and leads to uncontrolled air pollution and deforestation. A problem with chlorination is that the motivation to apply it is generally low because of the bad taste and smell of the resulting water. Other technologies are not effective for all water qualities, thus UV treatment is not very effective for surface waters with high turbidities. Furthermore, the investment costs for UV systems are high and they require a reliable supply of electricity.

Most of the low and moderate-cost POU technologies listed require everyday handling (SODIS, chlorination, combined coagulation with filtration and chlorination), while the others need monthly or annual maintenance (activated carbon filters, BSF, UV) or require the availability of spare parts and a certain level of education and training for their servicing.

Table 1
Overview of available POU/POE water treatment technologies for DC, ICs and TC

Water Treatment System	Type of supply	Estimated costs		Evaluation criteria						Source
		Investment $US	Operational $US*	Performance	Ease of use	Maintenance	Sustain-ability	Dependence on utilities	Social acceptability	
Developing countries										
Boiling with fuel	POU	Cook pot	Depends on fuel price	++	+	Depends on fuel availability	--	Fuel	++ tradition	Sobsey, 2002
Solar disinfection	POU	Plastic bottles	None	+, when low turbidity	+	Regular, time consuming	+	None	-/+	Sobsey, 2002
UV disinfection with lamps	POU	100-300	10-100	+, when low turbidity	+/ training required	Cleaning, annual replacement	-	Electricity	+	Sobsey, 2002
Free Chlorine	POU	2-8 (vessel)	1-3	+	+	Regular	-	None	Taste problem	Sobsey, 2002
Biosand filters	POU	10-20	None	81-100%, viruses - ?	++	Required once in few month	+	None	+	Kaiser *et al.*, 2002
Ceramic filters	POU	10-25	None - 10	+/viruses-?	++	Cleaning, replacement	+	None or tap pressure	+	Clasen *et al.*, 2004
Coagulation, filtration, chlorination	POU	5-10	140-220	+	+/training required	Regular, time consuming	-	None	Taste problem	Sobsey, 2002
Transition and Industrialized countries										
Activated carbon filtration	Faucet-mounted Under a sink POE	25-50 50-300 500-800	25-50 50-100 n.a.	+ if replaced	++	Annual replacement	+	Tap pressure	+	WSC, 2007; Ecosoft, 2007; WSC, 2007
Microfiltration **	POU SSS	3 n.a.	12 n.a.	+/viruses-?	+/++	Cleaning, replacement	-/+	None	-/+	LifeStraw,2007 Li & Chu, 2003; Pillay, 2006
Ultrafiltration	POU POE SSS, 250-1000 people	40 2700-3000 178000	none n.a. n.a.	++	++	Backflushing Cleaning, replacement	+	Gravity Tap pressure or electricity	+	LifeStraw2008 Homespring, 2007
Reverse Osmosis	Single tap SSS, 50 m^3/day	300-600 29900	80-120 9000	++	++	Required annually	-	Tap pressure or electricity	-/+	WSC, 2007; AMPAC, 2007 (Schoeman , 2003)
Bottled water	For a family of 4 people per year	None	360-720	Depends on the region	Depends on delivery distance	None	--/+ when in own bottles	None	+	WSC, 2007

n.a.: data not available ; * Operational costs for POU/POE systems are given for the family of four; ** Ceramic filters are considered separate

Time-consuming or complicated maintenance is one of the main problems limiting the application of available POU technologies.
Some of the systems described can also be used on a community scale. One of the examples is a slow sand filtration. This technology is cheap and may be completely built from locally available materials, however inadequate maintenance is often a main reason of system malfunction or breakdown. UV lamps are also used in multistage small scale systems for disinfection (Triangular Wave technologies, 2008). Also this technology requires a high level of maintenance which limits its suitability for POU application.

Table 1 shows that an "ideal" solution, namely one whose maintenance is limited to the delivery of water and whose costs are low, does not yet exist for POU systems. This may explain the low success of these systems so far. Therefore, further development is needed to simplify the maintenance of existing low-cost systems or reduce the costs of more advanced ones.
For the situation in the IC and TC, the costs of most solutions including membranes can be considered appropriate for middle-income households. Factors limiting their application in TC and remote areas of IC are the annual maintenance, the level of education necessary to operate the systems correctly, and feed water quality. Moreover, most systems rely on tap pressure and external energy sources (electricity), which may be not available in TC
The investment costs of SSS are generally too high for communities in DC and TC. These communities also lack trained personnel to maintain these systems and often do not want or cannot assume the responsibility for their performance after their construction by the government or NGOs. The provision of regular maintenance by regional maintenance centers, such as is practiced in some regions in South Africa, needs a certain organization and control and would not be possible in many other countries. There is also a need to develop robust, reliable and easy-to-maintain technologies for community supply systems for DC and TC.

5.2 Available membrane systems for decentralized application in DC/TC

The evaluation criteria discussed above for decentralized systems in general, also apply for membrane-based systems, however some of the criteria have to be discussed more in detail. The technical complexity of the available system varies quite substantially. Some processes consist of a membrane treatment unit only, others also include pretreatment or a post-treatment steps. This influences the system complexity, investments and maintenance. Furthermore, the required energy supply differs among the systems. An important additional criterion for membrane systems is the acceptable feed water quality and the possibility to deal with varying feed water quality as is the usually the case with surface waters. Systems which are designed to operate on tap water quality only will therefore not be suitable for such applications. Finally, the energy concept is of importance. Some systems rely on tap water pressure, while other systems require electricity or solar power, and some systems work on gravitational pressure. Table 2 summarizes these criteria as well as the capacity, and the application area for which the system is intended.

For an effective long term operation, rare but regular maintenance is needed (chemical cleaning, UV lamp replacement (Norit), repair of pumps and energy suppliers), which may be not always possible in DC or emergency situation. The systems working on hydrostatic pressure (gravity) are generally simpler. Except for the disposable systems (FilterPen) these systems however require everyday supervision and/or maintenance (e.g. manual

backwashing). In addition, most available membrane systems need periodic cleaning with chemicals that have to be transported and stored. Depending on the type of chemicals and their amounts, skilled personnel is needed in order to prevent the risks associated with the handling of chemicals.
The costs of many of the systems listed are not yet known because they are still in a state of development and are not available on a commercial scale. In general, however, it can be stated that the investments for pumps, solar-powered systems and measurement & control systems are high, so that many of the systems listed will not be affordable for people with low or middle incomes. However, the cost of the membrane itself should not be prohibitive for a POU application: UF membrane costs are currently around 40 US$/$m^2$ and declining. Furthermore, the permeability of UF membranes is relatively high with clean membrane permeability in the range of 500-1000 l/m^2/h/bar. Also if only a fraction of the clean membrane permeability is assumed for long-term continuous operation, the required membrane surface for a POU application is low. For example, assuming 5% clean water permeability at 0.2 bar would give a water production of 5 l/m^2/h or 10 l/m^2/h. Considering that only 20 – 50 l/day is required for a POU application, the membrane area needs to be only 0.17 – 0.42 m^2, corresponding to US$ 7 – 17 per family per system. The annual costs of the system will depend on the service life of the membrane.
For POU systems, the membrane life time is indicated as the volume of water which can be filtered until the filter gets clogged. This volume is dependent on feed water quality and the membrane surface. For example for LifeStraw Family this volume is estimated to be 18000L of filtered water (basic water quality parameters: Turbidity 15 NTU and TOC 5 mg/L). Assuming a daily drinking water consumption of 20 L, this corresponds to approx. 2.5 years of operation. The average service life of a clay pot is approx. 6 month (source). Personal-use devices are able to filter from 100 L (Filtrix) to 700 L (lifeStrawPersonal) of water, which corresponds to 1-7 month of use. In contrast to POU systems, which are mostly designed to be disposed once they are clogged, the membrane used in SSS may be cleaned in or out of module with chemicals which may restore its permeability. Thus, we can expect a longer membrane service life. For example, the membrane service life for SkyJuice is indicated to be approx. 2 years in DC.
Thus, assuming that the average membrane service life in DC is several years, the membrane costs themselves are relatively low and affordable even for the very poor (based on the assumptions above and a service life of 2 years, the membrane costs are 0.8-2.2 $ per person and year). In addition to the membrane, however, a system is required to operate it, and in some cases pre-treatment may be required. The total costs of the system will depend on the sum of the investment costs of its components and the operating costs, including membrane replacement costs. Among all the systems listed, the investment costs of only LifeStraw Family and SkyJuice are in the range of affordability for DC (LifeStraw Family - approx. 2.5-3 $ per person per year for drinking water; SkyJuice: 3-4 $ per person per year for water for basic domestic needs).

5.3 System requirements for decentralized membrane systems

Table 2 summarizes systems on RO, UF and MF. RO systems, which intended to be used for desalination, require high pressures and therefore depend on cost- and maintenance-intensive pumps. UF and MF based systems are intended for disinfection purposes. It should however be noticed that due to the pore size of MF membranes, no complete protection for viruses can be provided (see § 4.2.3). Considering the fact that a large number of diseases can be transferred by waterborne viruses (e.g. *Adenovirus, Enterovirus, Hepatitis A,* see: WHO, 2004b), the use of MF membranes brings important limitations. Furthermore, the size range of

ceramic pots is less defined and, depending on production process and operation, no complete protection against bacteria can be provided. In view of these limitations, we will confine the discussion below on UF membranes.

For application in urban areas of DC and TC, decentralized systems evidently should be low-cost and low-maintenance. If tap pressure is available, this provides a free form of energy to drive membrane processes, and is the preferred option. However, no such systems seem to be available on the market which are specifically designed to meet the cost criteria for developing countries. If no tap pressure but partially treated water is available, a hydrostatic pressure or a pump can be applied. A disadvantage of pumps however is the need for maintenance and spare parts. Thus, in view of these criteria, the LifeStraw Family appears to be a suitable POU system for this type of application. However, no SS system meeting the above mentioned criteria seems to be available.

For application in rural areas of DC, systems should be able to operate with untreated surface water, and should be independent on electricity or tap pressure. Systems which have been operated with surface waters not necessarily work trouble-free with other water qualities. As generally known, membrane processes can easily clog due to fouling factors, which are mainly related to NOM fractions and inorganic compounds (e.g. Fe, Mg). Long-term test results with a broad range of feed water qualities should be available in order to be able to predict the performance in each possible situation. In a large number of cases therefore, a pretreatment step may be required. However, pretreatment processes increase the costs and chance of failure of the systems, and the whole system finally should meet the low-costs and low-maintenance criteria. Therefore a clever design and extensive practical testing of such systems is essential for success.

As pointed out before, a critical aspect of membrane based SSS and POU systems is the operation, maintenance & control. Most of the currently available membrane systems need regular flushing, back-flushing and chemical treatment (see Table 2). Systems equipped with automatic flushing and cleaning however require complicated instrumentation and use chemicals that should be transported, stored and handled. This makes them less suitable for use in DC and TC. The solution should be sought in “low-tech” systems that can be operated intuitively and controlled by the local population.

Membrane fouling itself is an indicator of the system performance: once membrane is clogged, a household or an operator is forced to act and clean or replace the membrane. However, the system integrity is a critical factor of polymeric membrane filtration. Membrane integrity tests cannot be done on a low costs and by untrained personal, thus increasing the risk of unnoticed system breakdown. However, the membrane surface may be protected by installation of a simple particle screen and limiting access of the untrained person to the membrane surface. In addition, central monitoring systems can be installed which activate an alarm when the installation operates beyond its specification. SSS can then be run unmanned and a large number of installations can be controlled by a single centralized expertise center.

In summary, the following research and development needs exist for membrane-based decentralized systems:

- Development of membrane systems operating on tap pressure for treatment of tap water in urban areas, which meet the cost criteria for DC
- Development of UF-based SS systems using hydrostatic pressure
- Long-term tests of membrane systems with a wide range of feed water qualities to enable prediction of process performance depending on the local conditions

Table 2
Available membrane systems for decentralized application in DC/TC and their properties.

Membrane system		Capacity (L/day)	Pretreatment (post treatment)	Feed water quality	System investment costs ($)	Maintenance / operation	Energy	Application
RO, POU	Tabletop or under a sink systems	145-340	MF, activated carbon, multistage	tap water	ca. 400	catridges replacement 2 times per year	Tap pressure	IC/TC, applied
RO, SSS	ROSI	1000	UF	Brackish water	high	3 cartridges, 1-2 times per year	Autonomous; (Solar energy)	DC, tested
	Emergency Seawater, Aquamove, etc.	720000	MF/UF	Sea or brackish water	ca. 10000	Requires operator	Fuel or electricity	Emergency, applied
FO, POU	Hydration bags	3 (9 L/system) **	None	Surface water	30	none	osmosis pressure	DC, emergency
UF POU	LifeStraw Family	20-30 18000 L/system **	Chlorine	Surface/ground water	ca. 40	daily backflushing	Gravity	DC, tested
UF POE **UF SSS**	Homespring, POE Homespring, SSS	25000 60000 240000	Active carbon None None	Tap or ground water	2700-3000 141000 178000	Cartridge replacement; annual maintenance	Tap pressure / electricity	IC/TC applied
	"Arnal" system	1000*	- Coarse filter - Microfilter - Security filter	Surface water	n.a.	n.a.	Manual rotation wheel	DC, tested
	Skid-mounted systems	≤ 6000	Different configurations	Surface/ground water	Depending on lay-out	Depending on lay-out	Depending on lay-out	DC, emergency, applied
	"Pryor" system	10 m^3/day	None	Surface water	n.a.	Chemical cleaning	River flow and electricity for the recycling pump	DC, tested
	Perfector E (Norit)	48000	multistage MF, UV	Brackish water	ca. 26000	maintenance on a long term	Fuel	Emergency, applied
MF, POU	FilterPen LifeStraw Personal	100 L/system** 700 L/system**	None	Surface water	49.95 3	(Disposable product)	Human power (suction)	DC, applied
	Ceramic filters (pots) Ceramic candles Katadyn	ca. 5000L/system** 10000 L/system** 100-750 L/system**	None MF, active carbon	Surface water	10-25 150-300 200-400	None or cleaning None	Gravity Manual pump	DC, applied
MF, SSS	SkyJuice	10000	None	Surface/ground water	ca. 1000-2000	Manual backflushing and cleaning	Gravity	DC, applied
	MBR based	n.a.	None	surface water	n.a.	Chemical cleaning	Electricity	DC, tested ?
	Skid-mounted systems	≤ 5760000	Different configurations	Surface/ground water	Depending on lay-out	Depending on lay-out	Electricity	DC, emergency applied

*Capacity per membrane module; ** Capacity per system service life
n.a.: data not available
The literature references for this table are discussed in the text, the data on costs and capacity for the market products are obtained from producer

- For highly fouling feed waters: The development of efficient and robust pretreatment processes for membrane systems and the integration of such pretreatment processes with the membrane step
- The coupling of decentralized membrane systems with centralized supervision and service centers
- Systems requiring low maintenance and control, which can be operated by the local population

The recent development of few membrane based decentralized systems seem to fulfill at least a part of the criteria for applications in DC. This underlines the high potential of membrane technology in this field. However, better understanding of the membrane fouling processes and further developments are needed in order to develop systems that fulfill most of the criteria thus enabling gradually increasing implementation. By joining efforts in this direction, membranes could contribute substantially to solve the tremendous problems associated with drinking water as outlined in the millennium development goals.

6 Conclusions

A huge effort is required in order to reach the drinking water objectives set out in the Millennium Development Goals, and so far a centralized treatment approach has not been very successful in this respect. In rural areas, problems occur because the entire population is not connected to a water supply system. Moreover, available central systems are often not maintained properly and fall into disrepair. Urban areas face high population growth rates in many areas, especially in Asia and sub-Saharan Africa. In many cases, informal settlements appear which are not or only partially provided with safe drinking water. Even in urban areas where a water supply is available, the quality of the tap water is often unreliable, and decentralized systems are being installed by those who can afford it.

In order to cope with insufficient water quantity, groundwater wells are installed by the population or rainwater is harvested. In both cases, the water quality is very dependent on the local conditions, so that the water is not safe to drink in all cases.

A range of decentralized systems is available to cope with water quality problems. The focus of this review is on decentralized systems. Decentralized systems include Point-of-Use (POU) systems, which are defined as systems which treat only the potable (drinking and cooking) water of one household, corresponding to approximately 25 l/day, Point-of-Entry (POE) systems, defined as systems to treat all the water entering a house, and Small Scale Systems (SSS) used for community water treatment or in emergency. POU systems generally employ the following treatment principles: heat and/or UV, physical removal processes and chemical treatment. Small Scale Systems in general employ similar processes as in a large scale water treatment plants.

Performance criteria for decentralized systems in DC and TC include ease of use, low maintenance, the independence on utilities (energy and chemicals), and low costs. Many systems are available which meet several of the criteria, but not all criteria at the same time, which may explain the moderate success of the technologies so far.

Decentralized membrane systems can be based on microfiltration (MF), ultrafiltration (UF) or reverse osmosis (RO). RO-based systems are mainly intended for desalination purposes. RO requires relatively high pressures and therefore the process is dependent on cost- and maintenance-intensive pumps. MF- and UF-based systems are intended for disinfection. Not all available MF filters however have pore sizes enabling complete removal of bacteria. Moreover, the pore size of MF is per definition too large for complete removal of viruses. Therefore, MF-based systems can only provide a partial protection against viruses. Several

UF-based systems are on the market or in development. Some of these systems seem to meet the low-cost and low-maintenance criteria and some of them are operating on hydrostatic pressure, thus avoiding the need for pumps and additional energy sources. Only one POU system and no single SS system seem to meet all the criteria. Thus, efforts are required to develop POU processes meeting all the performance criteria. From the literature only limited data are available on the long-term performance with all possible water qualities. Considering the high fouling capacity of certain water types, the introduction of appropriate pretreatment processes should be considered.

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Abbreviations

DC: developing countries
TC: transition countries
IC: industrialized countries / developed countries
POE: point-of-entry
POU: point-of-use
SS: small-scale
SSS: small scale systems
MF: microfiltration
UF: ultrafiltration
NF: nanofiltration
RO: reverse osmosis
ED: electro dialysis
BSF: biosand filtration
DALY: disability adjusted life years

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Chapter 2

Stabilization of flux during dead-end ultra-low pressure ultrafiltration

Maryna Peter-Varbanets, Frederik Hammes, Marius Vital, Wouter Pronk

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Stabilization of flux during dead-end ultra-low pressure ultrafiltration

Maryna Peter-Varbanets [1, 2], Frederik Hammes [1], Marius Vital [1], Wouter Pronk [1]
[1] *Eawag: Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, 8600 Dübendorf, Switzerland*
[2] *Institute of Environmental Engineering, ETH Zürich, 8093 Zürich, Switzerland*

Abstract
Gravity driven ultrafiltration was operated in dead-end mode without any flushing or cleaning. In contrary to general expectations, the flux value stabilized after about one week of operation and remained constant during extended period of time (several months). Different surface water types and diluted wastewater were used as feed water and, depending on the feed water composition, stable flux values were in the range of 4-10 $L \cdot h^{-1} \cdot m^{-2}$. When sodium azide was added to the feed water to dinimish the biological activity, no stabilization of flux occurred, indicating that biological processes play an important role in the flux stabilization process. Confocal laser scanning microscopy revealed the presence of a biofouling layer, of which the structure changed over time, leading to relatively heterogeneous structures. It is assumed that the stabilization of flux is related to the development of heterogeneous structures in the fouling layer, due to biological processes in the layer. The phenomenon of flux stabilization opens interesting possibilities for application, for instance in simple and low-cost ultrafiltration systems for decentralized drinking water treatment in developing and transition countries, independent of energy supply, chemicals, or complex process control.

1 Introduction
Ultrafiltration (UF) provides an effective barrier for microorganisms, suspended particles and colloids and is increasingly implemented for the treatment of drinking water. Membrane fouling is one of the major limitations of membrane technology. Fouling can occur due to membrane adsorption, pore blocking, cake layer formation, precipitation or biofilm formation ("biofouling"). In the process of biofouling, microorganisms retained by the membrane tend to adhere to the membrane surface (Wang et al., 2005; Pang et al., 2005), excreting extracellular polymeric substances and leading to severe flux reduction (Ramesh et al., 2007). Thus, biofouling is considered one of the major problems during membrane filtration with Ultrafiltration, Nanofiltration (NF) or Reverse Osmosis (RO) (Vrouwenvelder, et al., 1998; Ivnitsky et al., 2005, 2007; Kim et al., 2006; Flemming et al., 1997). NF and RO membranes are usually applied in spiral-wound modules. In these modules, biofouling is dominantly a feed-spacer problem (Vrouwenvelder, et al., 2009a,b) and thus the mechanisms of biofouling are different to biofouling observed on UF membranes.
Biofouling has been studied intensively in membrane bioreactors for the treatment of wastewater (e.g. Lee et al., 2008; Hwang et al., 2008; Kimura et al., 2005; Meng and Yang, 2007) and a comprehensive reviews are available by Meng et al., (2009) and Le-Clech et al., (2006). In membrane bioreactors, biofouling starts by the deposition of cells and cell clusters on the membrane surface which multiply. Soluble microbial products and extracellular polymeric substances excreted by bacteria form a biocake, causing increase of hydraulic resistance (Ramesh et al., 2007). Yun et al., (2006) and Yang et al., (2007) showed that the

permeability of the fouled membranes is related to the structure of the biofouling layer. Confocal laser scanning microscopy (CLSM) has become the preferred method for the characterization of the structure in MBR's (Yang et al., 2007; Ivnitsky et al. 2007; Yun et al., 2006) and in drinking water systems (Bjørkøy and Fiksdal, 2009). In order to visualize specific groups of compounds, such as polysaccharides, proteins, nucleotides, and also of living and dead cells, different staining methods can be used (Yang et al. 2007).
In membrane bioreactors biofouling is controlled by shear stress of aeration (e.g. Ueda, et al., 1997; Psoch and Schiewer, 2008; Sofia et al., 2004) or by chemical cleaning (e.g. Guglielmi et al., 2008). In order to prevent biofouling in full-scale drinking water systems, membrane modules are usually flushed with hypochlorite in combination with frequent backflushing. Conventional ultrafiltration systems are operated at a transmembrane pressure of around 0.5 - 1.0 bar and require pumps for operation and backflushing. Decentralized systems designed in a similar manner are expensive due to the relatively high costs of auxiliary equipment (Peter-Varbanets et al., 2009). If operated by gravity, pump costs are avoided, and this can be an attractive option for decentralized, small-scale applications. Presently, only few gravity-driven ultrafiltration systems for decentralized application exist (SkyJuice, LifeStraw) (Peter-Varbanets et al., 2009; Clasen, et al., 2009). These systems can be operated at ultra-low pressure (100-150 mbar) and require little maintenance compared to the conventionally operated UF (Peter-Varbanets et al., 2009). To control fouling and prevent biofouling, irregular backflushing and disinfection with slow eluting chlorine tablets is used in LifeStraw (Clasen et al., 2009) and manual chemical cleaning is applied in SkyJuice (SkyJuice, 2009). However, no systems are known so far which are not dependent on cleaning or flushing.
In the present study we investigate the fouling behavior of direct dead-end ultrafiltration operated with surface water without flushing or cleaning under ultra-low pressure conditions (40-110 mbar). The focus is on the structure of the fouling layer and its impact on the hydraulic resistance of the fouling layer during long-term operation. The role of biological activity in the fouling layer and its influence on the structure of the layer is investigated.

2 Experimental Section

2.1 System set-up

The system set-up is shown in Figure 1. Feed water was pumped to the stirred storage tank placed at the heights corresponding to the required pressure. A pressure of 65 mbar was used unless indicated otherwise. The level of water in the tank was kept constant due to an overflow. The tank was connected by Teflon tubing to the membrane module. At least three modules were operated in parallel under similar conditions. The permeate flux was measured and logged with an Ohaus Adventure Pro scale and the hydraulic resistance of the fouling layer calculated according to the Darcy law. All the experiments were conducted at 20 ± 2ºC.

2.2 Feed water

Four basic types of water were used: (1) natural river water, (2) natural lake water, (3) diluted wastewater of two different dilution rates and (4) disinfected river water. TOC, DOC and NOM composition of the feed waters were determined by Size Exclusion Chromatography according to Huber and Frimmel (1992).
(1) River water was pumped directly from the Chriesbach river (Dübendorf, Switzerland) to the storage tank. The river water was characterized by a TOC of 2 - 3 $mg \cdot L^{-1}$ and a turbidity of 0.2 - 2 NTU. During rain events, which typically lasted 0.5 - 1 day, the TOC and turbidity reached values around 4 $mg \cdot L^{-1}$ and 30 NTU respectively.

(2) Lake water was collected from the lake Greifensee (Switzerland). The lake water was characterized by a TOC of 3.5-3.9 and turbidity of 0.5 - 1 NTU. The lake water in the storage tank was daily renewed with the lake water stored at 4ºC and pre-heated to 20ºC immediately before the replacement.
(3) Combined wastewater was collected from the city of Dübendorf after the primary clarifier and screen filtration (2 mm mesh size) and diluted with river water. Two different dilution ratios were used. Due to the fluctuations of wastewater quality, the TOC and Turbidity of the diluted wastewater fluctuated in the range of TOC 3.5-5.5 $mg \cdot L^{-1}$, turbidity 3-6 NTU and of TOC 9.7-15.3 $mg \cdot L^{-1}$ and turbidity 8-20 NTU respectively. Diluted wastewater in the storage tank was daily renewed.
(4) Sodium azide was added to the river water at a concentration of 0.35% to decrease biological activity in the river water. 3.5 g of Sodium Azide was dissolved in 1 L of river water and stirred for 1 h at 20ºC. The solution was immediately transferred to the feed water tank of the ultrafiltration system. The solution was daily renewed.
Total ATP, concentrations of NOM fractions and total cell count were measured after 1 h of stirring of a new solution and at the end of a 1-day cycle. To confirm that no biological growth was possible, both samples were incubated at 30°C for four days and the resulting total cell count was measured with flow cytometry as described in Berney et al., 2008. All measurements were done in triplicate on 9 different days during a period of 30 days.

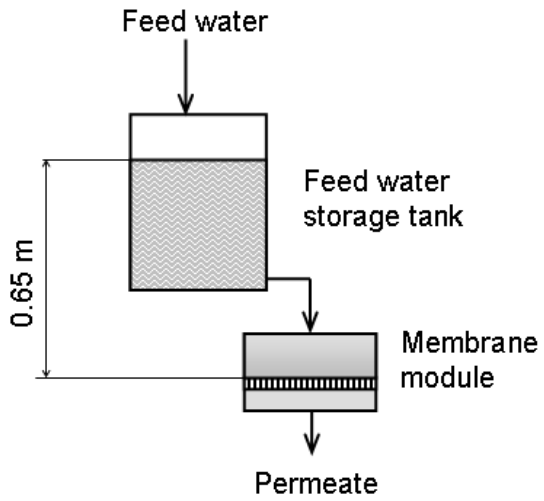


Figure 1 - Schematic presentation of the dead-end UF system

2.3 UF membranes and membrane test units

For each experiment we used a new flat sheet polyethersulfone membrane (PBHK, Biomax) with a nominal cutoff of 100 kDa. To remove conservation agents, the new membranes were stored for at least 24 h in de-ionized water and filtered with 1 L of de-ionized water under pressure used in the system. The efficiency of this procedure was assessed by DOC measurements of the de-ionized water permeate according to Huber and Frimmel, (1992). The clean water permeability of the membrane was 1200 ± 100 $L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$ (at 20°C). The membrane test units were standard polycarbonate filter holders of 48 mm inner diameter purchased from Whatman.

2.4 Confocal Laser Scanning Microscopy

2.4.1 System set-up and sample preparation

To investigate the development of the fouling layer structure over time, at least 15 membrane modules were operated in parallel under similar conditions. The system set-up and the flux measurements were done as described in section 2.1. The samples for the CLSM investigations were prepared as follows: at least 2 fouled membranes were removed from the modules at the same time, immediately fixed with formaldehyde (2.5 %), washed and cut in sections of approx. 0.25 cm^2. Upon fixation and cutting, samples were stained, incubated in the dark (4 h, 20ºC) and washed. SYBR® Gold nucleic acid gel stain (1000 fold diluted stock solution, Invitrogen, Switzerland) was used to detect all microorganisms independent on their viability. When Concanavalin A (50 fold diluted stock solution, Invitrogen, Switzerland) was used in addition to SYBR® Gold to stain the α-D-mannose and α-D-glucose groups of biopolymers, the staining was done sequentially. Then the sample was washed and Concanavalin A was added. The sample was incubated in the dark (4 h, 20ºC) and washed again. Staining was followed by a six-step dehydration with a glycerol/water gradient (40 - 100%). The dehydration was done as follows. The solutions of glycerol in water of 40, 60, 70, 80, 90, 95 and 100% (wt) were prepared. The samples were immersed in each of the solutions for at least 30 min to allow slow replacement of water with glycerol due to a concentration gradient. The dehydration with glycerol was done in order to increase the resolution of the images obtained with 63x glycerol Leica objective. In order to confirm that no artifacts occurred during the sample preparation procedure the images of not dehydrated and not stained samples were obtained in parallel (see supplementary information, section SI 3).
Fluorescein was used to trace the flow path of the liquid phase through the fouling layer. 200 mL of 0.01% fluorescein in river water was filtered through the module, and the membrane was removed from the module. The fixation and dehydration procedures were as described above, but fluorescein was added to every solution at a concentration of 0.01%. The samples containing fluorescein were not stained. 0.22 μm filtered bottled water (Evian, France) was used to dilute all stock solutions and to wash the samples (Berney et al., 2008).

2.4.2 CLSM image acquisition

CLSM images of the stained membrane samples were captured using a Leica SP5 Microscope equipped with the 63x glycerol immersion Leica objective. All images of the membranes were captured within 12-14 h after the membrane was removed from the system. At least 10 different sections of the membrane were investigated. Each section was scanned randomly over its whole area excluding the edges of the membrane, and at least 10 images, most typical for the sample were captured. The fluorescence of SYBR® Gold was detected by excitation at 488 nm and emission at 495 - 540 nm. Excitation at 514 nm and emission at 550 - 620 nm were used to detected Concanavalin A. Fluorescein was excited at 488 nm and emission detected at 500 - 575 nm. To detect the reflection from surfaces impermeable for light the excitation and detection wavelength were set at 633 nm and CLSM reflective mode was used.

2.5 Thickness of the fouling layer determined by CLSM

The thickness of the biofouling layer was determined as an average of at least 100 individual thickness measurements taken on at least 10 sections of the biofouling layer (Murga et al., 1995). An interval of 10-15 μm was kept between individual thickness measurements on each section of the biofouling layer. The thickness was measured from the beginning of the operation until the formation of channel networks and dendrite-like structures was clearly observed in the samples after the 9th day of operation. After this, the estimation of thickness

was not possible due to high inhomogeneity of the fouling layer surface. The thickness of detached layers was estimated as a distance from the top of the layer to the border of the layer still visible on the overexposed images.

2.6 ATP analysis

ATP analysis was used to determine the total active biomass in the water (Velten et al., 2007) and in the membrane fouling layer. The concentration of ATP in the membrane fouling layer was determined as follows: 5 membrane pieces with an area of 0.283 cm^2 each were cut from the fouled membrane, transferred into an Eppendorf tube containing 150 µL of phosphate buffer (pH 7.0), and incubated (30ºC). 150 µL of pre-heated (30ºC) BacTiter-GloTM reagent (Promega Corporation, Madison, WI, USA) was added to the membrane sample. The resulting luminescence was measured over a time period of 5 min every 30 seconds. The highest value of luminescence of each individual sample was then used to calculate the corresponding ATP concentration based on a calibration curve established using pure ATP and a pristine membrane.

3 Results

3.1 Stabilization of flux during dead-end operation

Flat-sheet UF membrane modules were operated in dead-end mode without cross-flow, backflushing or cleaning at gravitational transmembrane pressures of 65 mbar. No pre-treatment or disinfection was used. At least three modules were operated in parallel. Figure 2 shows that the flux decreased considerably during 2-3 days and stabilized at a value of 7-10 $L \cdot h^{-1} \cdot m^{-2}$ after 7-9 days of ultrafiltration of river water (Figure 2). Stabilization of flux at slightly lower values (5-6 $L \cdot h^{-1} \cdot m^{-2}$) was observed during ultrafiltration of lake water. When diluted wastewater was used as a feed solution, stabilization of flux occurs at a value of 4-7 $L \cdot h^{-1} \cdot m^{-2}$. In this case, a faster flux decline was observed during the first days than in the case of river or lake water. Increase of turbidity up to 30 NTU observed on days 2, 17 and 35 did not affect the stabilization of flux during ultrafiltration of river water (Figure 2). For all waters, the flux remained stable during at least 120 days with all feed water types (the first 30 days are shown in Figure 2).

The experiments at 40, 150 and 250 and 500 mbar showed that the level of flux stabilization does not depend on pressure (Figure 3a). Figure 3b shows that the total resistance of the fouled membrane increases with the increase of pressure during long term operation.

The integrity of the membranes and the membrane modules was verified by adding fluorescently labeled standard filter testing bacteria (*Brevundimonas diminuta*) to the feed water and measuring bacterial count in feed and permeate using flow cytometry according to Berney et al. (2008). The feed water containing labeled bacteria was permeated in several membrane modules that were operated prior to the experiment for 30 days with river water. As shown in Figure SI 1, the amount of organisms detected in the permeate by flow cytometry is below the detection limit, which confirms that the membrane was intact and did not have any leakage.

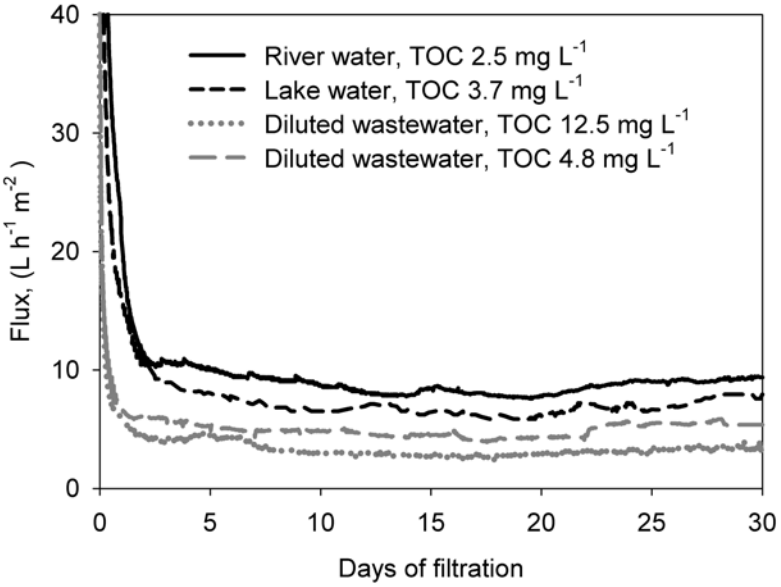


Figure 2 - Membrane flux during 30 days of dead-end operation for different water types

3.2 Biological activity in the biofouling layer

3.2.1 Impact of biological activity on the resistance of the fouling layer

The impact of biological activity on the stabilization of flux was investigated as follows. River water was filtered through two systems operated in parallel. In order to prevent biological growth and decrease biological activity, sodium azide was added to one of the systems (see section 2.2). The flux was measured in both systems and the resistance of the fouling layer compared. Figure 4 shows that the resistance increased continuously in the system with azide, while stabilization of resistance was observed for not disinfected river water.

No significant changes in the NOM composition of the water due to sodium azide were observed in the river water directly after azide addition or after storage during 25 h (Table 1).

Table 1 - NOM composition, cell count and ATP in river water with and without addition of sodium azide, and changes in composition after incubation during 25 h.

Concentration	River water		River water with sodium azide	
	1 h	25 h	1 h	25 h
Concentration of NOM fractions $\mu g \cdot L^{-1}$				
DOC	1767	1775	1798	1730
Biopolymers	65	69	75	62
Humic acids	748	745	803	758
Building blocks	216	230	202	220
Low molecular weight compounds	235	294	259	327
Total cell count, $cell \cdot mL^{-1}$	$1.7 \cdot 10^6$	$1.42 \cdot 10^6$	$1.66 \cdot 10^6$	$1.36 \cdot 10^6$
Total cell count after incubation (4 days, 30ºC), $cell \cdot mL^{-1}$	$3.41 \cdot 10^6$	$2.94 \cdot 10^6$	$0.80 \cdot 10^6$	$0.90 \cdot 10^6$
ATP total, $\mu g \cdot L^{-1}$	0.103	0.123	0.116	0.097
ATP cellular, $\mu g \cdot L^{-1}$	0.059	0.083	0.004	0.005
pH	7.96	7.97	8.01	8.01

The total cell count remained similar for river water and disinfected river water, while the concentration of cellular ATP in water with azide decreased to about 6% of the cellular ATP measured in river water (Table 1). These results show that the cells lose most of their activity after addition of sodium azide but they remain intact and are not disintegrated. To confirm that no biological growth occurred after addition of sodium azide in river water, both water types were incubated for 4 days at 30ºC and the total cell count was measured before and after incubation. As shown in Table 1, the number of cells in river water doubled after incubation, while the number of cells in disinfected water decreased.

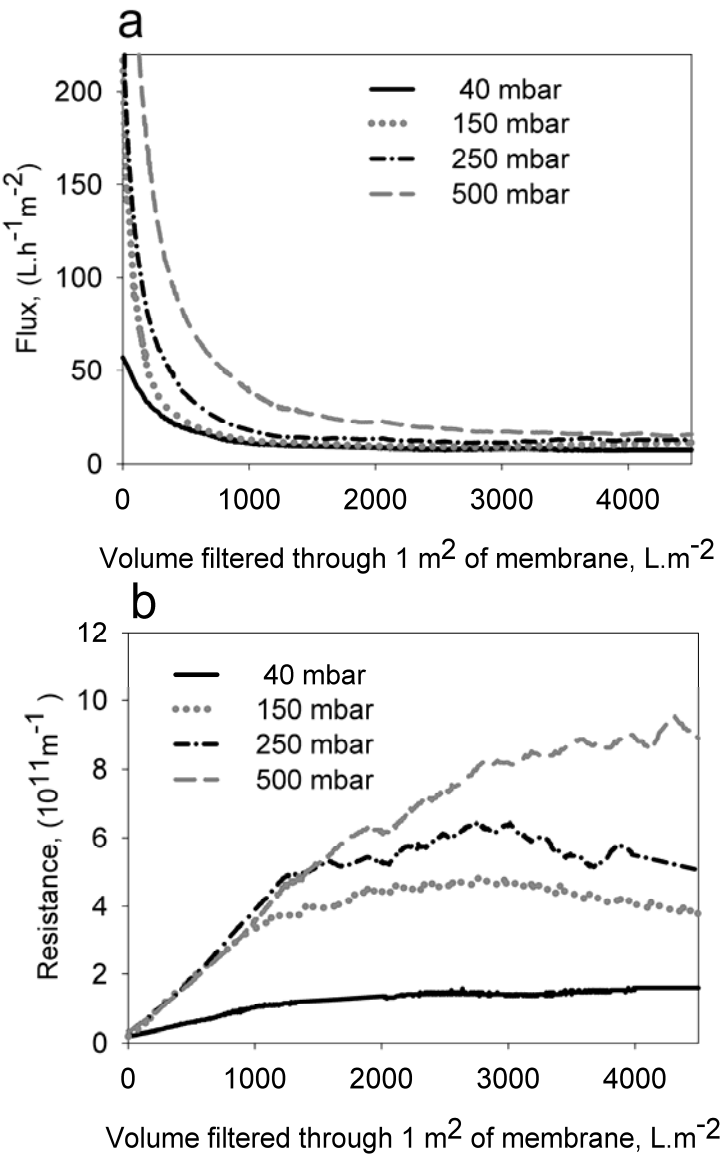


Figure 3- Membrane flux (a) and resistance (b) during dead-end ultrafiltration of river water at 40, 150, 250 and 500 mbar.

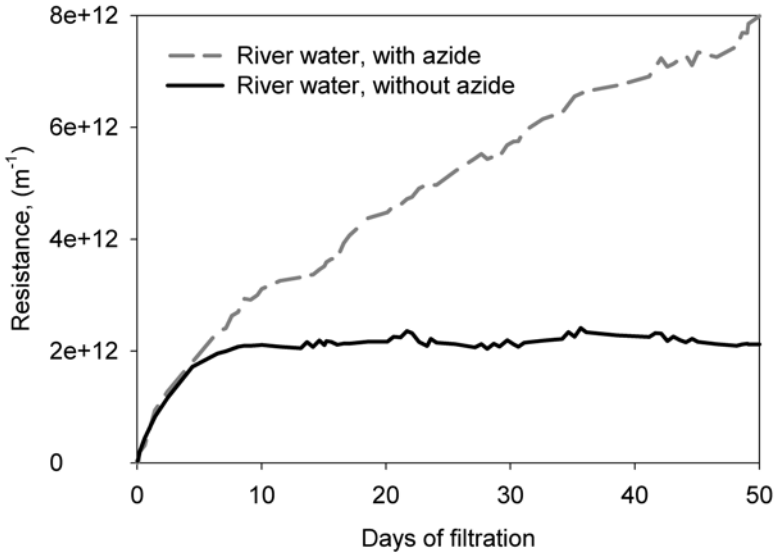


Figure 4 - The hydraulic resistance of the fouling layer formed during ultrafiltration of river water with and without suppression of biological activity with sodium azide.

3.2.2 ATP in the fouling layer

In order to further elucidate the biological activity in the system, adenosine tri-phosphate (ATP) was measured in the feed water and in the biofouling layer, and plotted against time for the system with and without azide (Figure 5).

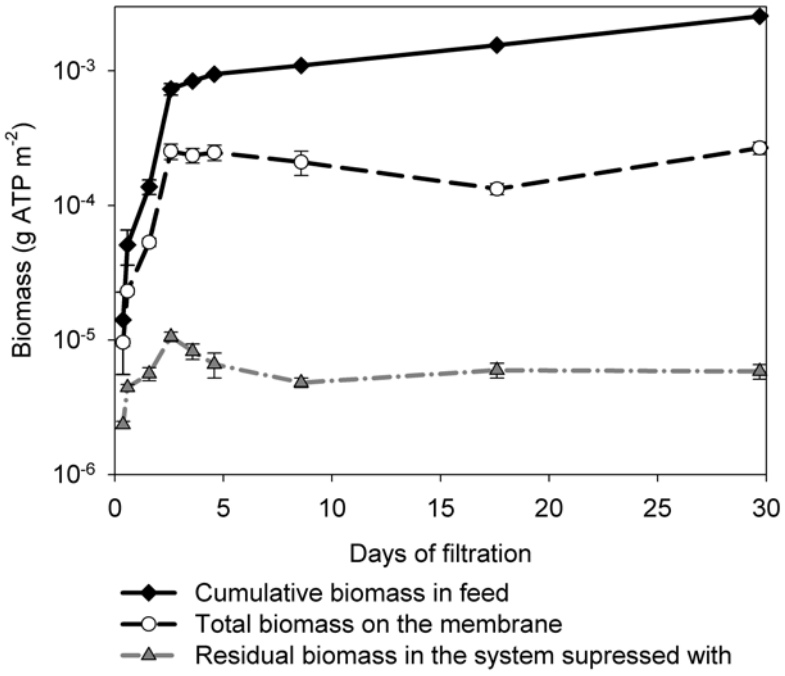


Figure 5 - Cumulative ATP in the feed water and ATP in the fouling layer at different points of time after start of river water filtration.

As shown in SI, Section SI 2, all cells are retained by the membrane, and thus, if no change of activity would occur, the amount of ATP in the fouling layer would correspond with the cumulative amount of cellular ATP in the feed. As shown, the observed biomass in the biofouling layer increased similar to the cumulative feed during the first 3 days, but then stabilized at a constant level of about 0.22 mg ATP·m^{-2}, while cumulative biomass increased continuously (Figure 5). This indicates that after prolonged operation, a loss of ATP occurs in the fouling layer.
Figure 5 shows that a reduction of about 95% of the total ATP was observed in the fouling layer during filtration of river water with addition of sodium azide compared to river water without azide.

3.3 The structure of the biofouling layer

The development of the structure of the fouling layer over time was investigated using Confocal Laser Scanning Microscopy (CLSM). The samples were prepared and stained as described in section 2.5. Figure 6 (a-d) shows representative optical cross-sections of the fouled membrane made on days 3 (a), 7 (b), 11(c), 24 (d) after starting the filtration of river water (the method to select representative pictures is described in the Materials and Methods section). In order to increase the contrast between the fouling layer and water phase and trace the water path, fluorescein was added to the river water during filtration and on all stages of the sample preparation procedure. Figure 6 (e-f) shows the structure of the fouling layer on days 9 (e) and 50 (f) visualized with fluorescein.
From the beginning of the experiment until the 7^{th} day of operation, the fouling layer remained homogeneous (Figure 6a) and its thickness increased to about 26 μm. During this first phase, the hydraulic resistance of the fouling layer increased proportionally to its thickness (Figure 7). From the 7^{th} day of operation, the layer started to detach from the membrane surface, forming cavities under the layer (Figure 6b). The penetration of fluorescein between the fouling layer and the membrane observed on Figure 6e implied that these areas were void spaces and not image artefacts. After 11 days of operation, channels started to be formed within the fouling layer (Figure 6c). At a later stage (day 24 to 50), the structure became increasingly heterogeneous, leading finally to the formation of mushroom-like dendrite structures (Figure 6d and f). The presence of channels in between these dendrites was visualized with fluorescein (Figure 6f).

In order to investigate the impact of decreased biological activity on the structure of the fouling layer, CLSM images of the fouling layer formed during ultrafiltration of river water with and without sodium azide were made. Figure 8 shows optical cross-sections of the fouling layer after 9 (a, b) and 27 (c, d) days of parallel filtration of river water without (a, c) and with (b, d) addition of sodium azide. Figure 8 (b,d) shows that a homogeneous and a compact fouling layer was formed in the system with azide. Without azide, the formation of heterogeneous structures, similar to those shown on Figure 6, was observed.
In order to make sure that no artefacts occurred during sample preparation procedure, the impact of the fixation, staining procedure and de-hydration with glycerol on the observed structure of the fouling layer was investigated as discussed in the Supplementary information (section SI 2).

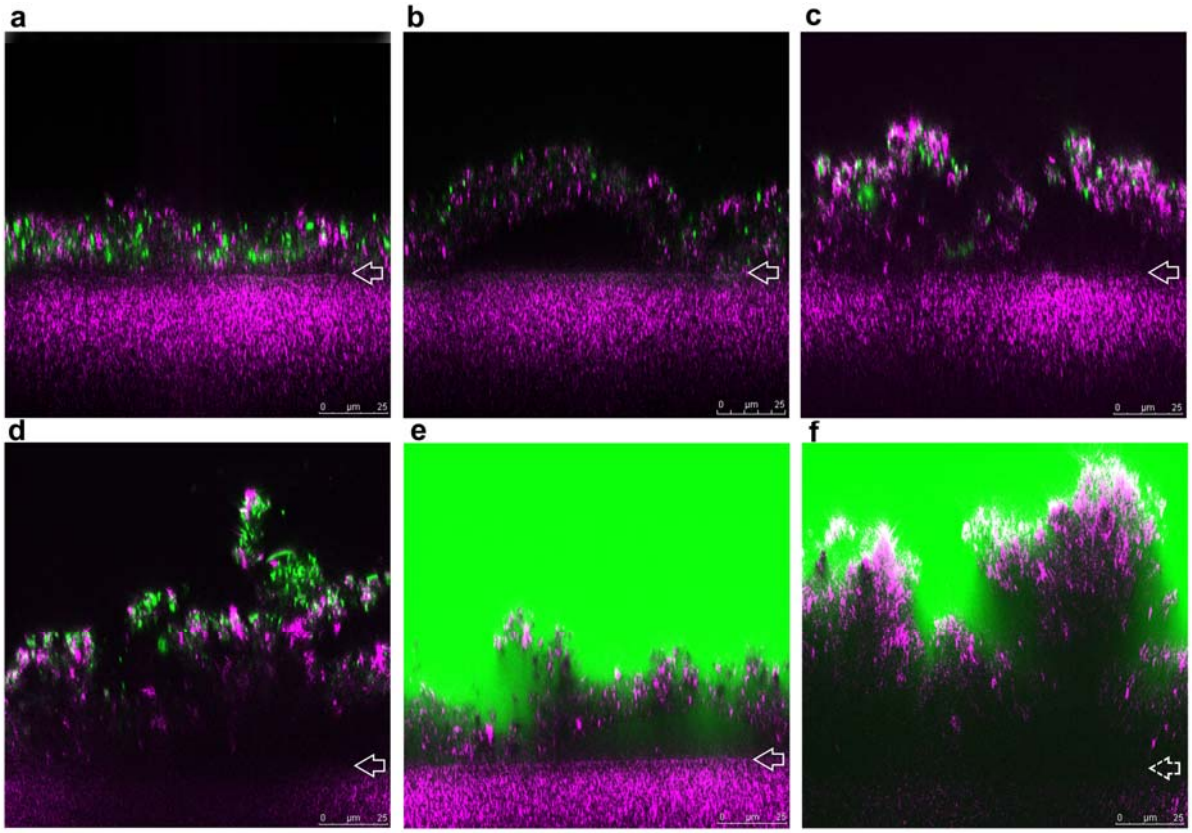


Figure 6 - Development of the fouling layer structure in time, visualized by CLSM (river water filtration). Images of the membrane cross-sections were made on days 3 (a), 7 (b), 11(c), 24 (d); images with the flow path traced by fluorescein on days 9 (e) and 50 (f). The arrows show the separation plane between the membrane and the fouling layer. The dashed arrow shows the probable separation plane. All images have dimensions of 140 µm x 140 µm, the length of the bar is 25 µm. On the images a-d, green indicates all biological cells independent of viability (SYBR® Gold stain); on the images e,f green indicates the presence of fluorescein in the water phase. Purple indicates the reflection of the solid surfaces in every sample.

4 Discussion

4.1 Flux stabilization and the role biological processes

As shown in Figure 2, flux stabilization was observed during dead-end UF of different types of surface waters and diluted wastewater, and this was not reported before in any other study. Generally accepted membrane filtration theory assumes the formation of a fouling layer during dead-end ultrafiltration, leading to a continuous increase of hydraulic resistance and decrease of flux (see SI, Section SI 1, eq.1). As shown in Figure 3a, flux stabilization is achieved for all pressures tested (40, 150, 250 and 500 mbar), but the flux level does not increase substantially with increasing pressure. As shown in Figure 3b, this implies that the resistance of the fouled membrane increases with increasing transmembrane pressure, which also cannot be described by conventional membrane fouling theory.

Figure 2 shows that the level of flux stabilization depends on the quality of the feed water. Faster flux decline and stabilization of flux at lower values observed in Figure 2 for the lake water and diluted wastewater in comparison to river water can be explained by the higher

concentrations of TOC and NOM (see Section 2.2), as well as by the higher turbidity of the wastewater.

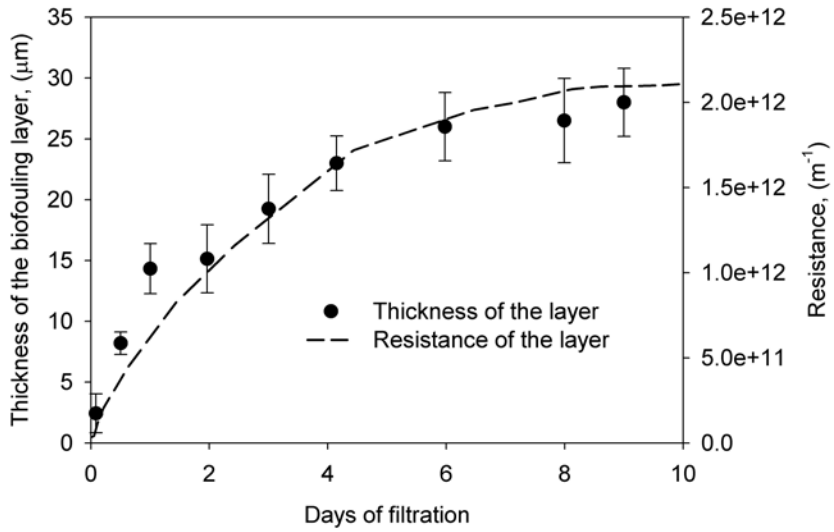


Figure 7 - Thickness and hydraulic resistance of the fouling layer for the first 9 days of river water filtration. The thickness of the layer during days 7-9 was determined as the thickness of the fluorescent top layer, not including the thickness of cavities.

To study the impact of biological activity on the flux and resistance of the fouling layer, sodium azide was added to the river water. The results shown in Table 1 and Figure 5 confirm that sodium azide prevents biological growth and leads to a reduction of biological activity in water and in the fouling layer but does not considerably affect the NOM composition of the river water. Figure 6 shows that the resistance of the fouling layer formed during filtration of river water with sodium azide increases, while the stabilization of resistance is observed for the river water without azide in a parallel experiment. This result indicates that stabilization of flux and resistance is related to biological activity in the fouling layer and does not occur when it is decreased.

The phenomenon of flux stabilization has not been reported previously. The reason that this has been overlooked so far can be that previous fouling studies have been conducted at higher pressures (e.g. 1.4 - 2.8 bar (Costa et al., 2006); 0.5 bar (Jermann et al., 2007); 0.3-1 bar (Lee et al., 2006)), at constant flux values higher than stable flux (e.g. at flux 27 $L \cdot h^{-1} \cdot m^{-2}$ (Yamamura et al., 2007); 20 $L \cdot h^{-1} \cdot m^{-2}$ (Kimura et al., 2004)) and/or during shorter periods of time (e.g. 1h (Katsoufidou et al., 2008); 40-50 min (Costa et al., 2006); 30 min (Yamamura, et al., 2007)) so that the flux stabilization was not observed.

4.2 Structural changes in the biofouling layer

When the biological activity was decreased by sodium azide, a homogeneous and compact fouling layer was formed (Figure 8b, d) as expected from conventional cake filtration theory. Without azide, a formation of homogeneous fouling layer was observed only until 7th day of filtration (Fig. 6a). During this first phase, the increase of the resistance of the fouling layer can be explained by an increase of the thickness of the layer, as indicated by Figure 7. From the 7th day of operation, a heterogeneous layer with channels and mushroom-like structures was observed (Fig. 6 b-f). Figure 6 shows that, although the thickness of the layer increases over time, the heterogeneity of the layer also increases. It can be assumed that the hydraulic

resistance of the fouling layer is determined mainly by the diameter and structure of cavities and channels. Furthermore, it can be expected that an increase in the thickness of the layer leads to an increase of hydraulic resistance of the channels and of the entire fouling layer. The formation of more heterogeneous structures and an increase of the diameter of channels counteract this effect. Thus, the fouling layer can be considered as a dynamic layer with steadily increasing thickness and heterogeneity.

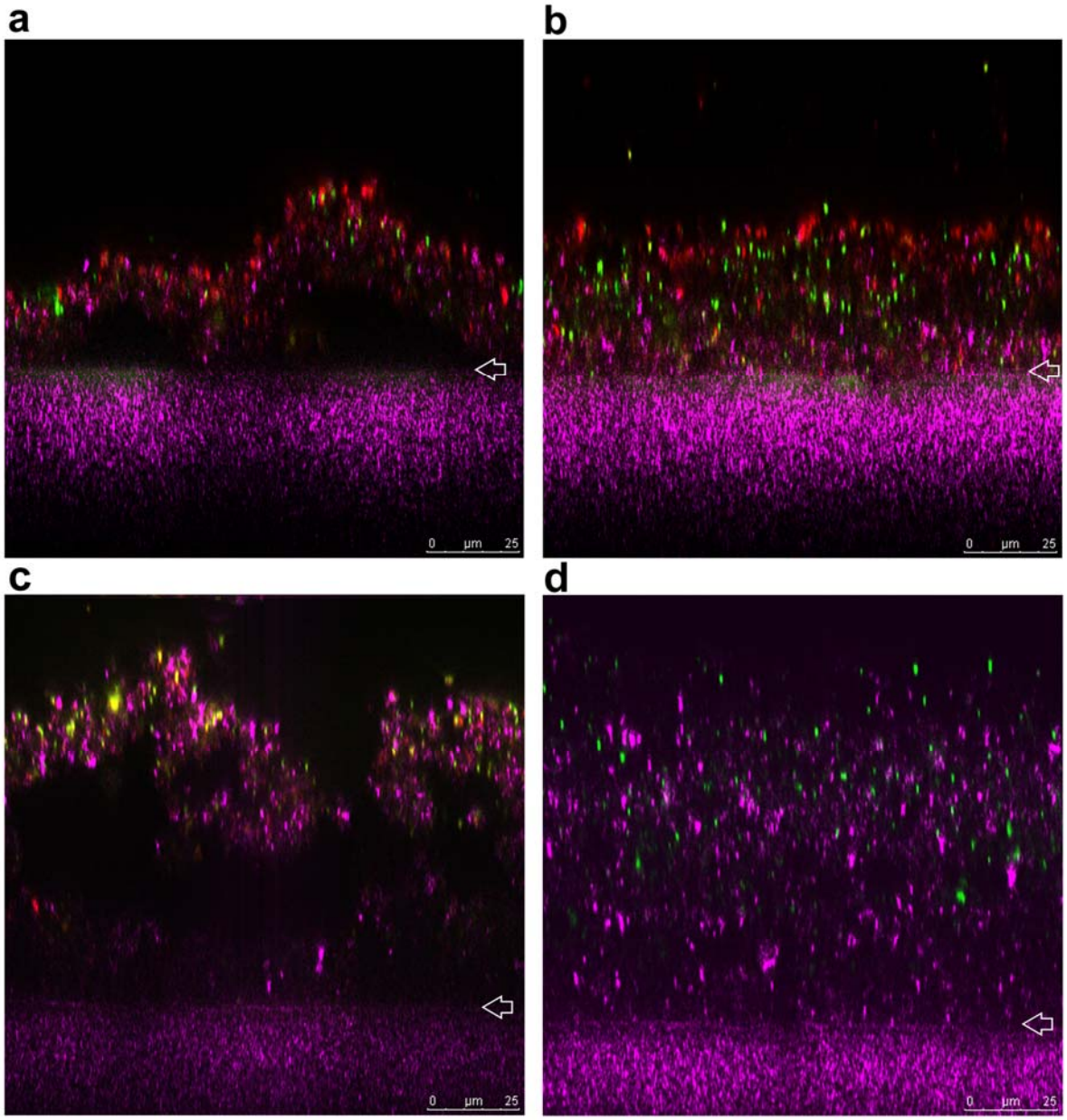


Figure 8 -The fouling layer structure formed during ultrafiltration of river water for 9 (a, b) and 27 (c, d) days without (a, c) and with (b, d) suppression of biological activity. The arrows show the separation plane between the membrane and the fouling layer. All images have dimensions of 140 µm x 140 µm, the length of the bar is 25 µm. Green – SYBR® Gold stain, indicating presence of all bacterial cells; Red - Concanavalin A stain indicating presence of α-D-mannose and α-D-glucose groups in biopolymers; Purple - reflection of the solid surfaces.

Increasing thickness of the fouling layer can be explained by the deposition of all non-dissolved material onto the membrane surface due to advective flow to and through the biofouling layer during dead-end UF. The results of the CLSM study (Figure 8), the study with sodium azide (Figure 4) and ATP balance (Figure 5) give strong indications that increasing heterogeneity of the biofouling layer over time is related to biological processes in the layer. It can be assumed that the flux stabilizes when deposition of non-dissolved material is in equilibrium with the biological processes.
The fact that pressure does not influence the stable flux considerably (see Figure 3 and Section 4.1) supports this hypothesis and can be explained as follows. During the first days of filtration the flux is high, resulting in a rapid deposition, dominating the biological processes, leading to a decline of flux. Under increased pressure the advective transport to the membrane is higher, thus increasing the deposition rate of material onto the membrane. However, it is expected that the rate of biological processes leading to the formation of cavities and channels depends only on water quality parameters and remains constant also under higher pressure. The level of flux stabilization is limited by the rate of biological processes, and thus, does not depend on pressure.

4.3 Mechanisms

The mechanism of biologically induced development of cavities and channels in the biofouling layer is still not completely understood and requires further investigations. However, in some types of biofilms on impermeable surfaces similar complex channel structures were observed (Lawrence et al., 1991; Stoodley, et al., 1994, Costerton et al., 1995, Battin et al., 2007). For biofilms, the formation of these structures is attributed to cell die-off (Webb, et al., 2003) and predation (Lawrence and Snyder, 1998) as well as degradation of extracellular polymeric substances (EPS) and bulk polymeric material (Ceyhan and Ozdemir, 2008; Sutherland, 2001). It is likely that processes such as degradation of cells, biopolymers and predation also occur in the biofouling layer and can lead to the formation of heterogeneous structures during dead-end UF. As presented in section 3.2.2 and Figure 5, a large part of ATP present in the feed water is lost in the biofouling layer. Although physiological changes cannot be ruled out, this reduction of ATP most probably can be ascribed to cell die-off in the fouling layer (Wang et al., 2009). The measurements of dissolved and assimilable organic carbon before and after the membrane suggest that nutrient limitation is not the cause of biomass inactivation or die-off in this case (Figure SI 3), although local nutrient limitation cannot be excluded. Furthermore, advective transport of low molecular weight compounds occurs through the biofouling layer in dead-end UF, thus leading to more favorable nutrient and oxygen conditions than in case of a biofilm on impermeable surface. Another explanation of the observed loss in ATP and the formation of heterogeneous structures could be the action of predators. However, further investigations are required in order to understand these processes.
Heterogeneous biofouling layers were observed also on nanofiltration (NF) and reverse osmosis (RO) membranes (Ivnitsky et al., 2005, 2007). In contrary to UF, nutrients are partly or completely rejected by the NF and RO membranes, which results in relatively high concentrations near the membrane surface and favor biological growth (Kim, et al., 2006; Vrouwenvelder, et al., 2009a). Furthermore, cross-flow filtration and high transmembrane pressure as usually applied in NF and RO result in more compact fouling layers subjected to detachment and sloughing (Ivnitsky et al., 2007). Hence, it can be expected that development of heterogeneous structures in biofouling layers on NF and RO membranes is governed by different mechanisms than in case of UF.

4.4 Potential for application

UF systems, based on the described phenomenon of flux stabilization, would not require any back-flushing, cross-flow, chemical cleaning or disinfection, which would greatly simplify the maintenance and operation of ultrafiltration systems. This makes ultra-low pressure ultrafiltration attractive for drinking water treatment on a decentralized scale. For decentralized applications (e.g. households), a pressure of 40 mbar required for ultra-low pressure UF can easily be obtained by gravity, e.g. by filling the feed water tank manually. The required capacity for drinking water for household or community systems is approx. 10 - 40 $L \cdot day^{-1}$ per family (Sobsey, 2002). Assuming a stable flux of 4 - 10 $L \cdot h^{-1} \cdot m^{-2}$, the membrane area needed is 0.17 - 0.42 m^2 per family. For conventional decentralized membrane systems, the costs of pumps and auxiliary equipment outweigh the membrane costs by far (Peter-Varbanets et al., 2009), which implies that the costs of gravity-driven ultra-low pressure UF can in principle be considerably lower than for conventional systems.

5 Conclusions

In this study, dead-end ultrafiltration without backflushing or cleaning under ultra-low pressure conditions was investigated and following conclusions can be drawn:

- After about one week of operation stabilization of flux was observed at a level of 4-10 $L \cdot h^{-1} \cdot m^{-2}$, depending on the type of feed water used (river-, lake- or diluted wastewater). The flux remained constant during several months of operation.
- The stable flux does not depend on the transmembrane pressure in the range of 40 - 500 mbar, which implies that the resistance of the fouling layer increases with increasing pressure.
- The formation of cavities, channels and dendrite-like structures is observed in the fouling layer formed, starting after about one week of operation.
- When the biological activity in river water is decreased by sodium azide, the formation of a compact fouling layer is observed. In this case, the stabilization of flux and resistance does not occur.
- On basis of the results, it can be assumed that flux stabilization occurs as a result of biological processes in the biofouling layer, leading to formation of channels and cavities in the fouling layer. The stable flux level is reached when the biological processes leading to increase of flux are in equilibrium with the processes leading to decrease of flux (deposition of retained material).
- The phenomenon of flux stabilization has a potential for application in simple gravity-driven ultrafiltration systems suitable for applications on a decentralized scale.

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Supplementary Information

SI 1 Basic membrane filtration principles

Flux (J, $L \cdot h^{-1} \cdot m^{-2}$) relates to the total hydraulic resistance of the pristine membrane (R, m^{-1}) as described by Darcy's law (Mulder, 2000):

$$J = \frac{10^3 \cdot \Delta P}{2.778 \cdot 10^{-9} \cdot \mu \cdot R} \qquad (1)$$

where ΔP (bar) is the transmembrane pressure and μ (Pa·s) is the viscosity of the filtered media. During ultrafiltration (UF) of drinking water, membrane fouling associated with bulk natural organic matter (NOM) (Amy, 2008) causes an increase of the membrane resistance due to pore blockage and cake or gel layer formation (Kimura et al., 2004). Thus, the hydraulic resistance of the fouled membrane should be determined as follow:

$$R = R_m + R_{fc} + R_b \qquad (2)$$

where R_m is resistance of the pristine membrane, R_{fc} is resistance of the cake fouling layer and R_b is resistance caused by pore constriction and blockage (Broeckmann et al., 2006). It has been shown that pore constriction is caused by NOM adsorption and occurs at the initial stage of filtration (Costa et al., 2006). In dead-end UF without backflushing as reported here, a cake forms on the membrane as all components larger than the pore size are retained. The fouling layer resistance (R_{fc}) can be described by the Karman-Kozeny equation:

$$R_{fc} = \frac{75 \cdot (1-\varepsilon)^2}{2 \cdot \varepsilon^3 \cdot \alpha^2} \cdot H \qquad (3)$$

where ε (dimensionless) is the porosity of the fouling layer formed on the membrane surface, α (m) is the characteristic radius of the particles forming the cake layer, and H (m) corresponds to the thickness of the layer (Katsoufidou et al., 2005).

During dead-end filtration without backflushing, all retained material is deposited on the membrane, causing an increase of fouling layer thickness. According to eq. 3, the hydraulic resistance of the fouling layer is defined by the thickness of the layer and its structural parameters. Assuming that the formation of a fouling layer occurs according to the cake filtration theory, the porosity of the layer is expected to remain constant. The resistance of the fouling layer therefore is expected to increase proportionally with the filtrate volume.

SI 2 Membrane integrity

The structural integrity of the membranes and the membrane modules was examined as follows: *Brevundimonas diminuta* (ATCC 19146), a standard filter testing organism of the American Society for Testing and Materials (ASTM, 2005), was cultivated in Luria-Bertani medium (30°C, 48 h). The bacteria were stained with SYBR® Green I (Hammes et al., 2008), separated by centrifugation (3000 rpm), re-suspended in 1 mL of tap water and diluted with river water to a final cell concentration of $3 \cdot 10^5$ cells·mL^{-1}. This solution was permeated in several membrane modules that were operated prior to the experiment for 30 days with river water. The fluorescent bacterial count was measured in the feed as well as in the permeate vessel at 0, 20 and 50 minutes after start of the permeation by flow cytometry according to (Berney et al., 2008). As shown in Figure SI 1, the amount of organisms detected in the permeate by flow cytometry was below the detection limit, which confirms that the membrane was intact and did not have any leakage.

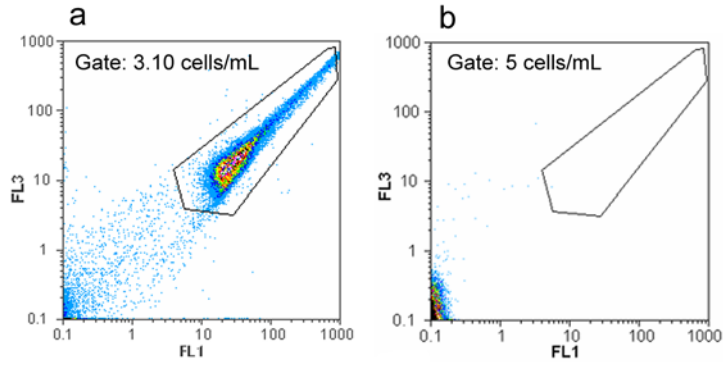


Figure SI 1 - Flow cytometry dot plots of the feed (left) spiked with fluorescently labeled B. diminuta, and the permeate (right) collected after 50 min filtration. FL1 denotes green fluorescence intensity (520 nm) and FL3 denotes red fluorescence intensity (615 nm) in arbitrary units. The same settings and electronic gates were used to distinguish labelled bacterial cells from background in all samples.

SI 3 Impact of staining and de-hydration during CLSM sample preparation on the structure of the fouling layer

In order to make sure that no artefacts occurred during sample preparation procedure, we investigated the impact of the fixation, staining procedure and de-hydration with glycerol on the observed structure of the fouling layer. The images of the fouling layer of a sample treated according to the procedure described in the methods section were compared to the image of a non-preserved and non-stained sample, processed within 1 h after it was removed from the membrane module and the images of the untreated samples in water phase. Figure SI 2 shows that the structures observed were similar, indicating that the sample preparation procedure does not change the sample structure. Another fact confirming that structures observed on the images were not created by sample preparation procedure is the fact that cavities and channels were not observed in samples with azide (see Figure 8 b,d).

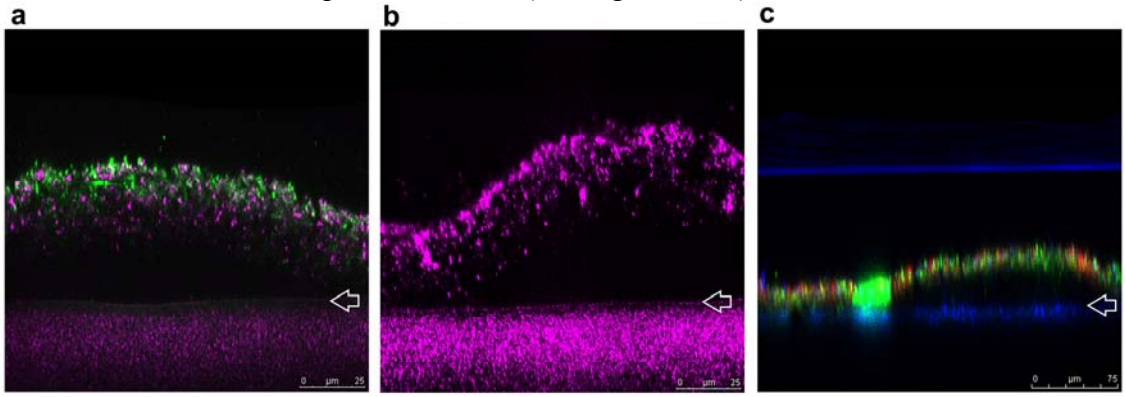


Figure SI 2 - CLSM images of the 9 day old sample. (a) Stained and processed according to the usual procedure (see methods), (green - SYBR® Gold, purple - reflection); (b) Not fixed and not stained sample processed within 1 h after extraction from the module, (purple - reflection); (c) Image of the sample taken in water with a 10x magnification dry lens (blue - reflection, green – SYBR® Gold, red - Concanavalin A). All images have dimensions of 140 x 140 µm.

SI 4 Assimilable organic carbon (AOC) analysis

AOC was determined with a batch growth assay and flow cytometry total cell counts as described previously (Hammes and Egli, 2005). In short: the pasteurized and filtered water samples (15 mL) were inoculated with 10 µL (1 x 10^4 cells·mL^{-1} initial concentration) of a bacterial AOC inoculum. These suspensions were then incubated at 30°C for four days (until stationary phase was reached) and the resulting growth was measured with flow cytometry as described in (Berney et al., 2008). The AOC inoculum originated from river water (Chriesbach river, Dübendorf, CH) and was prepared as described previously (Vital et al., 2007).

Figure SI 3 shows that AOC in permeate was similar or higher than in feed, which indicates that nutrient limitation did not occur during filtration and was not the cause of biomass inactivation or die-off. However, this result does not exclude possibility of local nutrient limitation.

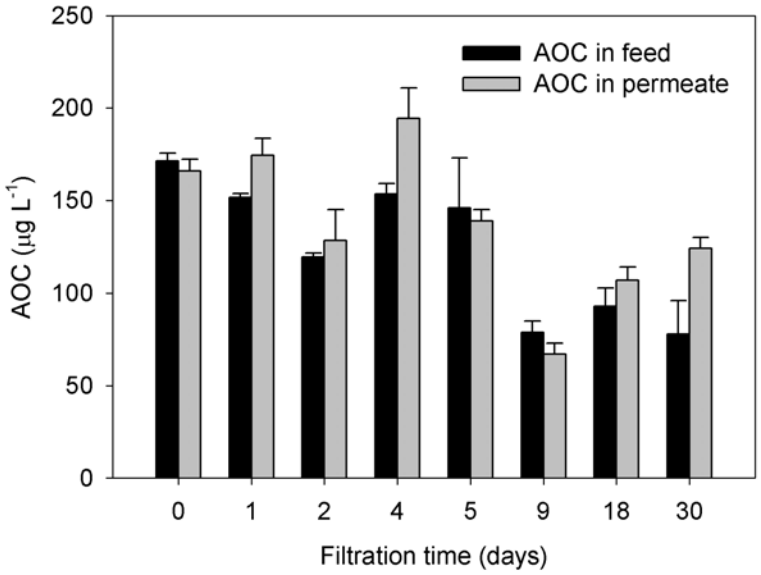


Figure SI 3 - Assimilable organic carbon concentration in the feed and permeate.

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Chapter 3

Mechanisms of membrane fouling during ultra-low pressure ultrafiltration

Maryna Peter-Varbanets, Jonas Margot, Jacqueline Traber, Wouter Pronk

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Mechanisms of membrane fouling during ultra-low pressure ultrafiltration

Maryna Peter-Varbanets [1, 2], Jonas Margot [1], Jacqueline Traber [1], Wouter Pronk [1]
[1] *Eawag: Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, 8600 Dübendorf, Switzerland*
[2] *Institute of Environmental Engineering, ETH Zürich, 8093 Zürich, Switzerland*

Abstract
Gravity-driven, dead-end ultrafiltration of surface water, performed at ultra-low pressures without backflushing, cross-flow or chemical cleaning, results in flux stabilization during extended periods of time. This principle can be used for direct ultrafiltration of surface water without an external energy supply and low maintenance for decentralized drinking-water treatment. Here we investigate the mechanisms of membrane fouling and flux stabilization during gravity-driven, ultra low-pressure UF (ULP-UF). The impact of natural organic matter on the structure and resistance of the fouling layer is studied for seven different types of water, namely river water, pre-treated river water, river water with addition of sodium azide, aerobic diluted wastewater, diluted wastewater with a low dissolved oxygen content and river water spiked with humic acids or kaolin. Our results show that the deposition of non-dissolved material, biologically-induced structural changes in the fouling layer and development of irremovable fouling are three major processes determining the fouling and flux stabilization in ULP-UF. The biologically-induced structural changes in the fouling layer lead to heterogeneous structures and channel networks there and cause a decrease of the specific resistance of this layer over time. Flux stabilization occurs when the decrease of the resistance due to structural changes in the fouling layer balances the increase of resistance due to deposition and irremovable fouling.

1 Introduction
Ultrafiltration (UF) is an effective technology for the treatment of drinking water. It acts as an effective barrier for microorganisms, suspended particles and colloids. Full-scale water treatment UF plants are usually operated at a transmembrane pressure of around 0.5-1.0 bar. Regular backflushing, disinfection and chemical cleaning are used to control membrane fouling and maintain fluxes in the order of 50-100 $L.h^{-1}m^{-2}$. Decentralized UF systems (household or small-scale systems) designed in a similar way are expensive due to the relatively high costs of the auxiliary equipment. Furthermore, such systems depend on electricity for pumps and process control, and require pre-treatment as well as regular maintenance, which is unfavourable for decentralized application, especially in developing countries.
In previous investigations, we studied dead-end UF of surface waters under ultra-low pressure (ULP) conditions (40-100 mbar). We observed a flux stabilization without any backflushing, chemical cleaning or an external energy supply (Peter-Varbanets et al., 2010). With different feed water types, stable flux values in the range of 4-10 $L.h^{-1}m^{-2}$ could be obtained for at least 6 months of operation. The flux stabilization allows the development of low-maintenance UF systems for decentralized application, operated by gravity at a height difference of 40 - 100 cm.

Flux stabilization occurs during long-term operation of ULP-UF and is caused by biological processes leading to structural changes in the fouling layer (Peter-Varbanets et al., 2010). The development of cavities, channel networks and heterogeneous structures causes a decrease in the resistance of the fouling layer, counteracts the increase of its thickness and leads to flux stabilization. Similar structural changes in the fouling layer can be observed in membrane bioreactors (Meng et al., 2009, Le-Clech et al., 2006), although the feed water composition and hydrodynamic conditions there are different.
Biopolymers and humic acids are known to be the major foulants occurring in natural waters (Amy, 2008). It has been shown that biopolymers are retained by UF membranes and interact with particles and some metal ions (Jermann et al., 2008a). Retained biopolymers form a gel or a cake layer which is usually assumed to be homogeneous and porous (Katsoufidou et al., 2005). Humic acids adsorb in and on the membrane, causing pore constriction and increasing adhesion properties of the gel layer formed by biopolymers and particles (Yuan and Zydney, 1999, Jermann et al., 2007). Cake layer formation due to the deposition of extracellular biopolymers is suggested to be a main cause of fouling in MBR systems (Meng 2009). Several studies have shown that soluble microbial products, which are organic compounds of low molecular weight (LMW), released into solution from substrate metabolism and biomass decay, were found to have a great impact on fouling (Barker and Stuckey 1999). In wastewater applications (MBR), the structure of the cake layer is recognized to be more complex. A three-dimensional flow pattern in the cake layer and inter-connectivity of the neighbouring pores in its structure were observed in MBR (Yang et al., 2007).
It is not known which fractions of organic matter affect flux stabilization and how they impact the development, structure and adhesion properties of the fouling layer in ULP-UF. Thus, the limitations of the process regarding water quality parameters are unknown. Understanding the mechanisms of flux stabilization and factors affecting the development of permeable fouling layers will help to increase the stable flux values and capacity of ULP-UF systems.
Here we investigate membrane fouling and flux stabilization in ULP-UF. The focus is on the role of various fractions of organic, particulate and colloidal matter as well as dissolved oxygen (DO) conditions in the membrane fouling. The impact of these factors on the resistance of the fouling layer due to the deposition of foulants as well as structural changes in this layer is investigated. Furthermore, the impact of irremovable fouling on the flux decline and stabilization is studied.

2 Materials and Methods

2.1 Feed water

Seven types of water were investigated: (1) river water (RW); (2) river water pre-treated with biological sand filtration (PRW); (3) river water with addition of sodium azide (RWA); (4) microfiltered wastewater diluted with river water to 7, 20 and 30% (MFDWW); (5) non-microfiltered wastewater diluted with river water to 10, 30 and 50% (DWW); (6) river water with increased concentration of humic acids (RWHA); (7) river water with increased concentration of inorganic particles (RWK).

Every type of water was pre-treated or prepared as described below and pumped to the storage tank. The tank was placed at appropriate heights above the membrane to create the required pressure, thermostated at 20 ± 2 ºC and connected by Teflon tubing to circular membrane modules (Whatman, diameter 48 mm). At least three modules were operated in parallel under similar conditions. A pressure of 65 mbar was used in all experiments. The permeate flux was measured and logged with an Ohaus Adventure Pro scale and the resistance of the fouling layer calculated according to Darcy's law.

(1) RW: River water was pumped directly from the Chriesbach River (Dübendorf, Switzerland) to the storage tank. The Chriesbach river water can be characterized by the following parameters: TOC = 2 - 3 $mg \cdot L^{-1}$; Turbidity = 0.2 - 2 NTU. During rain events, which typically lasted 0.5 - 1 day, the turbidity and TOC reached values of around 30 NTU and 4 $mg \cdot L^{-1}$ respectively.
(2) PRW: Slow sand filtration was used as pre-treatment to reduce the concentration of biodegradable LMW compounds and biodegradable biopolymers. The river water was pre-heated to 20 ± 2 ºC and pumped directly to a slow sand filter with a linear flow rate of 0.05 m/h. A sand fraction with a particle size of 0.25 mm was used. The effluent of the filter was collected in the water storage tank. The pre-treated water was used as feed water to the membrane module installed only after a "schmutzdecke" developed in the upper sand layer and on top of it and concentrations of NOM fractions in the filter effluent stabilized.
(3) RWA: Sodium azide was added to the river water at a concentration of 0.35% to suppress biological activity there: 3.5 g of sodium azide was dissolved in 1 L of river water and stirred for 1 h at 20 ºC. The solution was immediately transferred to the feed water tank of the ultrafiltration system. The solution was renewed daily. The fact that biological activity was suppressed and no biological growth was possible, while the NOM composition of water remained unaltered, had been confirmed previously (see Peter-Varbanets et al., 2010).
(4) MFDWW: Combined wastewater was collected from the town of Dübendorf after primary sedimentation and screen filtration (2 mm mesh size), pumped through a microfiltration membrane (Polypropylene, 0.2 μm, Microdyn-Nadir, Wiesbaden, Germany), oxygenated and collected in a wastewater tank. The microfiltered wastewater and river water were simultaneously pumped into three feed-water tanks with flow rates necessary to dilute wastewater to 7, 20 and 30% of the initial TOC. The feed-water tanks were stirred. The TOC of the raw and diluted wastewater was measured by liquid chromatography coupled to an organic carbon detector (LC-OCD) as described in Section 2.4. The wastewater had a TOC of 60-110 $mgC \cdot L^{-1}$ and a turbidity of 50-120 NTU. Due to re-growth and sedimentation during and after MF and in mixing tanks, the TOC of the diluted wastewater was always lower than the additive TOC of the raw wastewater and river water. The dissolved oxygen content of the diluted wastewater was measured by a dissolved oxygen meter (LDO HQ10, HACH, Germany) in a flow-through module installed in front of the membrane module.
(5) DWW: The same set-up without a microfiltration stage was used for the experiments with non-microfiltered wastewater of 10, 30 and 50% dilution.
(6) RWHA: 1, 2 and 3 mg of dry humic acids (Sigma-Aldrich, Switzerland) were dissolved in 1 L of river water pre-heated to 20 ºC. The solutions were stirred for at least 2 h, sonicated in an ultrasonic bath and transferred to stirred storage tanks. The solutions of humic acids in river water were renewed every 48 h. A system fed by RW was operated in parallel to RWHA under similar conditions.
(7) RWK: Kaolin was used to model the impact of inorganic particles: 30 and 300 $mg \cdot L^{-1}$ of kaolin were dissolved in river water. The solutions were stirred for at least 4 h, sonicated in an ultrasonic bath and transferred to the stirred storage tanks. The solutions were renewed every 24-48 h.
All the experiments were carried out at 20 ± 2 ºC.

2.2 UF membranes and membrane test units

For each experiment we used a new flat sheet polyethersulfone membrane (PBHK, Biomax) with a nominal cutoff of 100 kDa. To remove conservation agents, the new membranes were stored for at least 24 h in de-ionized water, and 1 L of this water was filtered under the same

pressure used in the experiments performed afterwards. The efficiency of this procedure was assessed by DOC measurements of the de-ionized water permeate according to the method described below. The clean water permeability of the membrane was 1200 ± 100 $L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$ (at 20 °C). The membrane test units were standard polycarbonate filter holders of 48 mm inner diameter purchased from Whatman. The integrity of the membranes and modules was verified as described previously (Peter-Varbanets et al., 2010).

2.3 Membrane cleaning and flux recovery

For experiments on irremovable fouling, the membrane was carefully removed from the membrane module and placed into prefiltered (0.22 μm) river water during a defined period of time. The fouling layer was removed by gentle shaking of the membrane in the filtered river water. The flux of the cleaned membrane was determined by filtration of nanopure water under the conditions of the long-term ultrafiltration experiment. Most experiments were conducted in triplicate (in duplicate for diluted wastewater).

2.4 NOM characterization, TOC and AOC determination

The various NOM fractions, including total and dissolved organic carbon (TOC and DOC respectively), biopolymers, humic acids, LMW humic acids, organic acids and neutrals, as well as hydrophobic organic carbon, were characterized by liquid chromatography coupled to an organic carbon detector (LC-OCD). The system was described in detail in Huber and Frimmel, (1992). The detection limit of the method was 10 μgC/L.

LC-OCD in by-pass mode was used to determine TOC as described in Huber and Frimmel, (1992). The detection limit of this method was 10 μgC/L.

For the experiments with addition of humic acids, the concentrations of dissolved and non-dissolved humic acids were determined. The dissolved humic acids were detected by LC-OCD as described below. The non-dissolved humic acids were determined as a difference between the particulate organic matter (POC) measured in river water with addition of humic acids and the POC of river water alone. POC was determined as the difference between TOC and DOC measured by LC-OCD as described above. The total humic acids were determined as the sum of the dissolved and non-dissolved humic acids.

All samples for the LC-OCD analysis were taken directly in front of the membrane module and measured in triplicate. For the experiments with RW, PRW, RWA, MFDWW, and DWW, the concentrations of the NOM fractions, TOC and DOC were measured on at least nine different days, and the average value of these measurements is shown unless indicated otherwise. For the experiments with RWHA and RW operated in parallel to RWHA under similar conditions, the concentrations of the NOM fractions were measured on at least four different days and the average values are shown. The standard deviation did not exceed 10% in all cases unless indicated otherwise.

The permeate samples were collected into Erlenmeyer flasks placed on ice. All samples were stored at 4 ºC and analyzed in triplicate within 6 h. To avoid any contamination, the glassware used for the ultrafiltration experiments, the samples and analysis equipment were cleaned and muffled during 4 h at 450 ^{0}C or more according to Hammes et al. (2006). The retention of NOM fractions was estimated as the difference between the concentration of these fractions in the feed and permeate.

Assimilable organic carbon (AOC) was determined with a batch growth assay and flow cytometry as described previously (Hammes and Egli, 2005).

2.5 Confocal Laser Scanning Microscopy

The samples for the CLSM investigations were prepared as follows: fouled membranes were removed from the modules, immediately cut into sections of approx. 0.25 cm^2 and fixed with formaldehyde (2.5 %). Upon fixation, the samples were stained with SYBR Gold® nucleic acid gel stain (1000-fold diluted stock solution, Invitrogen, Switzerland), incubated in the dark (4 h, 20 ^{0}C) and washed. If Concavalin A (20 mgL^{-1}, Invitrogen, Switzerland) was used to stain the α-D-mannose and α-D-glucose groups of biopolymers, the staining was performed sequentially following the same procedure. The same procedure and sequential staining were also used to detect inactive bacterial cells by propidium iodide (1000-fold diluted stock solution, Invitrogen, Switzerland). Staining was followed by a six-step dehydration with a glycerol/water gradient of 40 - 100 %.

CLSM images of the stained membrane samples were captured using a Leica SP5 microscope equipped with a 63x glycerol immersion Leica objective. All images of the membranes were captured within 12-14 h after the membrane was removed from the system. At least five different sections of the membrane were investigated. Each section was scanned randomly over its whole area excluding the edges of the membrane, and at least ten images most typical of the sample were captured.

The fluorescence of SybrGold® was detected by excitation at 488 nm and emission at 495 - 540 nm. Excitation at 514 nm and emission at 550 - 620 nm were used to detect Concavalin A. The fluorescence of propidium iodide (PI) was detected by excitation at 543 nm and emission at 560 - 620 nm. The reflection of surfaces impermeable to light was detected at a wavelength of 633 nm. Bottled water (Evian, France) filtered through a 0.22 μm microfilter was used to dilute all stock solutions and to wash the samples (Berney et al., 2008). The sample preparation procedure for CLSM has been described in more detail previously (Peter-Varbanets et al., 2010).

3 Results and discussion

3.1 Feed water origin and its impact on membrane fouling

3.1.1 Flux decline and stabilization

In view of the complex composition of surface waters, only natural waters were used as feed water to study the impact of different fractions of natural organic matter (NOM) and turbidity on fouling of the membranes. To obtain waters with different concentrations of TOC, NOM composition, dissolved oxygen (DO) and turbidity, we used untreated and pre-treated river water and primary wastewater effluent, humic acids and kaolin diluted with river water. The following seven water types (with 14 different water qualities) were studied:

(1) RW: River water
(2) PRW: River water pre-treated by biological sand filtration
(3) RWA: River water with biological activity suppressed by sodium azide
(4) DWW: Wastewater diluted with river water at three different dilution rates
(5) MFDWW: Microfiltered, oxygenated wastewater of three different dilution rates
(6) RWHA: River water spiked with humic acids (three different concentrations)
(7) RWK: River water spiked with kaolin (three different concentrations).

Figure 1 shows the flux measured during dead-end ultrafiltration without cross-flow or backflushing for six types of water. After an initial flux decrease during 2-3 days, flux stabilization was observed for RW and PRW (Fig. 1-a) and RWK (Fig. 1-c). In the case of MFDWW (Fig. 1-b), the flux stabilized, although fluctuations could be observed, with a considerable flux increase after 30 days of operation. Stable but lower flux values were

observed for water types with increasing TOC, as can be seen by comparing the flux curves for PRW, RW and MFDWW (Fig. 1-a, b). A steadily decreasing flux and no flux stabilization could be observed for RWA (Fig. 1-a), DWW (Fig. 1-b) and RWHA (Fig. 1-d).

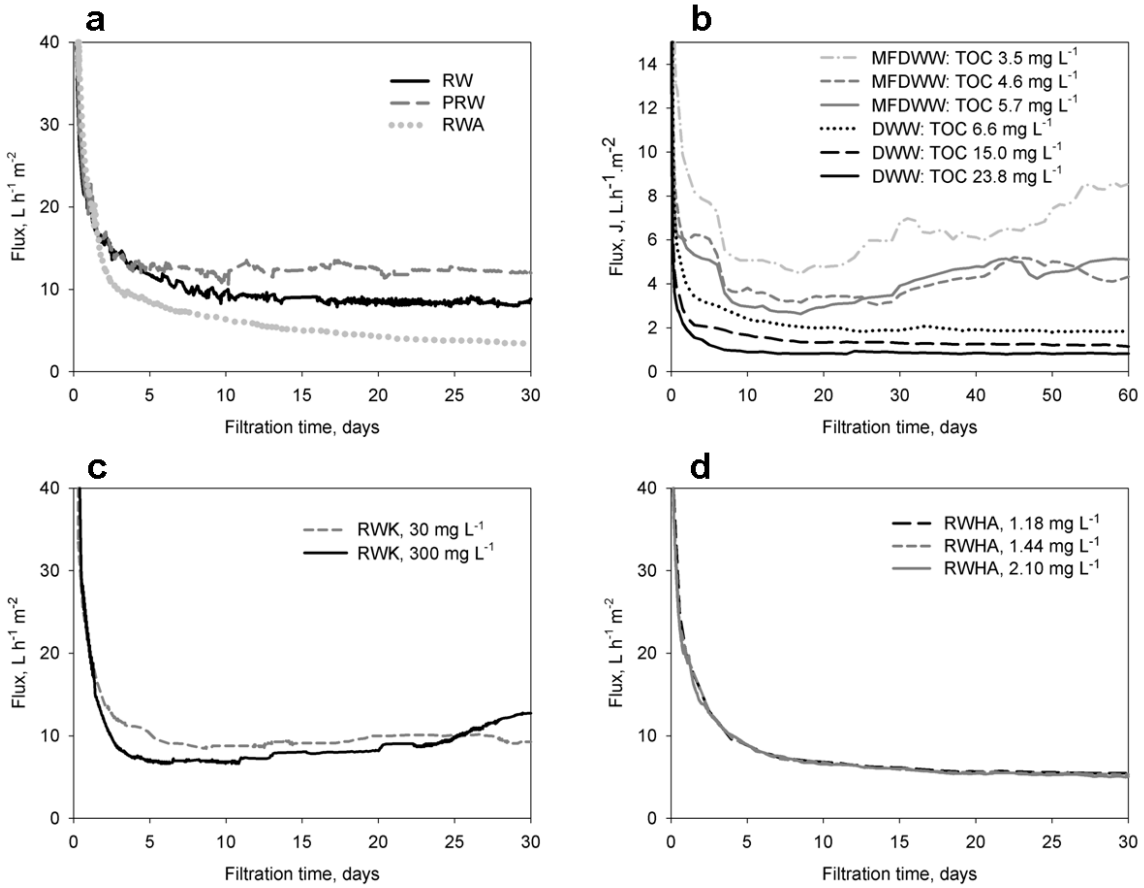


Figure 1 - Membrane flux during dead-end ultrafiltration of (a) river water (RW); (b) microfiltered diluted wastewater (MFDWW) and diluted wastewater (DWW); (c) river water with addition of kaolin (RWK); (d) river water with addition of humic acids (RWHA).

Comparison of Fig. 1-a and Fig. 1-c shows that kaolin added to river water at 30 and 300 mgL^{-1} does not influence the level of flux stabilization. When the turbidity of the river water increased to about 30 NTU (corresponding to 30 mg kaolin·L^{-1}) during periods of rainfall (on days 10-11, 45 and 52), no influence on flux was observed either (Fig. 1-a). This indicates that the deposition of inorganic particles does not influence the resistance of the fouling layer. However, pre-treatment of river water (PRW, Fig. 1-a), addition of diluted wastewater (Fig. 1-b) and humic acids (Fig. 1-c) had a significant impact on flux stabilization and the rate of flux decrease. Thus, the water quality has an important influence on the flux stabilization, and this was consequently studied in more detail. The NOM composition of all water types was characterized and the retention of NOM fractions by the UF membrane was measured as described in the Materials and Methods section.

3.1.2 Characterization of NOM in the feed water and retention of NOM fractions through the membrane

Table 1 shows the TOC and concentrations of several NOM fractions in RW, PRW, MFDWW and DWW, as measured by LC-DOC, as well as the average flux measured during days 10-25 and the dissolved oxygen content (DO).

Table 1 - Average flux, TOC, dissolved oxygen and concentrations of NOM fractions in river water (RW), pretreated river water (PRW), microfiltered diluted wastewater (MFDWW) and diluted wastewater (DWW)

Type of feed water	Stable flux $L.h^{-1}.m^{-2}$	TOC, $\mu g.L^{-1}$	NOM fractions, $\mu g.L^{-1}$				Oxygen, $mg.L^{-1}$
			Bio-polymers	Humic acids	Building blocks	LMW total	
PRW	11.1	1915	27	852	300	346	5.3
RW	8.9	2906	69	1312	504	650	7.9
MFDWW dilution factor:							
7%	6.3	3493	164	1332	528	853	3.7
20%	4.0	4573	294	1454	694	1310	3.1
30%	3.9	5733	377	1458	749	1790	1.0
DWW dilution factor:							
10%	1.9	6545	138	1525	733	2949	0.5
30%	1.3	15004	400	1713	1972	6434	0.1
50%	0.8	23794	392	1638	2027	14704	0.1

When river water was mixed with wastewater (MFDWW and DWW), biological growth occurred in the mixing tank, causing a decrease in the concentrations of biodegradable LMW compounds and biopolymers and a decline of dissolved oxygen content (DO). As shown in Table 1, the ultrafiltration of diluted non-MF wastewater was conducted under low DO conditions ($DO \leq 0.5\ mg \cdot L^{-1}$), and DWW with 30 and 50% dilution rates are considered as anaerobic in this study. Biological growth also occurred in the case of MFDWW, causing a decline of the concentration of LMW compounds. In contrast to DWW, MFDWW was oxygenated prior to mixing with river water. An increase of the oxygen content by oxygenation intensified biological growth in the system. As a consequence, the TOC of MFDWW was lower and the DO was higher than in DWW with the same dilution rate (Table 1). Thus, all water types with the exception of DWW were aerobic (Table 1).

The concentrations of dissolved and total humic acids in RWHA were determined as described in the Material and Methods section in order to assess the aggregation of humic acids in the storage tanks, as also reported in other studies (e.g. Costa, et al., 2006). The data are shown in Table 2. The concentrations of other NOM fractions in RWHA were similar to RW operated under similar conditions and are not shown in Table 2.

Table 2 - Concentrations of dissolved and particulate humic acids

	TOC, $\mu g(C).L^{-1}$	Humic acids total, $\mu g(C).L^{-1}$	Humic acids dissolved, $\mu g(C).L^{-1}$	Turbidity, NTU
RW	2027	982	982	0.8
RWHA	2390	1180	1173	2.1
	2837	1443	1419	3.3
	3577	2097	1673	4.6

Only biopolymers and the humic acid fraction of NOM were retained to some extent during filtration of all types of water. For RW, PRW, RWK, MFDWW and DWW, the retention data are shown in Fig. 2 as a function of the average flux. For RWHA, the retention of dissolved and aggregated humic acids and biopolymers is displayed as a function of the concentration of humic acids in Fig. 3.

The impact of the concentration of different NOM fractions, particulate and colloidal matter on the deposition, structure and structural changes of the fouling layer and on irreversible fouling is discussed in detail in the following sections.

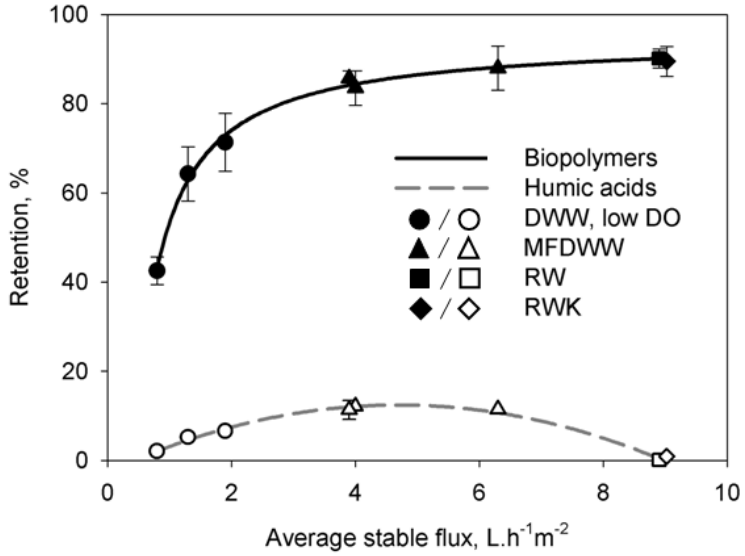


Figure 2 - Retention of biopolymers (closed symbols) and humic acid (open symbols) fractions depending on the stable flux values measured during filtration of RW, RWK and DWW and MFDWW with different dilution rates.

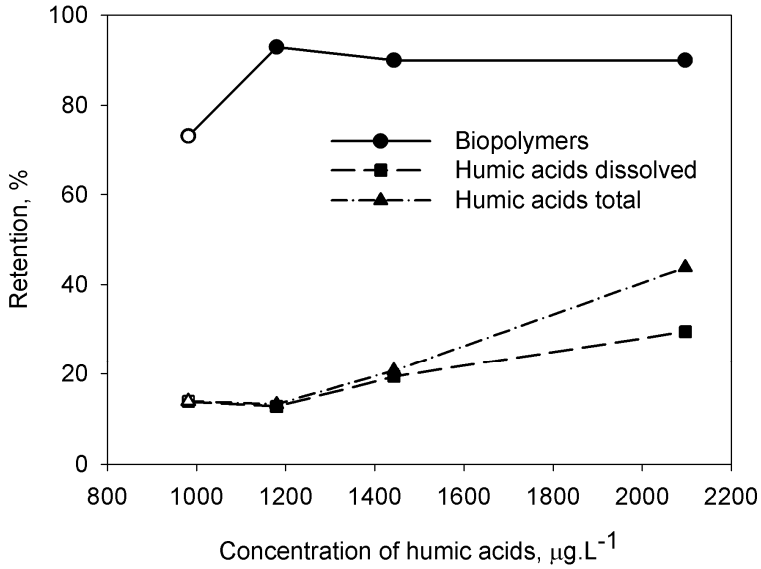


Figure 3 - Retention of biopolymers and total and dissolved humic acids as a function of the concentration of humic acids in RW (open symbols) and RWHA (closed symbols).

3.2 The impact of deposition of NOM, particulate and colloidal matter on fouling mechanisms

3.2.1 The impact of biopolymers

Figure 1-b shows that the flux stabilization does not occur on the same level for different types of aerobic wastewater. The decline of flux and increase in resistance of the fouling layer is generally assumed to be related to the deposition of biopolymers on the membrane surface

and formation of a gel layer (Amy, 2008, Ye et al., 2005, Ji and Zhou, 2006). As shown in Fig. 2, biopolymers are rejected effectively, which would imply that the thickness and resistance of the fouling layer increases with permeated volume and with the concentration of biopolymers. Indeed, Table 1and Fig. 4 show that for all types of aerobic waters, namely pre-treated river water, untreated river water and diluted MF wastewater, the stable flux decreases with increasing concentration of biopolymers.

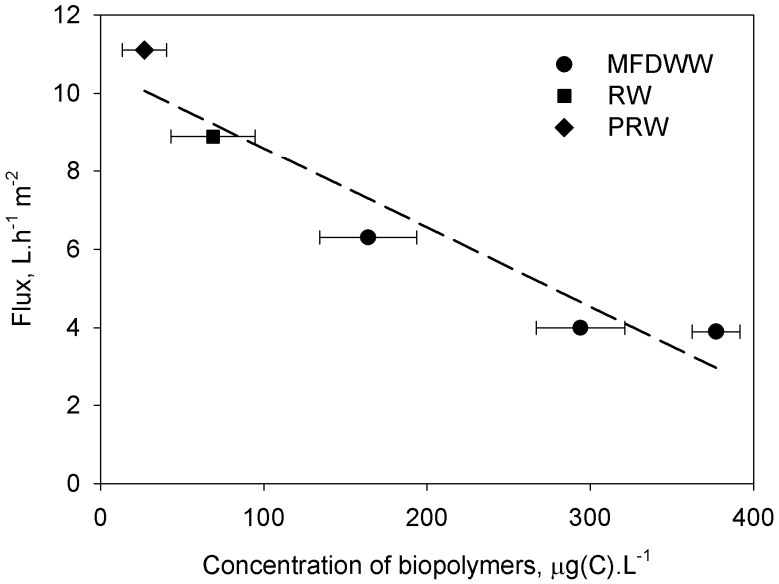


Figure 4 - Stable flux depending on concentration of biopolymer fractions of NOM measured in RW, PRW and MFDWW.

Thus, an increasing rate of deposition of biopolymers in the fouling layer could explain the decreasing flux for all types of aerobic waters. However, in the case of anaerobic DWW, there is no clear correlation between the flux and the measured concentration of biopolymers (Table 1) as will be further discussed in Section 3.3.2.

3.2.2 The impact of dissolved and colloidal humic acids

Figure 2 shows that besides biopolymers, only the humic acid fraction was partly retained by the membrane. The concentration of humic acids is comparable for RW, MFDWW diluted to 7% and DWW diluted to 30 and 50%. Nevertheless, a significant flux difference is observed in these cases, which indicates that autochtonous humic acids do not influence the flux stabilization.

Table 2 shows that in contrast to autochtonous humic acids, the addition of humic acids to river water leads to increased turbidity, while the difference between dissolved and total humic acids increases. This indicates that part of the added humic acids aggregates. The size of the aggregates was determined to be approx. 50-100 nm by photon correlation spectroscopy (PCN, Zetasizer NS, Malvern, UK). Figure 3 shows that approx.15-35% of the dissolved humic acids, all aggregated humic acids and 90% of the biopolymers are retained by the membrane. All other NOM fractions remain similar to river water, indicating that the deposition of colloidal aggregates of humic acids prevent flux stabilization, as shown in Fig. 1-d.

3.2.3 The impact of inorganic particles

Figure 1-c and Fig.1-a show that the deposition of inorganic particles has no impact on the flux stabilization. The high concentrations of particles in the feed water (30 and 300 mg.L^{-1} kaolin) and the fact that the flux does not depend on the kaolin concentration, indicate that the *specific* resistance of the cake layer formed by inorganic particles is considerably lower than the resistance caused by NOM. This has also been observed previously by Jermann et al., (2008 a, b). Thus, it can be concluded that the concentration of NOM fractions defines the flux and the resistance of the fouling layer, while the concentration of particles does not have a significant impact on the resistance.

3.3 Structural changes in the fouling layer

We have already shown that the flux stabilization and the resistance of the fouling layer are attributed to the formation of cavities, channels and heterogeneous structures in the fouling layer (Peter-Varbanets et al., 2010). It was shown that these cavities and channels are formed due to biological processes within the layer, namely growth, die-off and degradation of cells and EPS (Peter-Varbanets et al., 2010). When the biological activity is suppressed (RWA), no flux stabilization is observed (Fig. 1-a).

The availability of easily biodegradable building blocks (BB), LMW compounds and DO is expected to influence the biological processes leading to the formation of heterogeneous structures and thus to the resistance of the fouling layer. In addition to biological processes, physico-chemical processes could also potentially affect the structure of the fouling layer. The impact of BB and LMW compounds, DO and physico-chemical interactions between NOM, particles and colloids is consequently discussed in detail below.

3.3.1 The impact of BB, LMW compounds and AOC on structural changes in the fouling layer

When the average stable flux is plotted against the concentration of LMW fraction (Fig. 5), a clear (non-linear) relationship can be observed.

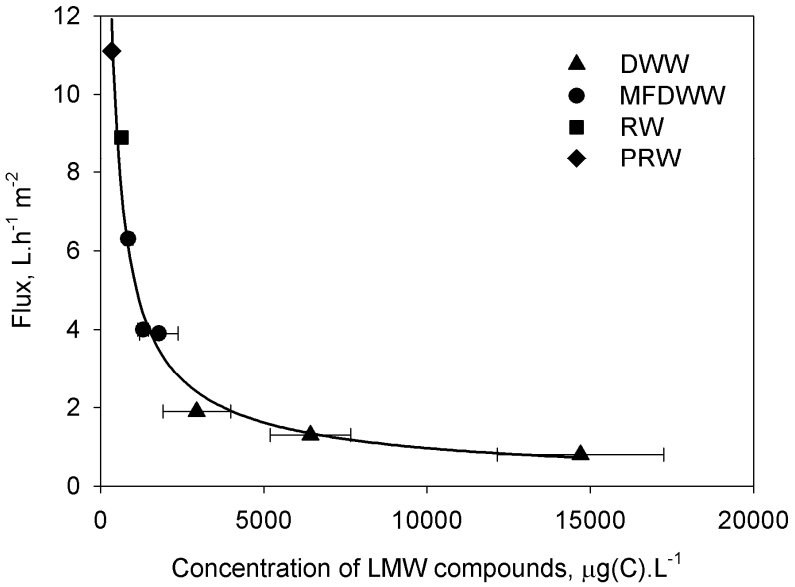


Figure 5 - Stable flux depending on concentration of LMW compounds

Table 1 shows that the average stable flux decreases with an increase in the concentration of the building blocks (BB), although no clear correlation can be observed in this case. The existence of the correlation for LMW compounds and decline of stable flux with an increase in concentration of BB can be explained as follows. As the concentration of LMW and BB increases, the concentration of assimilable organic carbon (AOC) can also be expected to increase. In order to assess this effect, the AOC, LMW and BB concentrations were measured at the same point of time in MFDWW with three different dilution factors as well as in RW. As shown in Table 3, the AOC values increased from 85 µg (C) $\cdot L^{-1}$ in RW to 2149 µg (C) $\cdot L^{-1}$ in MFDWW (30%) , while the measured concentration of LMW compounds increased from 510 µg (C) $\cdot L^{-1}$ in RW to 2206 µg (C) $\cdot L^{-1}$ in MFDWW (dilution factor 30%) and the BB increased from 359 µg (C) $\cdot L^{-1}$ in RW to 708 µg (C) $\cdot L^{-1}$ in MFDWW.

Table 3 - AOC and concentrations of building blocks and LMW compounds measured after 50 days of filtration

Type of water		LMW compounds, µg·L^{-1}	Building blocks, µg·L^{-1}	AOC, µg·L^{-1}
RW		510	359	85
MFDWW	7%	943	481	269
	20%	1295	696	1749
	30%	2206	708	2149

As mentioned above, biological degradation processes lead to the formation of heterogeneous structures and channels in the fouling layer, thus lowering its hydraulic resistance. Increased AOC concentrations under non-limiting DO conditions lead to increased microbial growth rates (Vital et al., 2007), which can be expected to counteract the process of microbial degradation. Furthermore, it can be expected that increased microbial growth leads to a higher amount of biomass in the fouling layer resulting in greater thickness of the layer and filling or narrowing of the channels. These processes cause an increase in the resistance of the fouling layer and a decline of the stable flux.

In addition, the increasing rate of deposition of the biopolymers in the fouling layer also causes an increase in the resistance of the fouling layer, as discussed in Section 3.2.1. Furthermore, part of the biopolymers retained in the fouling layer is biodegradable and can contribute to the processes of biological growth and degradation discussed above.

Thus our results show that all three factors, namely the deposition of biopolymers (1), the increase of microbial growth rate (2), and the decline of microbial and EPS degradation rate (3), can contribute to the increase in the resistance of the fouling layer and a decline of the stable flux. However, the data presented here do not give clear evidence as to which of these factors dominates.

3.3.2 The impact of DO on the structure of the fouling layer

A high concentration of biodegradable LMW compounds in the feed water intensifies biological growth, leading to a decline of the dissolved oxygen (DO) concentration in the feed water. Table 1 shows that for UF of diluted non-MF wastewater (DWW), the DO was low ($\leq$ 0.5 mg$\cdot L^{-1}$). Figure 2 shows that the retention of biopolymers and humic acids decreases at low DO (DWW), although the stable flux decreases and the resistance of the layer consequently increases. This result indicates that the concentration of soluble and colloidal macromolecules smaller than membrane cut-off increases, and the concentration of aggregated or colloidal macromolecules larger than cut-off decreases under DO-limited conditions, as also observed by Yun et al. (2006), Kang et al., (2003), Jin et al., (2006) and Min et al. (2008). The mechanisms of this process are unknown and require further investigation. However, it can be expected that the decrease in the size of accumulated

particles will lead to the formation of a more compact fouling layer structure and cause an increase in resistance.

3.3.3 Physico-chemical interactions within the fouling layer

Inorganic particles and aggregates of humic acids dominating in the fouling layers formed by RWHA and RWK are not easily biodegradable and thus do not play a significant role in the biological processes. Therefore it can be expected that the process of channel formation and aggregation is strongly limited or does not take place at all in these water types. With an increase of the filtered volume, the thickness of the fouling layer will continue to grow in time, leading to an increase in resistance as the structure remains unaltered. This explains the fact that no flux stabilization occurs in the case of added humic acids (Fig. 1-d). However, it does not explain why the resistance of the fouling layer stabilizes in the case of added kaolin (Fig. 1-c). The differences between these two types of systems are discussed below.

According to existing knowledge (Aoustin, et al., 2001, Jermann, et al., 2007), humic acids interact with metal ions (e.g. Ca) and form bridges between particles, biopolymers and the membrane surface. Furthermore, as humic acids are more hydrophobic than other fractions of NOM, they can interact within the fouling layer (Yuan and Zydney, 1999b). These intra-molecular interactions between humic acid aggregates are expected to cause the formation of a compact layer with high cohesion strength and low heterogeneity. The formation of such a compact fouling layer can be confirmed by the fact that the separation properties of the membrane fouled with aggregates of humic acids increase compared to the membrane fouled with river water in parallel experiments. This is indicated in Fig. 3, which shows that the retention of dissolved humic acids increases with the concentration of total humic acids, and the retention of biopolymers is higher than in river water.

It was shown in Fig. 1-c and discussed in Section 3.2.3 that the concentration of kaolin does not have a significant impact on the resistance of the fouling layer. Figure 2 shows that kaolin does not influence the retention of biopolymers and humic acids. This indicates that a relatively open fouling layer structure similar to RW is formed in the case of RWK. The intra-molecular interactions which are expected to result in the formation of a compact layer in the presence of humic acid aggregates do not occur in the presence of inorganic particles (Jermann et al., 2008 a,b). However, it is plausible that biological processes leading to these structural changes in the fouling layer would occur both in the presence and absence of particles. So it can be assumed that these biological processes define the structure and resistance of the fouling layer, while particles do not have a significant impact on the resistance.

3.4 The structure and resistance of the fouling layers observed by CLSM

Structural changes in the biofouling layer, namely biologically induced formation of cavities, channel networks, dendrite-like structures and detachment of the fouling layer were observed in a previous study. It was shown that the formation of cavities and channels reduced fouling layer resistance and heterogeneity and the thickness of the fouling layer increased with time (Peter-Varbanets et al., 2010). The development of these heterogeneous structures was found to be the cause of flux stabilization (Peter-Varbanets et al., 2010).
This study showed that DO-limited conditions and deposition of colloidal humic acids prevent flux stabilization and a compact and homogeneous fouling layer is expected to form in these

cases. In order to confirm this, the structure of the fouling layer formed under aerobic and anaerobic conditions as well as during filtration of colloidal humic acids was investigated using CLSM.

3.4.1 The structure of the fouling layers formed in aerobic and anaerobic waters

The structure of the fouling layer formed during ULP-UF of aerobic river water was investigated previously (Peter-Varbanets et al., 2010). A typical CLSM image of the fouling layer formed during 28 days of filtration of river water (RW) is shown in Fig. 6-c. Channels can be observed reaching from the top of the fouling layer down to the membrane. When the biological activity was suppressed by sodium azide (RWA), a compact and homogeneous fouling layer was observed (Fig. 6-d).
During long-term operation with RW, the formation of heterogeneous structures in the fouling layer can be observed visually without the microscope. In the case of filtration of MFDWW, this process is even more pronounced, finally leading to detachment of the fouling layer and self-initiated clearing of the membrane surface on a macro-scale as shown in Fig. 7. The release of patches from the fouling layer ("sloughing") causes a sudden increase in flux fluctuations, as shown in Fig. 1-b for MFDWW. In the case of RW, the detachment processes occur on a smaller scale and the flux fluctuation is consequently less pronounced. Thus in the case of MFDWW, just like for RW, the structure changes over time, leading to more heterogeneous structures of lower specific resistance and thus to flux stabilisation.

The CLSM images of the layer during the filtration of anaerobic wastewater (DWW 30% and 50%) show that the formation of cavities and channels observed between the layer and the membrane during filtration of river water (Fig. 6-c) is not observed for DWW (Fig. 6-a, b). Although a more heterogeneous structure is observed on the upper surface of the fouling layer, a layer of about 40 μm thickness on the membrane surface does not show any cavities or channels. This layer resembles the compact and homogeneous fouling layer formed during filtration of RWA (Fig. 6-d).
Thus, the fouling layer formed under anaerobic conditions has a more compact structure and lower heterogeneity than the aerobic fouling layer. Similar results were observed during filtration of aerobic and anaerobic wastewater in MBR (Yun, 2006).
The resistance of a homogeneous layer can be described by the Karman-Kozeny equation (Katsoufidou et al., 2005). While the structure remains unaltered and the thickness of the fouling layer increases over time, this equation predicts an increase of resistance with the increase of permeate volume in dead-end filtration. This corresponds to our findings that flux stabilization does not occur under DO-limited conditions (DWW) or in the case of disinfected river water (RWA).

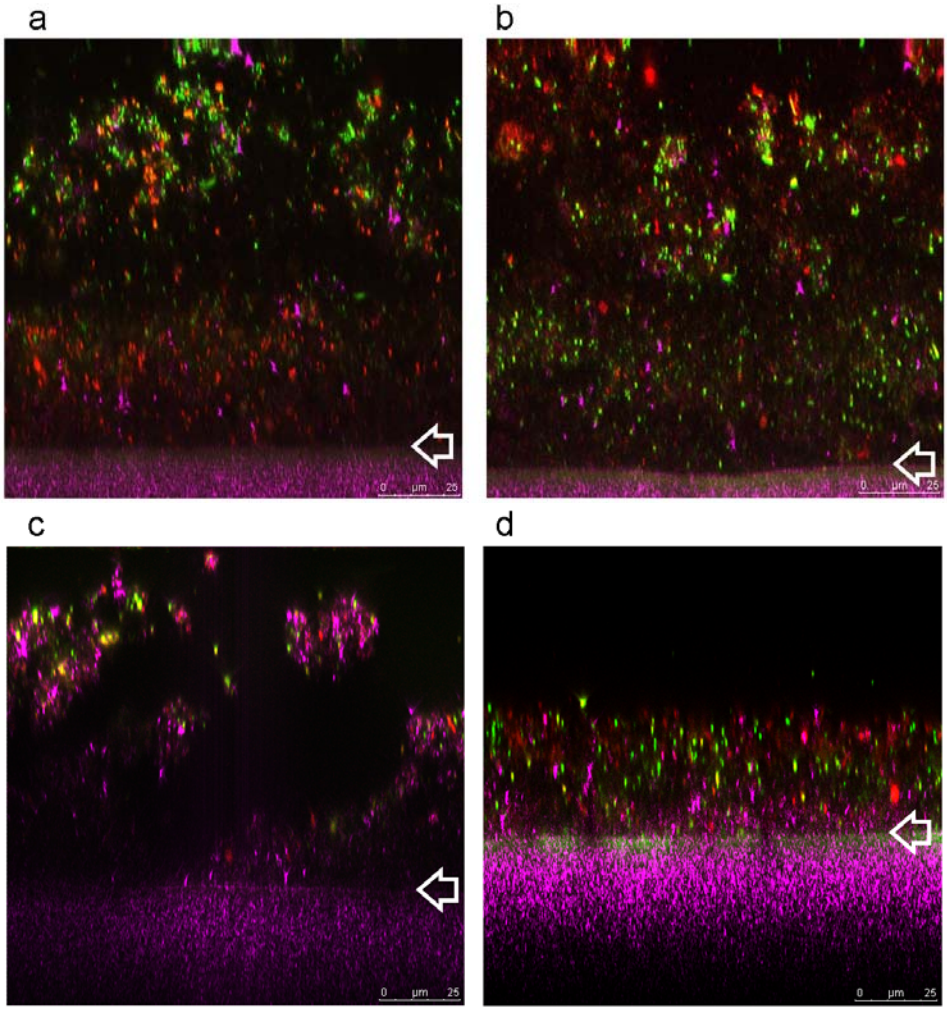


Figure 6 - Optical cross-section of the fouling layer formed on the membrane during ultrafiltration of DWW (30% wastewater) (a, b), RW (c) and disinfected RW (d). Green – SYBR® Gold stain, indicating presence of all bacterial cells; Purple - reflection of the solid surfaces; Red (a) - Propidium iodide stain indicating presence of inactivated bacterial cells; Red (b, c, d) - Concanavalin A stain indicating presence of α-D-mannose and α-D-glucose groups in biopolymers. All images have dimensions of 140 x 140 µm.

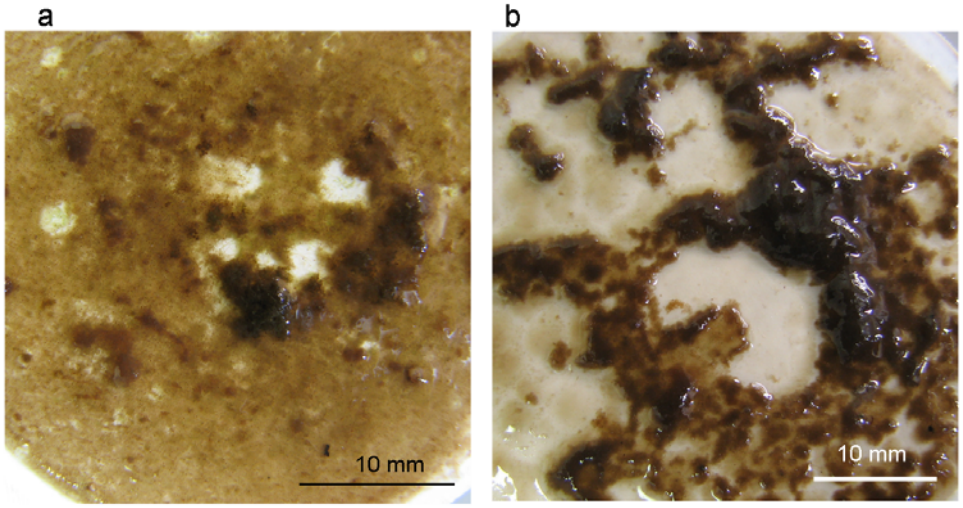


Figure 7 - Fouling layer formed during ultrafiltration of MFDWW diluted to 20% after 60 days of operation (a) and MFDWW diluted to 30% after 92 days of operation

3.4.2 The structure of the fouling layers formed by colloidal humic acids

The CLSM images show that reflecting particles dominate the fouling layer formed during filtration of RWHA (Fig. 8-a). Such particles are not observed in the layer formed during parallel filtration of RW (Fig. 8-b) and are thus identified as aggregates of humic acids. Detachment of the layer from the membrane surface is also observed with RWHA, indicating a relatively low adhesion strength of the layer to the membrane. However, channels and cavities in the layer which can be seen in Fig. 6-c and Fig. 8-a for river water are absent in the layer formed with spiked humic acids (Fig. 8-b). Thus, the formation of heterogeneous structures does not occur in the layer formed by colloidal humic acids and its resistance depends on the permeated volume and increases over time. As discussed in Section 3.3.3, the interactions within the fouling layer lead to the formation of a compact fouling layer, and, as shown in Fig. 8-b, dominate the attachment of the layer to the membrane.

3.5 Irremovable fouling during ULP-UF

Two terms, irremovable and irreversible fouling, are used in UF of drinking water and wastewater to describe fouling which cannot be removed by cleaning. Generally, in UF of drinking water, irreversible fouling is defined as the fouling which cannot be removed by physical methods of cleaning (backflushing), but can partly be removed by chemical cleaning (Kimura et al., 2004). In wastewater applications, irreversible fouling is considered to be refractory to removal by any methods, including chemical cleaning. The fouling which can be removed by chemical but not physical cleaning is considered to be irremovable (Meng et al., 2009). In ULP-UF, backflushing and chemical cleaning are not applied to remove accumulated fouling layer. However, gentle shaking of the membrane module and flushing the membrane surface after a standstill period of 2-7 days leads to complete removal of the fouling layer (Fig. 9-a) and partial flux recovery. The fouling layer removed after cleaning is defined as “removable fouling” in this study. The fouling which is not removed during this cleaning procedure is defined as “irremovable fouling”. Thus, the difference between initial flux and flux measured after cleaning is defined as flux decline due to irremovable fouling.

Figure 10 shows the flux recovery of membranes after removal of the fouling layer formed during filtration of RW, RWA, DWW, and RWHA. Only 40-60% of the resistance was recovered in all samples, although a fouling layer was not visible on the CLSM images (Fig. 9-a). As shown in Fig. 10, flux recovery decreases with filtration time and increases with the duration of the standstill period. Flux recovery is lower for disinfected river water (RWA) and anaerobic wastewater (DWW), but does not depend on the TOC of the diluted wastewater. Addition of humic acids to the river water (RWHA) causes an increase of flux recovery.

The main reason for irremovable fouling in drinking water applications of UF is known to be adsorption of the humic acid fraction of NOM into the pores of the membrane (Katsoufidou et al. 2008). Deposition of cells inside the pores of the membrane, known to cause irremovable fouling in MBR and increasing the resistance by 8% (Lee, et al., 2001), is unlikely in ULP-UF due to the small pore size of the membranes used (around 19 nm), which does not allow access of bacteria. We suggest two other reasons for irremovable fouling, namely pore constriction on the permeate side due to re-growth of microorganisms and formation of a so-called “base layer” on the membrane surface. A base layer is a thin fouling layer (but thicker than a single adsorption layer) which covers a surface and from which channels and mushroom-like structures can develop (Massol-Deya et al., 1995). These authors observed the formation of a base layer in aerobic biofilms in fixed-film reactors. The existence of such a layer on the membrane can be expected to lead to increased resistance. The mechanisms of adsorption, re-growth and formation of a base layer are discussed below in more detail.

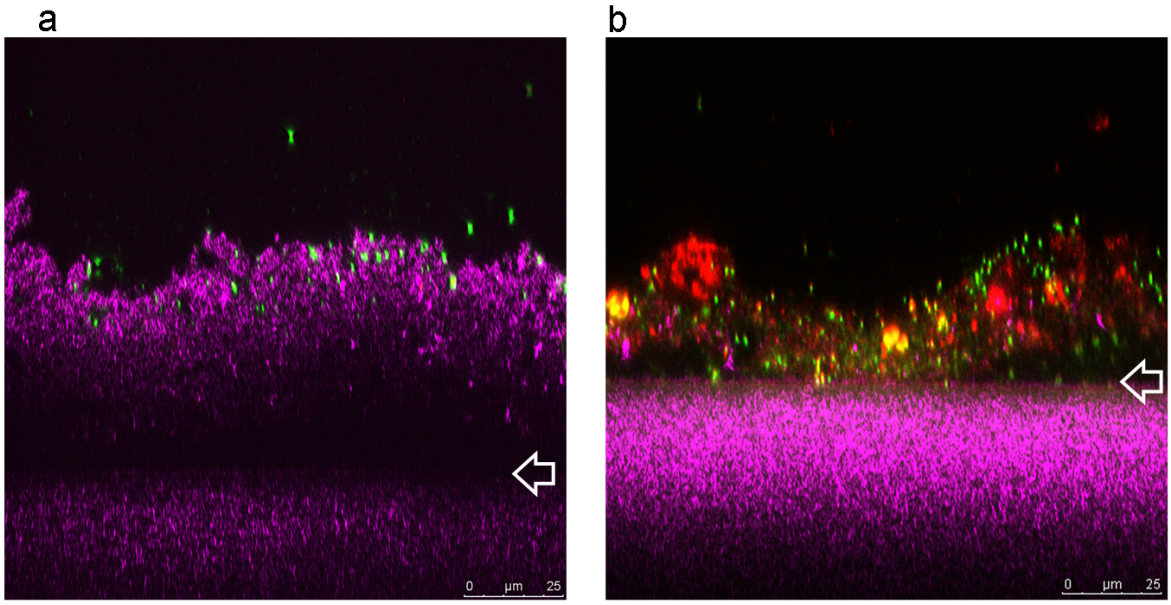


Figure 8 - CLSM image of fouling layer formed during ultrafiltration of (a) humic acids dissolved in river water (RWHA) and (b) RW in parallel experiments. Green – SYBR® Gold stain, indicating presence of all bacterial cells; Purple - reflection of the solid surfaces; Red (b) - Concanavalin A stain indicating presence of α-D-mannose and α-D-glucose groups in biopolymers. The image has dimensions of 140 x 140 µm.

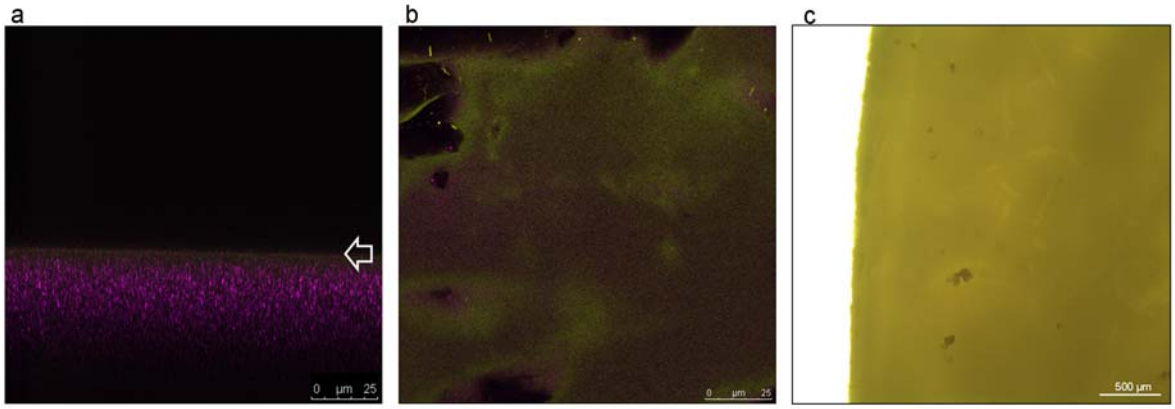


Figure 9 - CLSM images of an optical membrane cross-section (a), the membrane surface (b), and an image of the edge between the base layer and the clean membrane surface obtained with the optical microscope (c). All images are of the same membrane and were taken after 31 days of filtration of RW, a standstill period of one week and cleaning. For images (a) and (b), purple indicates reflection of the solid surfaces and yellow (b) is a Concanavalin A stain indicating presence of α-D-mannose and α-D-glucose groups in biopolymers. The image has dimensions of 140 x 140 µm.

Adsorption. Adsorption of soluble NOM into the pores of a clean membrane occurs typically in the initial stage of filtration and declines over time due to saturation of the adsorption centres in the pores and on the surface of a membrane (Katsoufidou et al., 2008). Over the long term, the resistance caused by adsorption should not depend on the operation time. However, Fig. 10 shows that flux recovery decreases with the increase of operation time, indicating that adsorption is not the only reason for irremovable fouling in ULP-UF.

Biological re-growth on the permeate side. UF membranes retain microorganisms but not LMW compounds, including AOC, and the permeate is therefore a suitable medium for re-growth. If re-growth of microorganisms is not inhibited, it will occur on the permeate side of the membrane. The support layer of PES membranes has a relatively open structure, composed of cellulose fibres, which can be colonized by microorganisms. Pore blocking of the support layer is unlikely due to the relatively large size of the pores. Furthermore, a low flux recovery was also observed in river water which contained sodium azide (RWA), although biological re-growth does not occur in these conditions, as was shown previously (Peter-Varbanets, et al., 2010). This indicates that biological re-growth on the permeate side is not the major reason for irremovable fouling.

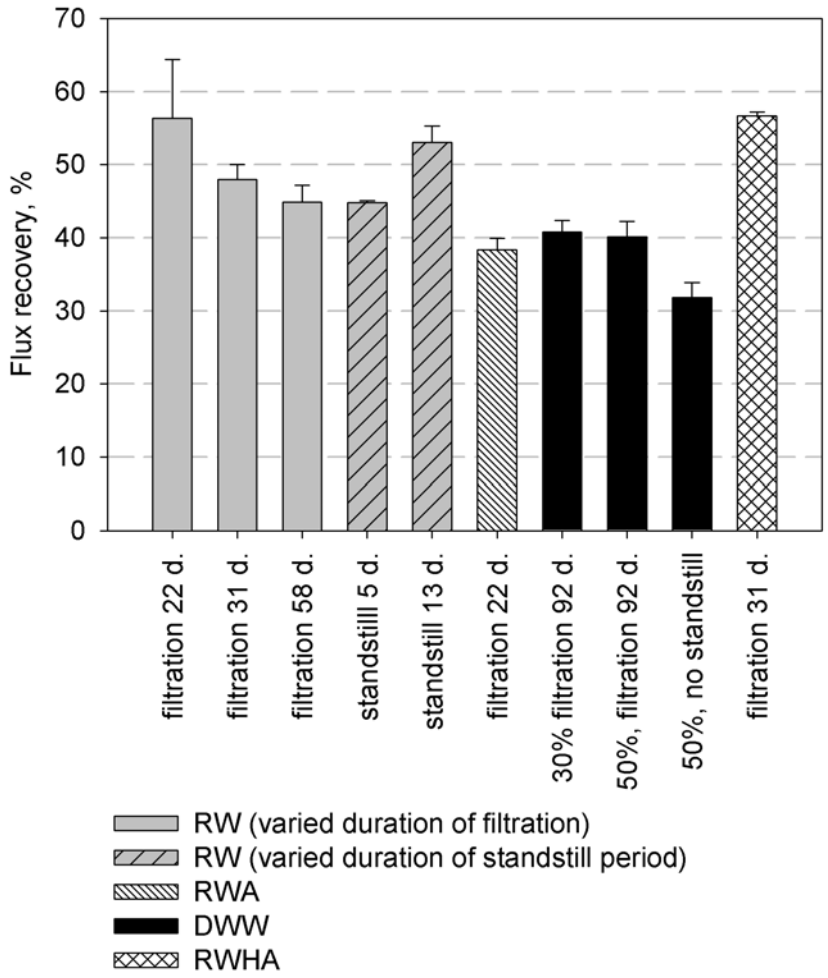


Figure 10 - Flux recovery after physical cleaning of the membrane surface for RW, disinfected RW, DWW and RWHA

Base layer. The CLSM image of a cleaned membrane shows that the fouling layer was completely removed from the membrane surface (Fig. 9-a). However, a patchy and thin coloured layer is still visible on the membrane (Fig. 9-c). Staining of this layer with a lectin stain of Concanavalin A shows that biopolymers are present on the membrane surface (Fig. 9-b). It is assumed that flux recovery is mainly due to the properties of this base layer, because it influences the interaction between the fouling layer and the membrane surfaces.

The CLSM images of the aerobic and biologically active fouling layers (Fig. 6-c, Fig. 8) showed local detachment of the fouling layer. This could imply that the interaction between the base and fouling layers varies over the membrane surface or that biological processes causing detachment of the fouling layer occur locally.
As discussed in Peter-Varbanets et al. (2010), one of the plausible reasons for the detachment of the fouling layer and hence its varying attachment strength is biologically induced degradation of EPS and bacterial cells inside the fouling layer and on the layer/membrane interface. During a standstill period, nutrient limitation intensifies degradation processes, further decreasing attachment strength of the layer and finally leading to its complete detachment from the base layer and the membrane surface. It can be expected that the efficiency of cleaning is high and thus resistance due to irremovable fouling is low for the layers with low attachment strength.
In contrast to the aerobic fouling layer, the fouling layers formed under anaerobic conditions as well as the biologically inactive layers do not detach, which indicates that the interaction between the base and fouling layers is relatively strong (Fig. 4a, b and d). The efficiency of cleaning can be expected to be lower for fouling layers with high adhesion strength than for those with low adhesion strength. Thus the resistance due to irremovable fouling is expected to be higher in the case of anaerobic waters.
This corresponds to the situation in MBRs where it was observed that the interactions between layer and membrane are higher under anaerobic than under aerobic conditions (Yun, 2006), resulting in a lower cleaning efficiency under anaerobic conditions.

3.6 The fouling mechanisms in ULP-UF

For a pristine membrane, the flux (J, $L \cdot h^{-1} \cdot m^{-2}$) is related to the total hydraulic resistance (R, m^{-1}) as described by Darcy's law (Mulder, 2000):

$$J = \frac{10^3 \cdot \Delta P}{2.778 \cdot 10^{-9} \cdot \mu \cdot R} \qquad (1)$$

where ΔP (bar) is the transmembrane pressure and μ (Pa·s) the viscosity of the filtered media.
During ultrafiltration (UF) of drinking water, membrane fouling causes an increase in membrane resistance over time. Our results show that the resistance of the fouling layer depends on the deposition of non-dissolved material and structural changes in the fouling layer. The deposition contributes to an increase in resistance over time (dR_d/dt). Irremovable fouling also leads to an increase in resistance (dR_{irr}/dt). The structural changes in the fouling layer due to physico-chemical interactions can also lead to an increase in resistance. However, structural changes in the fouling layer leading to the formation of cavities and channels were shown to cause a decrease in the resistance of the fouling layer over time ($-dR_{stch}/dt$). The resistance is expected to stabilize when the sum of these processes equals zero:

$$\frac{dR}{dt} = \frac{dR_d}{dt} + \frac{dR_{irr}}{dt} - \frac{dR_{stch}}{dt} = 0. \qquad (2)$$

Thus, under stable conditions, the increase in the resistance of the fouling layer due to deposition, physico-chemical interactions and resistance due to irremovable fouling counteracts the decrease in resistance due to structural changes in the fouling layer. These three processes define the mechanisms of fouling and flux stabilization in ultra-low pressure ultrafiltration. The major factors affecting these processes are summarized in Table 4, showing that concentrations of biopolymers and LMW compounds, DO conditions and concentration of colloidal humic acids are the major factors affecting the membrane fouling mechanisms in ULP UF.
The complex channel structures observed in fouling layers in river water and aerobic diluted wastewater during ULP UF resemble the heterogeneous structures found in fouling layers in

MBRs (Yang et al., 2007, Yun et al., 2006). The factors affecting membrane fouling mechanisms are reasonably similar in both systems, although the hydrodynamic conditions are different.

Table 4 - Mechanisms of membrane fouling in ULP-UF

Fouling mechanism		**Process**	**Factors affecting resistance**
Deposition	Fouling layer formation	Advective transport	Biopolymers
			Colloidal humic acids
Structural changes	Formation of heterogeneous structures, channels and cavities	Biological processes (growth, degradation)	AOC, LMW compounds Dissolved oxygen
	Physico-chemical interactions	Hydrophobic interactions, adsorption, metal bridge formation	Biopolymers, Colloidal humic acids
Irremovable fouling	Pore narrowing and constriction	Adsorption	Dissolved humic acids, biopolymers
		Re-growth on permeate side	AOC/LMW compounds
		Base layer	Biopolymers Microorganisms

4 Conclusions

In this study, seven different types of water were used to investigate the mechanisms of membrane fouling in ULP-UF. The following conclusions can be drawn:

(1) The deposition of non-dissolved material, structural changes in the fouling layer and development of irremovable fouling over time are three major processes that define the mechanisms of fouling and flux stabilization in ULP-UF. Flux stabilization and resistance occur when the increase in the resistance due to structural changes in the fouling layer counteracts the decrease in resistance due to deposition and irremovable fouling.

(2) In aerobic systems or systems without addition of colloidal humic acids, the level of flux stabilization depends mostly on the concentration of biopolymers and biodegradable compounds.

(3) DO-limiting conditions prevent the development of channel structures in the fouling layer, resulting in a more compact structure with higher resistance.

(4) An increase in resistance is also observed when colloidal humic acids are added to the feed water. In this case, channels and cavities are not formed and hydrophobic interactions between the colloids cause the formation of a compact fouling layer.

(5) Deposition of inorganic particles has no impact on flux stabilization.

(6) Irremovable fouling in ULP-UF contributes to 40-60% of the flux decline and is lower for aerobic and biologically active systems than for DO-limited systems. The most probable explanation for this irremovable fouling is the formation of a base layer on the membrane.

Acknowledgements

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Chapter 4

Intermittent operation of ultra-low pressure ultrafiltration for decentralized drinking water treatment

Maryna Peter-Varbanets, Weija Li, Willi Gujer, Wouter Pronk

in preparation

Intermittent operation of ultra-low pressure ultrafiltration for decentralized drinking water treatment

Maryna Peter-Varbanets [1, 2], Weija Li [1], Willi Gujer [1,2], Wouter Pronk [1]
[1] *Eawag: Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, 8600 Dübendorf, Switzerland*
[2] *Institute of Environmental Engineering, ETH Zürich, 8093 Zürich, Switzerland*

Abstract
Gravity-driven, dead-end ultrafiltration of surface water, performed at ultra-low pressures without backflushing, cross-flow or chemical cleaning, results in flux stabilization during extended periods of time. This principle can be used in household systems for drinking water treatment. In these systems, the treatment of drinking water takes place once or twice a day with regular interruptions. Therefore, these systems should be suitable for intermittent operation.
Here we investigate the impact of intermittent operation on stabilization of flux during ultra-low pressure ultrafiltration with and without forward flushing after standstill periods. Our results show that an increase of flux is observed after standstill periods of 3-312 h. Flux measured after a standstill period increases with the increase of standstill time and is higher for the systems operated with river water and with flushing than for the systems operated without flushing or with diluted wastewater. A simple model to predict flux and production capacity of the system depending on the duration of standstill during long term intermittent operation is proposed. It is shown that the production capacity of the system does not change significantly when operated with flushing, although operation time is reduced.

1 Introduction
Ultrafiltration (UF) provides an effective barrier for microorganisms, suspended particles and colloids and is an effective technology for the treatment of drinking water. The phenomenon of flux stabilization during gravity-driven ultrafiltration (UF) allows the development of low-maintenance systems operated at a transmembrane pressure of 40-100 mbar for decentralized applications. In previous investigations, we showed that the stabilization of flux occurs at 4-10 $L.h^{-1}m^{-2}$ for at least 6 month of operation with different water types, although no backflushing or chemical cleaning were used (Peter-Varbanets et al., 2010). These flux values allow treatment of 48-120 $L.day^{-1}$ of water with 0.5 m^2 of membrane which is sufficient for application of ultrafiltration at ultra-low pressure (ULP) conditions on household scale.
Household systems for drinking water treatment, also known as point-of-use systems are increasingly implemented in developing and transition countries (Peter-Varbanets et al., 2009). At present there are about 20 million users of such systems worldwide (WHO, HWTS). When applied in developing countries, these systems have been associated with considerable reductions in disease (Fewtrell et al., 2005). Household systems are designed to treat only the part of water used for drinking and cooking which amounts to 10-40 L/day for a 5 member family (Peter-Varbanets et al., 2009). In most available household systems the treatment is usually done once or twice a day, depending on the flow-rate of a filter or a batch size and local customs (Sobsey, 2002). Therefore, the decentralized system should be suitable for intermittent operation.

The impact of intermittent operation on membrane based decentralized systems for drinking water treatment has never been investigated before. However, intermittent operation has been already employed as a physical cleaning method for flat sheet membranes in wastewater treatment. Applied in membrane bioreactors, the process of stopping the permeate flux is called relaxation (van der Marel et al., 2009; Phattaranawik and Leiknes, 2009). Currently, relaxation is employed for about 15-120 s every 3-10 min (Drews et al., 2009; Grelot et al., 2009). An improvement of the flux in MBRs due to pressure relaxation is explained by the enhanced foulant back transport (Hong, et al., 2002). Aeration enhances back transport leading to the reduction of a fouling rate (Hong et al., 2002). Hong et al. (1997) showed 100% flux recovery by pressure relaxation during ultrafiltration of colloidal suspensions. However, relaxation is assumed to be ineffective when the deposition of foulants on the membrane surface is irreversible (van der Marel et al., 2009). Metzger et al., (2007) showed that relaxation can increase irremovable fouling compared to a long-term continuous operation due to removal of the cake layer which protects membrane surface from irreversible adsorption of soluble biopolymers (Metzger et al., 2007).
Thus, it is not known what impact intermittent operation can have on ultrafiltration. Furthermore, it is evident that intermittent operation in gravity-driven UF systems for decentralized applications differs from relaxation applied in MBRs. The relaxation periods in MBRs are shorter, compared to the standstill periods during UF for decentralized application (15-60 s for MBRs compared to 1-24 h for UF). Furthermore, aeration, which enhances back transport of foulants from the membrane surface, cannot be used for gravity driven decentralized applications due to high energy requirements. However, other methods may be applied to enhance removal of particles deposited in the fouling layer on a long term and to control fouling. In only few existing gravity-driven UF systems for decentralized application (SkyJuice, LifeStraw) irregular backflushing and disinfection with slow eluting chlorine tablets (LifeStraw) or manual chemical cleaning (SkyJuice, 2009) are applied to control fouling (Clasen et al., 2009, SkyJuice, 2009). Disinfection and chemical cleaning are not suitable for the systems based on the phenomenon of flux stabilization. We have shown previously that inactivation of biomass in the fouling layer leads to the clogging of the membranes (Peter-Varbanets et al., 2010). Backflushing decreases the capacity and increases the complexity of the gravity-driven system while it has to be done with treated water. However, forward flushing can be done manually with feed water and therefore may be used to increase the flux on a long term during continuous or intermittent operation. Due to back transport phenomenon described by Hong et al., (2002), it can be assumed that forward flushing is most effective after a standstill period.

Thus, in order to predict the behavior of a system operated intermittently on a long term, the impact of standstill periods on stabilized flux is investigated in this study. Standstill periods of 3-19 h/day are investigated for at least 3 month of dead-end ultrafiltration at 65 mbar of hydrostatic pressure. The effect of a simple method to control fouling such as regular forward flushing is explored in order to increase the capacity of the system. Regular forward flushing of the membrane surface is investigated during continuous and intermittent operation and its impact on the production capacity of the system is also studied.

2 Materials and methods

2.1 Feed water

Two basic types of water were investigated. River water was pumped directly from River Chriesbach (Duebendorf, Switzerland) to the storage tank. The Chriesbach river water can be

characterized by the following parameters: TOC = 2 - 3 $mg \cdot L^{-1}$; Turbidity = 0.2 - 2 NTU, Dissolved Oxygen = 7-7.5 $mg \cdot L^{-1}$. During rain events, which typically lasted 0.5 - 1 day, the turbidity and TOC reached values around 30 NTU and 4 $mg \cdot L^{-1}$ respectively.
Combined wastewater was collected from the city of Dübendorf after primary sedimentation and screen filtration (2 mm mesh size). The wastewater and river water were simultaneously pumped into a stirred feed water tank with a flow-rate necessary to dilute wastewater to 10% of the initial TOC. TOC of the raw and diluted wastewater was measured by liquid chromatography coupled to an organic carbon detector (LC-OCD) as described in Huber and Frimmel (1992). The diluted wastewater had a TOC of 5.5-7.6 $mgC \cdot L^{-1}$ and Turbidity of 6-9 NTU.

2.2 UF membranes and membrane test units

For each experiment we used a new flat sheet polyethersulfone membrane (PBHK, Biomax) with a nominal cutoff of 100 kDa. To remove conservation agents, the new membranes were stored for at least 24 h in de-ionized water and 1 L of de-ionized water was filtered under the same pressure as used in the experiments performed afterwards. The efficiency of this procedure was assessed by DOC measurements of the de-ionized water permeate according to the method described below. The clean water permeability of the membrane was 1200 ± 100 $L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$ (at 20°C). The membrane test units were standard polycarbonate filter holders of 48 mm inner diameter purchased from Whatman. For the experiments with forward flushing we used two-part plexi-glass membrane modules of our own design. The membrane (25 cm^2) was placed on a spacer on one part of the module and sealed with a silicon O-ring and a second part. The retentate volume of the module was 25 cm^3. The integrity of membranes and modules was verified as described before (Peter-Varbanets et al., 2010).

2.3 System set-up

River water or diluted wastewater were pumped into the feed water tank. The tank was placed at heights, corresponding to 65 mbar transmembrane pressure, thermostated at 20 ± 2 ºC and connected by Teflon tubing to the membrane modules (Whatman, diameter 48 mm). In each experiment, at least two modules were operated in parallel under similar conditions. The permeate flux was measured and logged with an Ohaus Adventure Pro scale with a precision of 0.1 g.
The membrane modules were operated continuously without flushing or cleaning for 10 or 21 days and the flow was interrupted for a standstill period of defined duration. After the standstill period, the systems were operated continuously till the flux stabilized.
The impact of forward flushing was studied in a similar way. However the membrane was flushed after the standstill period. Flushing was done with feed water at a flow-rate of 10 ml/min during 10 minutes which corresponded to a Reynolds number of 6.8 and implied laminar flow conditions.
To study the long-term impact of long term intermittent operation with and without forward flushing, 7 systems were operated in parallel for a period of 60 days. Forward flushing was carried out every day at the end of a standstill period. The standstill periods of 3h, 6h, 12h and 19h were studied. The duration of a standstill period was regulated by a magnetic valve and a timer. In addition, a system was operated with a standstill period of 12 h without flushing and two systems were operated continuously with and without flushing. Flushing was done with feed water as described above.

2.4 Confocal Laser Scanning Microscopy

To obtain CLSM images of the fouled membrane and membrane after standstill period with flushing, two systems were operated continuously for 21 days. One of the membranes was removed from the system before the standstill period, and the other was flushed after a standstill period of 168 h. Both membranes were fixed, prepared and investigated by CLSM as described previously (Peter-Varbanets et al., 2010).

2.5 Particle size distribution

The particle size distribution was measured in feed water and flush water weekly during 60 days of intermittent operation using a Single Particle Counter (SW-PE, Klotz, Bad Liebenzell, Germany) with a detection limit of 1 μm. The particle concentrations were multiplied by the volume of feed water and flush water to obtain total particle numbers. In total 14 measurements during a measurement period of 60 days were made.

3 Results

3.1 Flux stabilization and recovery

As reported before, the phenomenon of flux stabilization can be observed during dead-end ultrafiltration (UF) of river water without flushing, cross-flow or cleaning under ultra-low pressure (ULP) conditions (Peter-Varbanets et al., 2010). Figure 1 shows the decline and stabilization of flux during ULP-UF of river water and diluted wastewater filtered at 65 mbar for a period of 30 days.

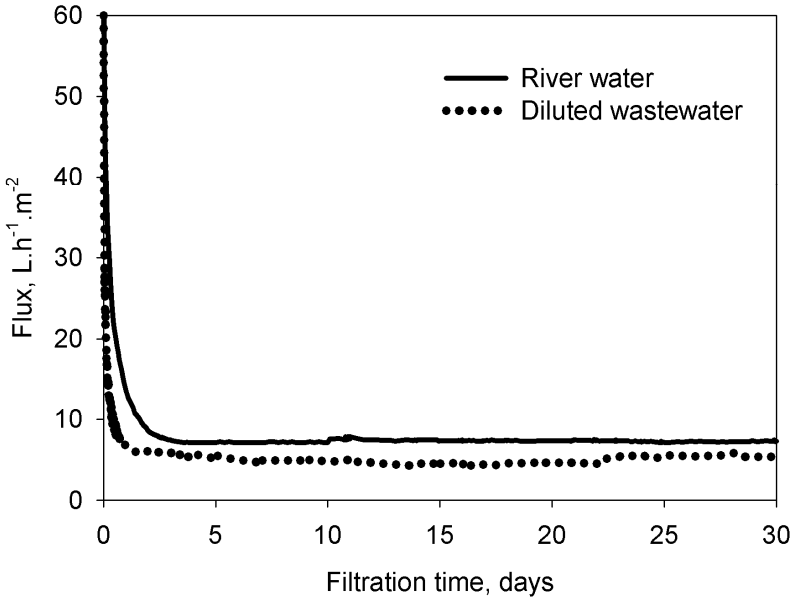


Figure 1 - Membrane flux during continuous dead-end ultrafiltration of river water and diluted wastewater

To study the impact of the duration of standstill period on flux during ULP-UF, membrane modules were operated continuously for 10 days. After 10 days, operation of the modules was interrupted by closing the feed and permeate channels of the modules. After a standstill period, the filtration was started again and a higher value of flux was observed, as shown in Fig. 2-a. After about 2 days of continuous operation which followed the standstill period, the flux decreased and stabilized at the value of stable flux observed before the standstill period.

Similar results were observed for a system continuously operated for 21 days before the standstill period (Fig.2-b).
When a membrane was flushed after a standstill period as described in Material and methods section, a higher recovery of flux was measured (Fig. 2-c,d). Also in this case, similar results were observed for a system continuously operated for 10 (Fig. 2-c) and 21 days (Fig. 2-d).

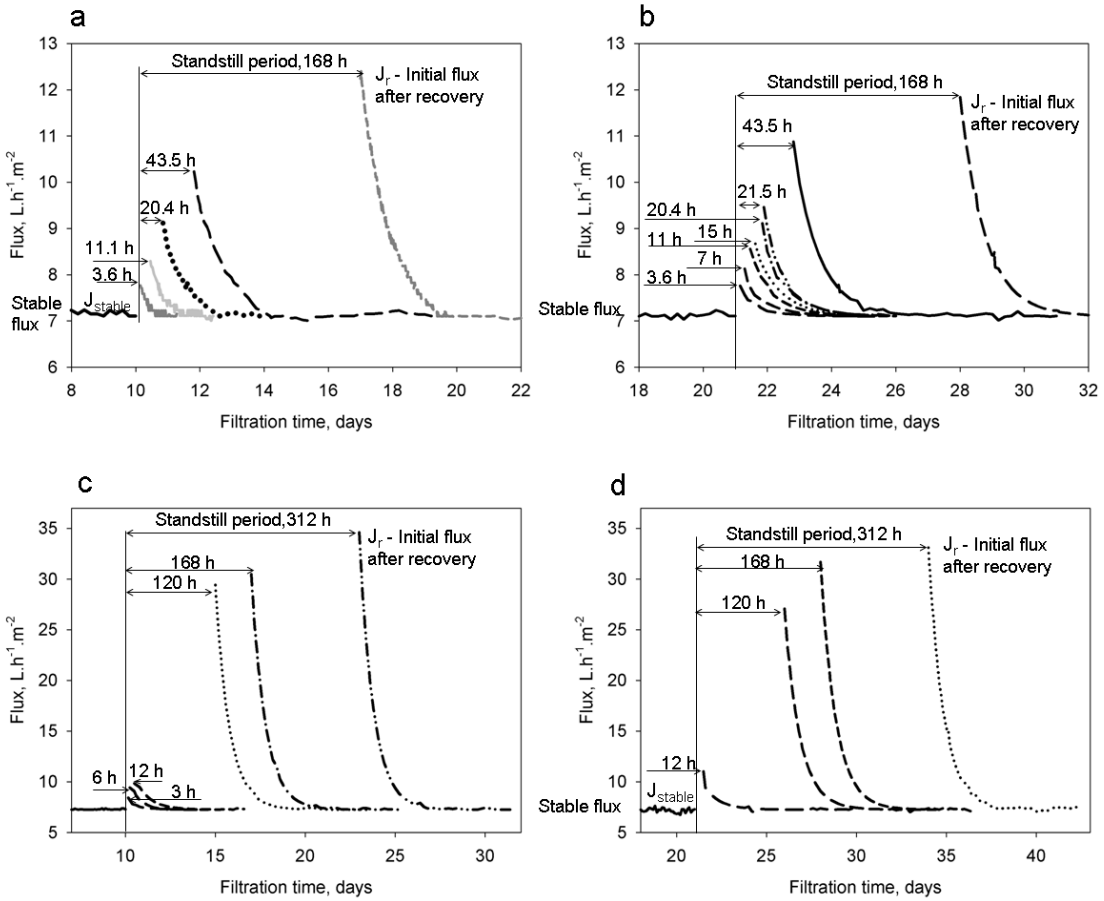


Figure 2 - Membrane flux during dead-end ultrafiltration of river water operated for 10 (a, c) and 21 (b, d) days followed by standstill periods with (c, d) and without (a, b) flushing.

Figure 3 shows the values of the flux after recovery plotted against the duration of a standstill period. Figure 3 shows that the initial flux after recovery J_r (L.h^{-1}m^{-2}) increased with the duration of the standstill period in all situations. The duration of operation of the system before the standstill period did not influence the recovery of flux, while flushing resulted in higher values of the initial flux after recovery, as shown in Fig. 3.
The recovery of flux after a standstill period occurred also when diluted wastewater was used. However, lower values of flux after recovery were observed for diluted wastewater than for river water (Fig. 3).

3.2 Intermittent operation

3.2.1 Impact of intermittent operation with and without flushing on flux

In order to simulate the long-term impact of intermittent operation on stable flux, ULP UF systems were operated intermittently with and without flushing after every standstill period with a fixed 24 h cycle for a period of 60 days. Figure 4 shows flux measured in systems operated continuously and intermittently for 12 h/day with and without flushing (a) and for

systems operated intermittently for 21, 18, 12 and 5 h/day with flushing (b). Figure 4-a shows that flushing does not influence the value of stable flux for the systems operated without a standstill period. However, an increase of flux due to flushing is observed for the systems operated during 12 h/day (Fig. 4-a). Figure 4-b shows that an increase of flux is observed with a decrease of daily operation period for the systems operated with flushing.

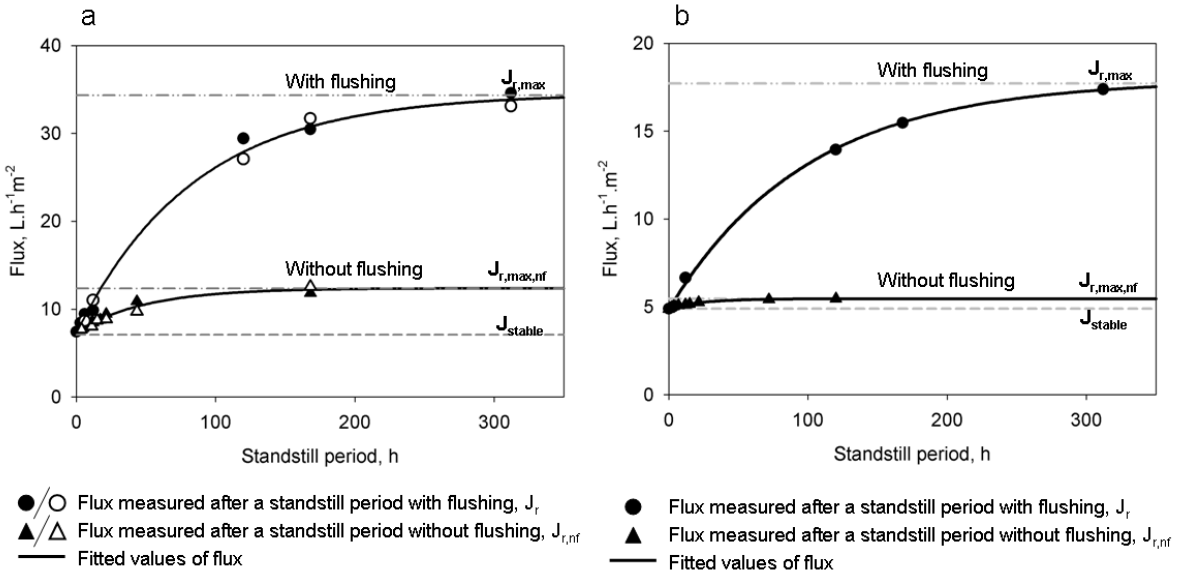


Figure 3 - Measured and fitted initial flux after recovery (J_r) depending on the duration of a standstill period for systems operated with and without flushing with river water (a) and diluted wastewater (b). Closed symbols correspond to the flux measured in the systems operated for 10 days before the standstill period, open symbols correspond to the 21 days of operation.

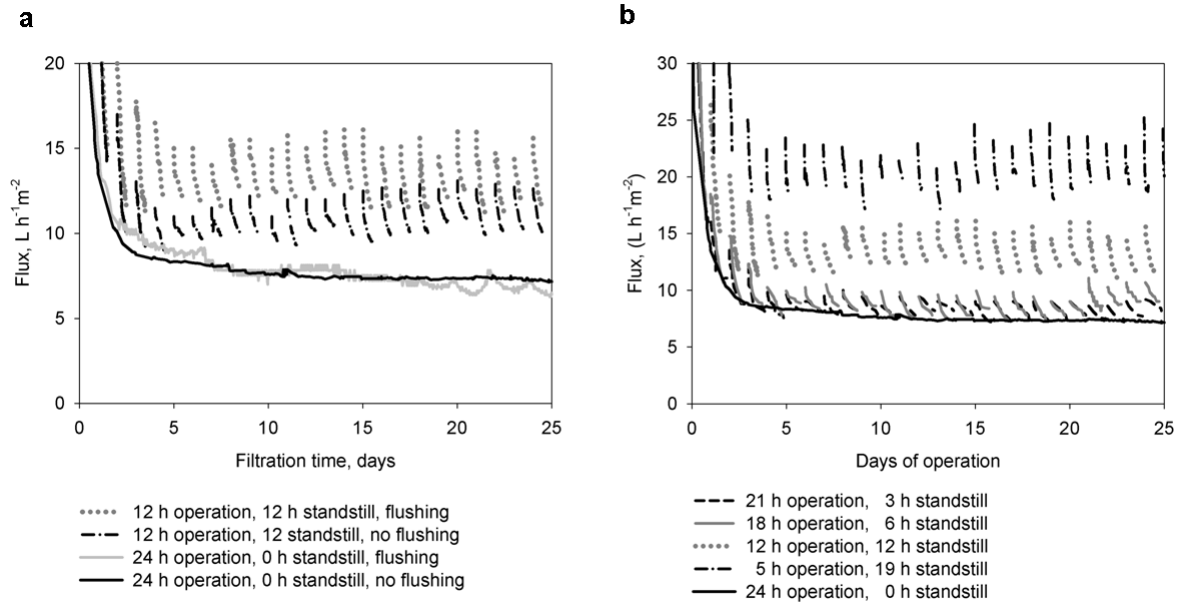


Figure 4 - Membrane flux during ultrafiltration of river water operated with and without flushing with no standstill and during 12 h/day (a), and intermittent ultrafiltration with flushing operated during 21,18,12 and 5 h/day (b)

3.2.2 Characterization of particles and dissolved organic matter

In order to gain more insight in the flux recovery processes during intermittent operation, the particle size distribution was measured in feed water and flush water as described in Section 2.5. Figure 5 depicts these accumulated particle numbers in the feed water and in the flush water for one single filtration cycle, whereby 5-a and 5-b represent different representative cycles during a total measurement period of 60 days.

Figure 5 shows that the particle size distributions in feed and in flush water are different. The relative amount of larger particles (above 20 μm) is higher in the both flush waters than in the feed and furthermore, the flush water contains significant numbers of larger particles which are not at all present in the feed water (above 73 μm for day 28 and 46 μm for day 36). The amount of small particles (below 20 μm) is not consistent: it is higher in the flush water at day 28, but somewhat lower at day 36. Figure 5 shows that the amount of larger particles in the flush water increases with the time of standstill.

It is evident from Figure 5 that the total mass of flushed material is higher than the total mass of particles in the feed. To explain this, dissolved organic carbon (DOC) retained by the membrane has to be taken into account. Figure 6 shows the material balance for DOC in feed and flush water measured by Size Exclusion Chromatography (as described by Huber and Frimmel, 1992). The values of DOC "retained" refers to the difference between the total DOC measured in feed and permeate during one filtration cycle. The DOC in flush refers to the total amount of DOC removed by flushing (see legend of the Fig. 6). Fig. 6 shows that more DOC is retained on the membrane (due to size exclusion, assimilation or dissimilation by microbial cells) than removed by flushing. This indicates that part of the DOC is bound in the fouling layer and is removed in a particulate form.

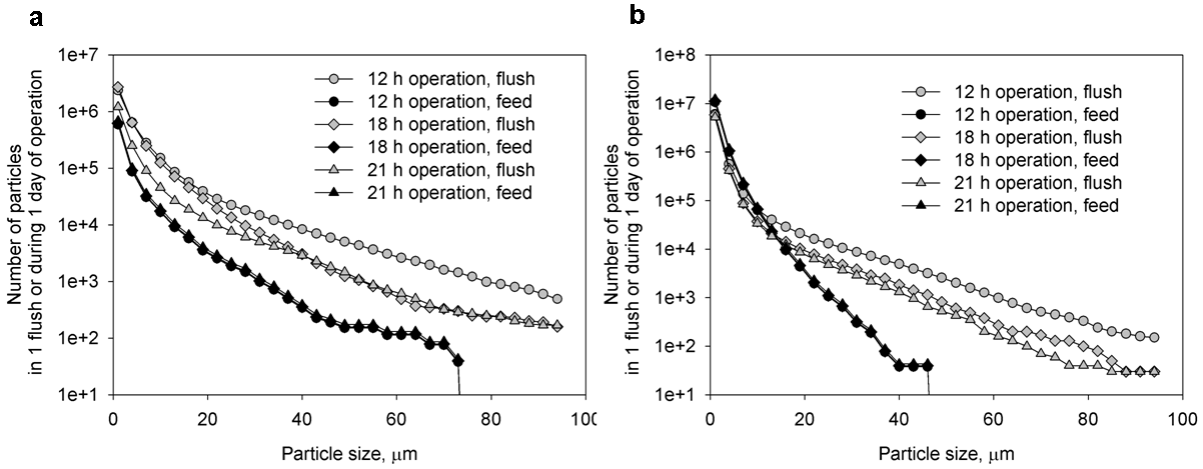


Figure 5 - Cumulative particle counts in feed water filtered (closed symbols) and flush water (open symbols) collected during one cycle, measured on days 28 (a) and 36 (b)

Thus, our results show that transformation and/or aggregation processes occur in the fouling layer during the operation and standstill period leading to the formation of larger particles. This can be confirmed by visual observation of the fouling layer: Figure 7 shows photographs of fouled membranes after 60 days of operation. Larger aggregate-structures can be observed in the fouling layer formed with intermittent operation (Figs. 7-b, c, d), while the fouling layer formed during continuous operation displays a relatively smooth structure (Fig. 7-a). The impact of aggregation on flux recovery during standstill is discussed in Section 4.1.

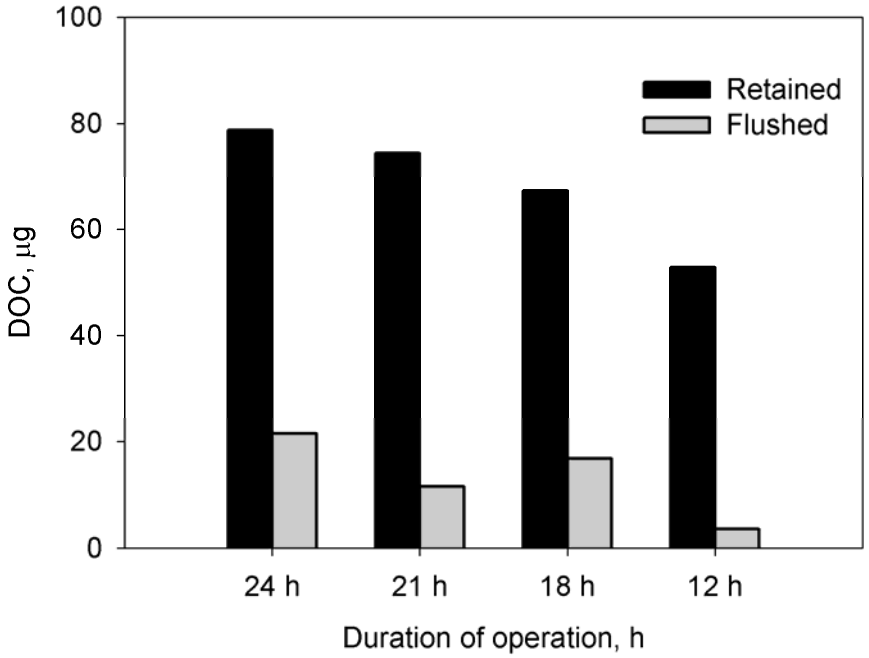


Figure 6 - Cumulative DOC retained by the membrane and flushed after one filtration cycle. The values of DOC were calculated as follows: retained DOC refers to a difference between DOC in feed and permeate for the volume of water filtered during 1 cycle; DOC in flush refers to the difference between total DOC measured in flush and background DOC in feed, for the flush water volume in 1 cycle.

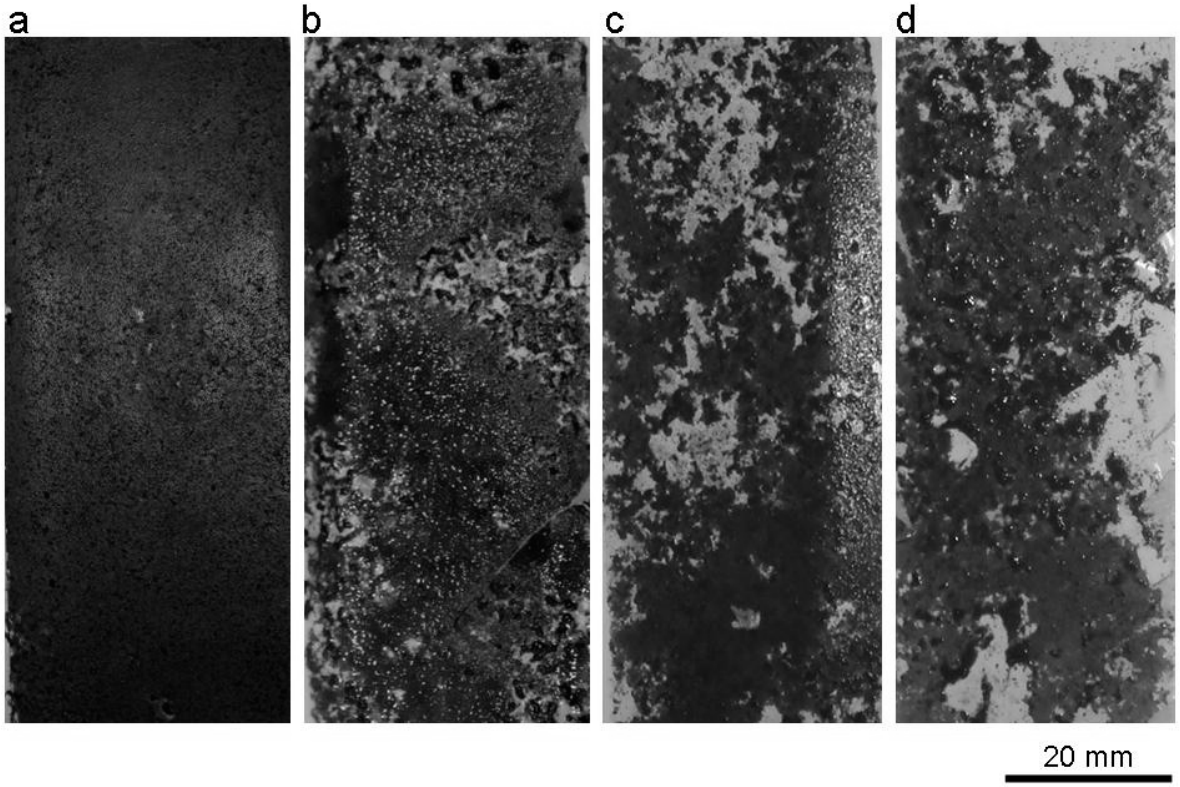


Figure 7 - Top view of the fouling layer after 60 days of continuous operation without flushing (a), intermittent operation for 18 h/day with flushing (b), intermittent operation for 12 h/day without flushing (c), intermittent operation for 12 h/day with flushing (d).

4 Discussion and model development

4.1 The mechanisms of flux stabilization and recovery

Flux stabilization. Figure 1 shows that stabilization of flux is observed, although advective deposition of foulants during dead-end filtration is expected to lead to an increase of the resistance of the fouling layer and decrease of flux, as described by generally accepted membrane fouling theory. This phenomenon is discussed in our previous study (Peter-Varbanets, et al., 2010), which shows that biological processes within the fouling layer lead to a formation of a heterogeneous layer (see Fig. 4) dominated by cavities and channels. It was concluded that the formation of such porous structures counteracts the decline of flux due to deposition and leads to the stabilization of flux (Peter-Varbanets, et al., 2010).

Flux recovery. Figure 3 shows that flux measured after a standstill period increases with an increase of the duration of the standstill period for river- and diluted wastewater operated with and without flushing. However, Fig. 3 indicates that the recovery of flux is limited by a maximal flux after recovery ($J_{r,max}$). Figure 3 shows that a lower $J_{r,max}$ value is observed for the systems operated without flushing and with diluted wastewater, than for the system operated with river water and flushing.

For the system with flushing, it can be expected that the recovery of flux occurs due to the removal of the fouling layer from the membrane surface by flushing. CLSM images of the fouled membrane before (a) and after (b) flushing after a standstill period of 7 days show that a complete removal of the fouling layer takes place (Fig. 8).

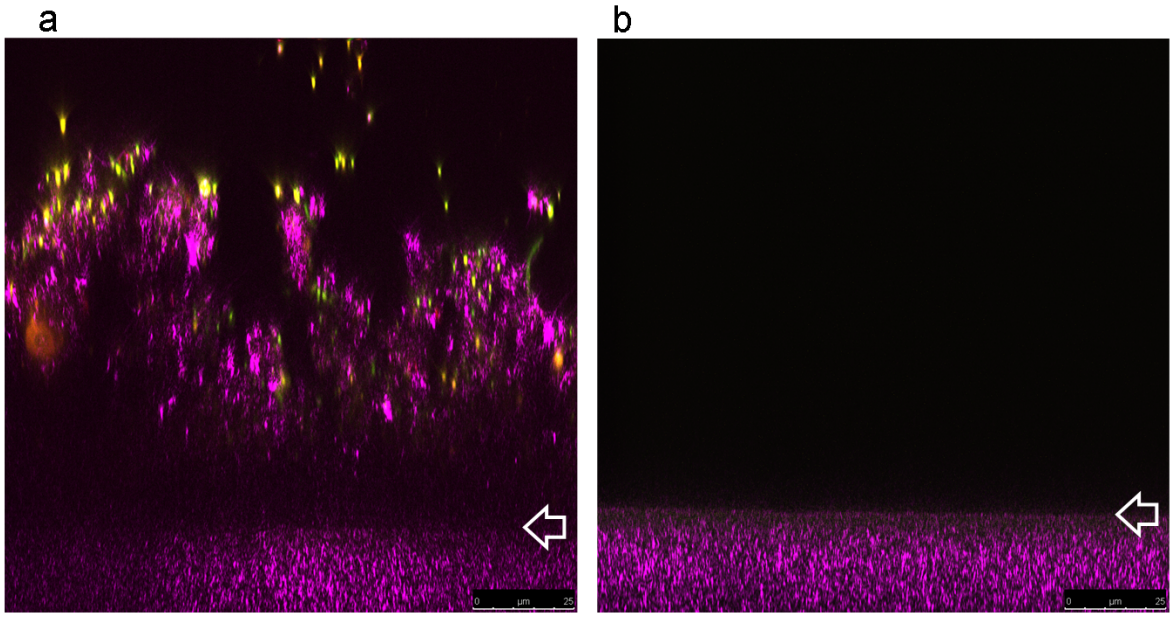


Figure 8 - CLSM images of the fouling layer before (a) and after (b) flushing. The system was operated for 21 days, the duration of standstill period before flushing was 7 days (168 h).

This result indicates that the flux observed after recovery, $J_{r,max}$ (see Fig. 3) is limited by irremovable fouling, which is defined as fouling which cannot be removed by flushing. Thus, lower maximal flux recovery in the case of diluted wastewater indicates that the irremovable fouling has increased. It can be assumed that this is related to the increased TOC content, leading to a higher extent of adsorptive fouling and pore constriction (Crozes et al., 1997; Jermann et al., 2007). When flushing is not applied, part of the fouling layer is expected to remain on the membrane surface after a standstill period leading to a lower flux after recovery.

The effect of standstill periods (or "relaxation" periods) on membrane fouling and flux has not been studied, except for the case of membrane bioreactors (MBR's). The increase of flux during periodical standstill periods in MBR's has been explained by the back transport of fouling components (Hong, et al., 2002). Furthermore, it has been hypothesized that back transport is ruled by diffusion, leading to the removal of foulants reversibly attached to the membrane surface back to the feed (e.g. Hong et al, 1997). As shown in Fig. 4, flux decline and recovery during intermittent operation with or without flushing are reversible. This is an indication that diffusional back transport also plays a role during the process studied here. However, the results shown in section 3.2.2 confirm that aggregation occurs in the fouling layer. The amount of larger particles in the flush water increases with the time of standstill as shown in Fig. 5. This result indicates that aggregation is favored during standstill periods leading to the release of larger structures and total mass with increasing standstill time. Figure 7-c shows that this process occurs also when no flushing is used. This indicates that shear stress due to flushing is not the main reason of increasing heterogeneity of the fouling layer observed in Fig. 7. Thus, aggregation in the fouling layer can be another reason of increasing flux values after standstill periods. The exact biological and physical nature of this process is not fully understood today, and further investigations are needed to better understand the mechanisms of flux recovery.

4.2 Modeling intermittent operation

During long term operation of ULP-UF in household applications, the system usually is filled manually. It can be assumed that filling of the system, and thus also treatment of drinking water takes place once or twice a day, mostly in regular intervals. Thus, the system can experience regular interruptions with a defined duration of operation and standstill time during any one-day cycle. Figures 2 and 4 show that a decline of flux is observed during operation and a recovery of flux occurs during standstill periods. Thus, the decline of daily operation time leads to an increase of flux. Assuming that the flux decline and recovery are reversible and reproducible processes, the impact of intermittent operation on flux and production capacity of the system can be predicted. The development of the model is discussed in the following paragraph.

4.2.1 Model development

Flux decline and stabilization. As discussed in section 4.1 and shown on Fig. 3, the recovery of flux is limited by maximal flux after recovery, $J_{r,max}$ which, in case of the system with flushing, corresponds to the possible flux due to irremovable fouling. It can be expected that at flux values lower than $J_{r,max}$ irremovable fouling does not affect the flux and the flux declines mostly due to advective deposition of foulants and formation of a fouling layer. The deposition of foulants can be defined by their concentration in the feed water and flux of water through the membrane. As discussed in section 4.1 biological processes limit the decline of flux and cause its stabilization at J_{stable}. Thus, assuming that the quality of water does not change, it can be expected that the decline of flux in time due to deposition of foulants in the fouling layer depends on flux and is limited by the stable flux J_{stable}. This can be described by the following relationship:

$$-\frac{dJ}{dt} = k_d\left(J - J_{stable}\right) \qquad \text{(Eq.1)}$$

where coefficient k_d (h^{-1}) is the rate of flux decline.

Flux recovery. Figure 3 shows that flux measured after recovery J_r ($L.h^{-1}m^{-2}$) asymptotically increases with the duration of a standstill period for the systems with and without flushing in all cases. The recovery of flux over time during a standstill period, J_r can be described by the following relationship (eq. 2):

$$\frac{dJ_r}{dt} = k_r \cdot \left(J_{r,\max} - J_r\right) \qquad \text{(Eq. 2)}$$

where the coefficient k_r (h^{-1}) is the rate of flux recovery and $J_{r,max}$ ($L.h^{-1}m^{-2}$) is the maximal flux which can be observed after a standstill period with or without flushing.

Thus, eqs. 1 and 2 predict the decline and recovery of flux during intermittent operation depending on the duration of operation and standstill period for the flux values lower than the flux due to irremovable fouling ($J_{r,max}$ for the system with flushing). Thus, assuming that the quality of water does not change, the production capacity of the system during intermittent operation can be estimated.

4.2.2 Estimation of parameters

The parameters of eqs. 1 and 2 were estimated applying SigmaPlot (v.10) software to the measured data, shown in Figs 1-3. The best estimates and the error information for the systems operated with river water and diluted wastewater with and without flushing are listed in Table 1. Table 1 shows that the parameters of eqs. 1 and 2 depend on water quality: the stable flux (J_{stable}) is lower, and the rate of flux decline k_d is higher for the system operated with diluted wastewater comparing to the system operated with river water.

The impact of water quality on the stabilization of flux during continuous operation was studied previously (Peter-Varbanets et al., 2010b), where it was shown that an increase of TOC leads to a decline of stable flux value. The increase of advective deposition of biopolymers on the membrane and the increase of the concentration of assimilable organic carbon (AOC) which intensifies biological growth on the membrane surface were the major reasons of the decline of stable flux (Peter-Varbanets et al., 2010b). We assume that the increase of k_d and the decline of J_{stable} is caused by an increase of advective transport of foulants to the membrane surface and an increase of the thickness of the fouling layer with an increase of TOC. Furthermore, Table 1 and Figure 3 show that the limiting flux ($J_{r,max}$) is lower for diluted wastewater than in the case of river water. This was discussed in section 4.1, which showed that this fact can be related to an increase of irremovable fouling with an increase of TOC content.

Table 1 - Parameters and error information estimated for the systems operated with river and diluted wastewater with and without flushing at a transmembrane pressure of 65 mbar

Recovery of flux	J_{stable} ($L.h^{-1}.m^{-2}$)		$J_{r,max}$ ($L.h^{-1}.m^{-2}$)		k_r (h^{-1})		k_d (h^{-1})	
	value	std. error	value	std. error	value	std. error	value	std. error
River water								
without flushing	7.39	0.04	12.28	0.066	0.020	0.0007	0.044	0.002
with flushing	7.26	0.20	34.52	0.44	0.012	0.0007	0.044	0.002
Diluted wastewater								
without flushing	4.91	0.02	5.39	0.02	0.036	0.0045	0.075	0.003
with flushing	4.86	0.16	13.06	0.39	0.01	0.0009	0.075	0.003

4.2.3 Model validation

In order to validate the model, the parameters k_d, and J_{stable} were estimated from the data shown in Fig. 3 for the systems operated intermittently with and without flushing (Table 2). Table 2 shows that the parameters estimated for the systems operated for 24-12 h/day differ at less than 10% from the value estimated for the continuously operated system (shown in Fig. 1). This result confirms the assumption that the parameters of Eq. 1 can be predicted using the flux values measured during continuous operation of the system. However, Table 2 shows that for the system operated 5 h/day, coefficients k_d and J_{stable} are considerably higher. The reasons of the increase of the stable flux and flux decline are not yet known and require further investigations.

Table 2 - Summary of the parameters for the systems operated intermittently

Operation	Standstill	flushing	k_d, (h^{-1})	J_{stable}, ($L.h^{-1}.m^{-2}$)
Reference system			0.044	7.44
24	0	no	0.041	7.69
24	0	yes	0.043	7.76
12	12	no	0.048	7.83
21	3	yes	0.046	7.65
18	6	yes	0.047	7.53
12	12	yes	0.046	8.19
5	19	yes	0.230	20.57

Fig. 9 shows the measured and fitted values of flux for the systems operated intermittently for 5, 12, 18 and 21 h/day with flushing. During most of the cycles the measured and fitted values overlap. However, fluctuation of flux was observed during operation of the system with river water. This can be attributed to the fluctuations of water quality, which were not taken into account for predicted flux values.

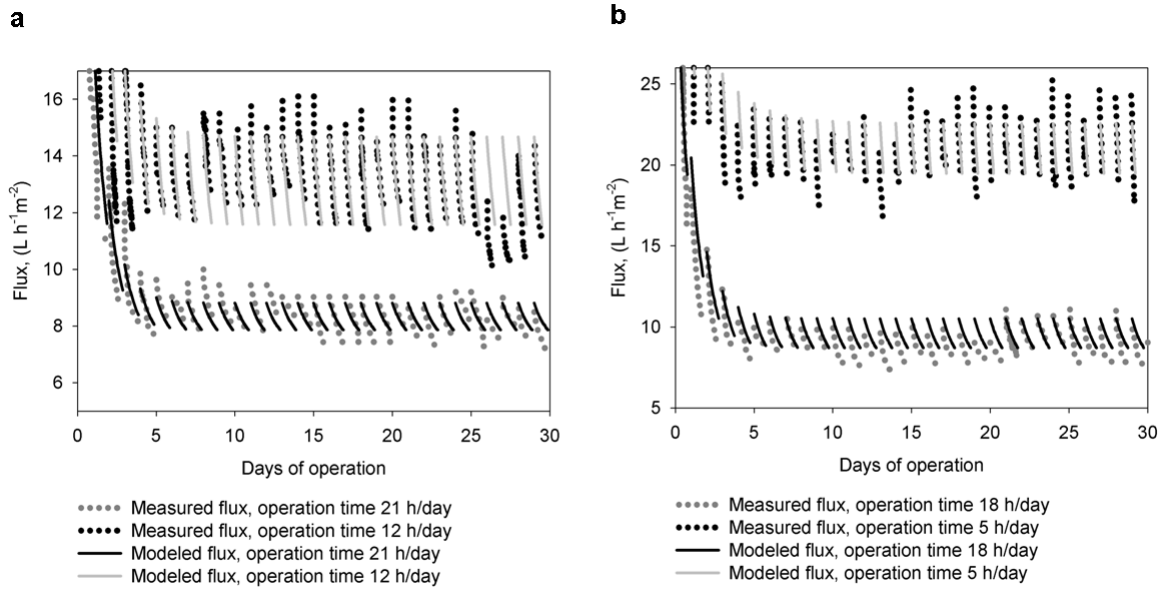


Figure 9 - Predicted and measured flux during intermittent ultrafiltration of river water operated during 21, 12 h/day (a) and 18, 5 h/day (b) with flushing

4.3 Application of intermittent operation and flushing in household and community scale systems

Summarizing, our results show that intermittent operation increases the flux of the system. Figure 10 shows the production capacity depending on the duration of operation, predicted as described in section 4.2.1 for the system operated intermittently with and without flushing. Figure 10 shows that for the system operated for 16-24 h/day with flushing, the production capacity of the system does not change significantly, although the operation time is reduced. Thus, intermittent operation does not limit application of ULP UF on household or community scale, but actually improves productivity of such systems. When the system is operated without flushing, intermittent operation leads to a decrease of the capacity due to the decrease of operation time and lower flux recovery after standstill periods.

Flushing increases operation requirements of the system and is likely not to be performed in households. However, it can be advised as a simple cleaning method, as it increases the flux up to about 50 % after a standstill period. For the systems operated on a larger scale (e.g. a small community), an operator or an automatic control of the system may be available. In such cases, flushing after a standstill period can be used as a periodical measure to improve performance of the system. Flushing without a standstill period showed to be ineffective (see Figure 4) and is not recommended.

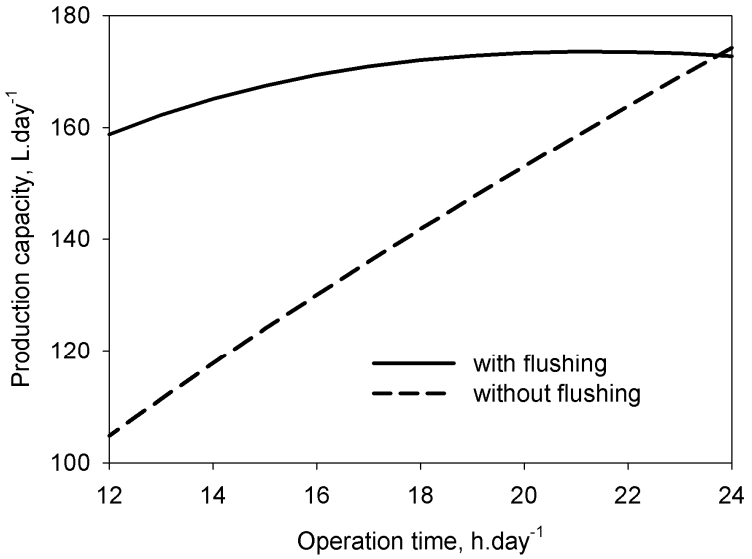


Figure 10 - Predicted production capacity depending on the daily operation time of the systems operated with and without flushing.

5 Conclusions

This study investigates the impact of intermittent operation and forward flushing on the stabilization of flux during dead-end ultrafiltration of drinking water under ultra-low pressure conditions for decentralized applications. The following conclusions can be drawn:

- Intermittent operation of ULP UF leads to an increase of flux. Flux recovery increases with the increase of standstill time and is higher for the systems operated with river water and with flushing than for the systems operated without flushing or with diluted wastewater.
- Flux decline and recovery during intermittent operation with or without flushing are reversible processes. In cyclic steady-state conditions, the absolute decline of flux during operation time is equal to the increase of flux during standstill time.

- The impact of intermittent operation on flux of the system can be predicted based on the duration of the standstill and operation time. This enables estimation of long term production capacity of the system operated intermittently.
- For the system operated for 16-24 h/day with flushing, the production capacity of the system does not change significantly, although operation time of the system is reduced. When flushing is not performed, intermittent operation leads to a decrease of capacity due to decrease of operation time and lower increase of flux after a standstill period.

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General conclusions and outlook

General conclusions

Decentralized systems

Decentralized systems are effective in reducing the risk of water-borne diseases. For application in developing and transition countries important boundary conditions for decentralized systems include efficiency, low costs, ease of use, sustainability, low maintenance and independence of utilities (energy sources, chemicals). Many systems are available which meet several of the criteria, but not all criteria at the same time, which may explain the moderate success of the technologies so far. Effective, low-cost, robust and less chemical- and energy-intensive technologies to disinfect water on decentralized scale are needed.

Decentralized systems based on membranes

Membrane fouling and biofouling are considered to be a major limitation of wide-spread application of ultrafiltration. Current approaches to prevent membrane fouling and to maintain stable membrane flux are energy intensive (e.g., high cross flow velocities) and chemical intensive (e.g., regular chemical cleaning). The decentralized membrane systems designed similar to conventional ultrafiltration systems are not suitable for applications in developing and transition countries. A need exists for research and development of membrane systems with low costs and low maintenance requirements, specifically designed for developing and transition countries.

A membrane system suitable for decentralized application

An ultrafiltration system suitable for application in developing and transition countries should be operated by gravity, without chemical cleaning, flushing, disinfection or cross-flow. As a feed, natural water (river, spring, well or rainwater) should be used without pre- or post-treatment. The set-up of such a system is shown on Fig. 1. According to generally accepted membrane filtration theory, operation of such a system on a long term leads to fouling and clogging of the membrane.

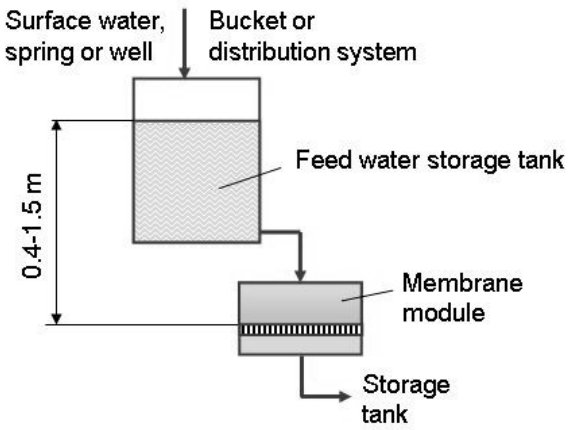


Fig. 1 - A schema of a membrane system

The phenomenon of flux stabilization

Generally accepted membrane filtration theory assumes the formation of a fouling layer during dead-end filtration, leading to a continuous increase of resistance and decrease of flux. In contrast to this common view, the stabilization of flux occurs at a value of 7-10 $L \cdot h^{-1} \cdot m^{-2}$

during ultrafiltration of river water and at a value of 3-7 $L \cdot h^{-1} \cdot m^{-2}$ during ultrafiltration of diluted wastewater. The flux remains stable during at least 120 days of operation.

The structure of the biofouling layer

Microscopic investigations (CLSM) confirmed that heterogeneous structures are formed in the biofouling layer. A conceptual model of this process is proposed in Fig. 2. During the first 2-3 days of operation a formation of a homogeneous fouling layer is observed (Phase I). The formation of cavities and local detachment (phase II) causes the development of a heterogeneous structure (phase III) and finally the formation of isolated colonies (phase IV).
Similar structures were observed in the case of biofilms developing on fixed surfaces (Wimpenny et al., 2000; Costerton et al., 1995). However, the formation process and intermediate stages in case of dead-end ultrafiltration are fundamentally different due to advective flow of substrate and solids to and through the fouling layer, and the absence of shear stress. Thus, the mechanisms of both processes should be carefully reconsidered.

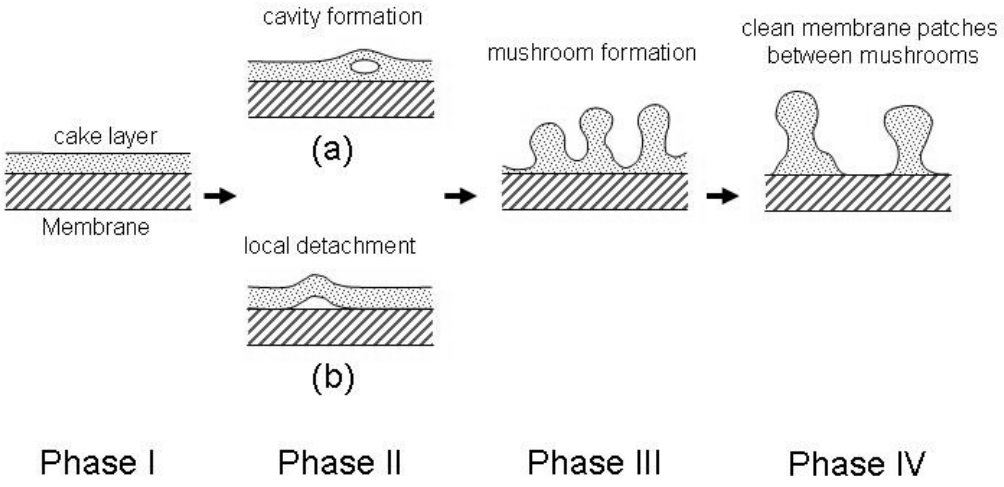


Fig. 2 - Structural changes in the biofouling layer formed during dead-end UF under ultra-low pressure conditions

The role of active biomass

The stabilization of flux is related to biological activity in the fouling layer and is not observed if the biological activity is inhibited (e.g. by disinfectants or cold temperatures). The biological processes cause the formation of heterogeneous structures in the fouling layer.

Irremovable fouling

Irremovable fouling in ULP UF contributes to 40-60% of the flux decline and is lower for aerobic and biologically active systems than for DO-limited systems. The most probable explanation for this irremovable fouling is the formation of a base layer on the membrane. However, adsorption plays a role in the initial stage of filtration, and re-growth on the permeate side can slightly contribute to the increase of resistance due to irremovable fouling during a long-term operation.

Membrane fouling mechanisms

The stabilization of flux is observed when the increase of resistance of the fouling layer due to deposition, physico-chemical interactions and irremovable fouling counteracts the decline of resistance due to structural changes in the fouling layer. These processes define the mechanisms of fouling and flux stabilization in ultra-low pressure ultrafiltration.

Parameters and limitations

Water quality. In aerobic systems or systems without addition of colloidal humic acids, the level of flux stabilization depends mostly on the concentration of *biopolymers* and *biodegradable low molecular weight compounds*. *Dissolved oxygen limited conditions* prevent development of channel structures in the fouling layer resulting in a more compact structure with higher resistance. Also an increase of the resistance is observed when *colloidal humic acids* are added to the feed water. In this case, channels and cavities are not formed and hydrophobic interactions between the colloids cause a formation of a compact fouling layer. It was shown that *inorganic turbidity* did not have an impact on the stabilization of flux.

Transmembrane pressure. The stable flux value does not increase considerably with initial pressure. This means that an increase of pressure leads to an increase of resistance of the fouling layer.

Intermittent operation. Intermittent operation leads to the increase of the average stable flux, and flushing after a standstill period further intensifies this process. The stabilization of average flux occurs when the decline of flux during operation time is equal to the increase of flux during standstill time. Intermittent operation during 21 h/day with flushing after a standstill period of 3 h results in a higher production capacity of the system, compared to continuous operation.

Relevance of flux stabilization

It is shown that UF systems, based on the phenomenon of flux stabilization, do not require any back-flushing, cross-flow, chemical cleaning or disinfection, which greatly simplifies the maintenance and operation of ultrafiltration systems. The pressure of 40 mbar required for ultra-low pressure UF can easily be obtained by gravity in most situations. Assuming a stable flux of 4 - 10 $L \cdot h^{-1} \cdot m^{-2}$, the membrane area needed is 0.17 - 0.42 m^2 per family for point-of-use application. With the recent decrease of membrane costs, operation of ultrafiltration under low flux and ultra-low pressure conditions can become an alternative to the conventional energy-intensive operation. Thus, ultra-low pressure ultrafiltration can provide an important technological contribution to address the drinking water problems in developing countries.

Outlook

This thesis challenges a conventional approach to ultrafiltration (UF) that has thusfar discouraged the application of UF membranes for potable water treatment in developing countries. The phenomenon of flux stabilization during UF under ultra-low pressure conditions was first observed, documented and investigated in this study. This phenomenon allows application of UF without any means of physical or chemical cleaning at hydrostatic pressure of 40-100 mbar which considerably reduces complexity and costs of decentralized UF systems.

However, only some aspects of the ultra-low pressure ultrafiltration and the phenomenon of flux stabilization were studied in detail. There is a great potential for further development of this technology. Four major directions can be identified:

- understanding of the mechanisms of flux stabilization;
- optimization of ultra-low pressure ultrafiltration to enhance flux and increase removal efficiency;
- development and implementation of decentralized membrane systems;
- exploration of the phenomenon of flux stabilization in other fields of membrane technology.

These directions are discussed in detail below.

The mechanisms of the phenomenon of flux stabilization

Structural changes in the fouling layer

The structural changes in the biofouling layer, namely the formation of cavities, channel networks and mushroom-like structures are found to be the major reason of the stabilization of flux.

The development of heterogeneous structures in the biofouling layer in time during dead-end ultra-low pressure UF was discussed in chapters 2, 3, 4 and summarized in the Fig. 2. In this model, the formation of cavities and local detachment (phase II) leads to the development of mushrooms (phase III) and finally the formation of mushroom-like structures separated by the channels (phase IV).

Although it is leading finally to similar structures as found in one type of biofilms developing on fixed surfaces (mushroom or tulip biofilm model (Wimpenny et al., 2000; Costerton et al., 1995)), the process of formation of "mushrooms" and intermediate stages are fundamentally different. One of the conventional biofilm theories assumes that active bacterial attachment, shear/sloughing and diffusion limitation are important mechanisms leading to the formation of colonies and structural changes (Picioreanu et al., 1998; van Loosdrecht et al., 1995; Costerton et al., 1995). In dead-end filtration systems, bacteria and other not dissolved material are transported to the membrane surface by an advective flow and there is no shear stress. Thus, the role of active bacterial attachment is less significant for a biofouling layer than for a biofilm. Furthermore, the advective flow to and through the fouling layer intensifies the transport of nutrients and oxygen through the biofouling layer.

Nevertheless we observe formation of similar structures in dead-end operated systems and in the biofilm formed in the cross-flow conditions. Therefore, the mechanisms assumed essential for biofilm formation need to be carefully reconsidered and a better understanding of the processes leading to the formation of cavities and development of channel networks during dead-end UF is required.

The cause of the structural changes in the biofouing layer has not been established conclusively so far. The major hypotheses were mentioned in chapter 2 and are listed below:

- *Degradation of biopolymers in the layer.* The biopolymer fraction of natural organic matter is present in the feed water and retained by the membrane at about 60%. As revealed by lectin staining and confocal laser scanning micrscopy, biopolymers are deposited in the fouling layer and are one of the major components of it.
- *Biomass die-off in the biofouling layer.* It was shown (chapter 2) that approx. 85% of the active biomass loses activity in the layer during the first week of filtration. However, measurements of assimilable organic carbon suggested that nutrient limitation was not the reason of biomass die-off in this case.
- *Predators (grazers).* The role of predators (grazers) is another plausible reason of the formation of cavities and channels within the biofilm and biomass die-off.

Local detachment of the fouling layer

The local detachment of the fouling layer (Phase II-b in Fig. 2) is am essential phase leading to the formation of channel networks. It is still not clear whether local detachment is a relevant process for biofilm formation in general, or wether it is specific for biofouling layer in UF system and therefore has not been observed before.

The interaction of the biofouling layer with the membrane is determined by membrane properties and the properties of the adhering substances, which can be either cells growing on the surface, their excretion products (EPS), or dissolved compounds (especially biopolymers) present in the feed water. Detachment occurs if the interactions between membrane and biofilm are lower than the external forces applied on it. In most biofilm research, shear is applied as external force. However, in dead-end operated UF, detachment occurs (Phase II in Fig. 2) without shear forces. The properties of the membrane surface, such as surface roughness, hydrophobicity, and charge (Pasmore et al., 2001), a base layer (discussed in chapter 3) and a fouling layer influence the attachment strength of the fouling layer to the membrane surface.

If the cohesion strength within the layer is higher than the attachment strength of the layer to the membrane surface, a tension of the layer can cause its detachment and braking.

The detachment could be caused by similar biological processes as discussed above and be an intermediate step between cavity formation and formation of channels. The detachment of the biofilm could also be caused by grazers, but this is less probable since the bacteria attached to a surface are not easily accessible for grazers. Another reason for this process can be an aggregation process within the biofilm, e.g. due to colony formation. A less plausible hypothesis, which however cannot be excluded from discussion, is a concentration polarization under the fouling layer. Assuming the fouling layer is a semi-permeable membrane with larger pore size than the membrane, part of the material can be retained between the layer and the membrane leading to an increase of concentration. Thus, an osmotic pressure can develop under the layer and counteract the advective force pushing the layer to the membrane surface and causing further detachment of the layer.

None of these hypotheses was confirmed so far and further research is needed to understand the reasons of the structural changes in the biofouling layer and relevance of these processes for the biofilms on fixed surfaces.

The role of microbial community

A key question is whether specific microorganisms proliferate in the conditions prevailing in a biofouling layer, and whether these organisms contribute to the stabilization of the flux through the membrane. The role of the microbial community in the stabilization of flux has not been studied so far. However, the fact that stabilization of flux is observed with different

type of waters may indicate that the various microbial communities may cause similar effects in the fouling layer.

The potential for optimization

Enhancing flux

Due to microbial activity, pores and channels are formed within the fouling layer which leads to a relatively permeable layer structure. Intensification of this process can lead to the decrease of the resistance of the layer and stabilization of flux at a higher value. For example, a pre-coating can be carried out to reduce adsorption of solutes and improve the removability of the layer. Modification or pre-coating of the membrane surface with anti-microbial agents actively disinfects bacteria attaching to the membrane surface and can intensify degradation processes in the base layer of the biofouling layer leading to the increased formation of cavities. The properties of the membrane surface, such as surface roughness, charge and hydrophobicity can influence the detachment of the fouling layer. Natural biological processes causing degradation of EPS and enhancing permeability of the fouling layer can be promoted by EPS degrading enzymes. Enzymes may be bound to the microspheres used to pre-coat the membrane surface and destabilize the structure of the biofouling layer during its development. Furthermore, the degradation processes can be intensified by combination of pre-coating with intermittent operation and flushing.

It is evident that any additional stage reduces the simplicity of the process. In many cases it can be more efficient (and cheaper) to increase the capacity of the system by increasing the membrane surface or applying simple cleaning procedure such as flushing or intermittent operation (discussed in chapter 4).

Enhancing rejection

The stabilization of flux observed during ULP UF of river water occurs on a similar level of the polyethersulfone (PES) membrane with a cut-off of 50, 150 kDa and PES MF membrane with a pore size of 0.2 μm, although the permeability of the new membranes differs significantly (Fig. 3).

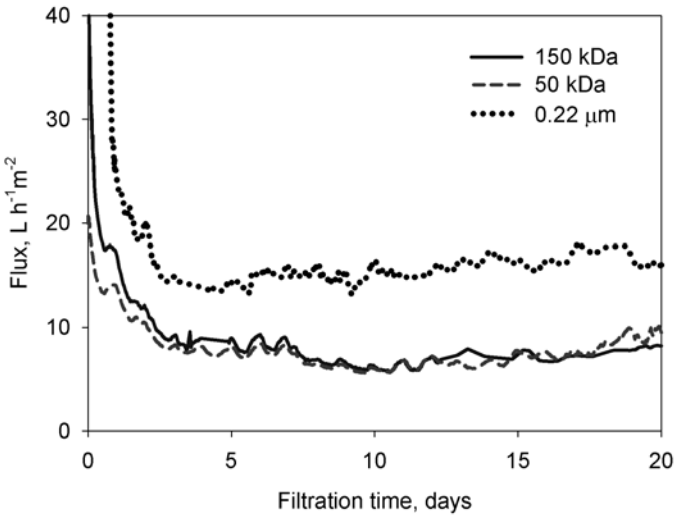


Fig. 3 - The impact of membrane cut-off on flux

This result indicates that more tight membranes can be used to increase the rejection properties of the system, while the capacity of the system remains the same. The permeability of 100 L/hm^2 (which corresponds to the flux of 10 L/hm^2 at 100 mbar) can be achieved

already with some nanofiltration membranes. It is expected that the stabilization of flux is observed also in this case. Thus, the gravity-driven approach may be applied to the nanofiltration increasing the quality of produced water.
Furthermore, the separation properties of the fouling layer itself can be challenged. It was observed that fluorescent microspheres are retained in the upper part of the fouling layer and not on the membrane (data not shown). This effect can be reduced when channels are formed in the fouling layer. Furthermore, the base layer (chapter 3) may play itself a role of a secondary membrane with higher separation properties than the membrane itself.

Development and implementation of decentralized systems

Potential for application

It is shown that UF systems, based on the phenomenon of flux stabilization, do not require any back-flushing, cross-flow, chemical cleaning or disinfection. The pressure of 40 mbar required for ultra-low pressure UF can easily be obtained by gravity in most situations. In conventional UF plants, pumps are applied for feeding raw water, circulation and backflushing. Furthermore, automated process control and dosing systems for cleaning/disinfection agents are required. Such plants are typically operated at a flux of about 100 $L \cdot h^{-1} \cdot m^{-2}$. If operated by gravity (with a flux of 4 - 10 $L \cdot h^{-1} \cdot m^{-2}$), a much higher membrane area is required. The costs of the membrane in such plants are an important fraction of the total costs, and therefore it is questionable if ultra-low pressure UF systems would be competitive in this case.
However, for existing household and small-scale systems, the costs of equipment dominate. The design of the system based on ULP UF can be kept relatively simple. Besides the membrane module, a household system based on ULP UF requires two tanks for storage of raw and treated water. The required pressures of 40 - 100 mbar can be easily obtained by manually filling the storage tank, and thus no pumps are needed. If the water tanks can be produced locally, the costs of these are expected to be relatively low. However, the standardized membrane modules have to be manufactured by international membrane manufactures and delivered to the developing country. Thus, the total costs of the system will be determined mainly by the costs of the membrane. The estimation of the costs of the membrane is discussed in the following paragraph.

Estimation of costs of the ULP UF systems for decentralized applications and potential for adoption in developing countries

Table 1 shows an estimation of the costs of the membrane for point-of-use and small scale community water treatment. The average stabilized flux assumed for the calculation is based on a feed water containing 2-12.5 $mg \cdot L^{-1}$ of dissolved organic carbon (DOC). An increase of DOC of the feed water will result in a decrease of the flux, increasing the required membrane area and membrane costs.
The assumed membrane service life expectancy is a best guess and is not based on experimental data (the maximum duration of the experiments so far is about six months, and the membrane was still intact after that period). The exact lifetime will depend on the local conditions and the level of training of the users, and this has to be investigated in individual situations. In the case of small scale systems, a somewhat larger life time is assumed due to improved operation conditions and process control in comparison to household applications. The costs of the membrane modules were assumed to be 40 US$$\cdot m^{-2}$ (Churchhouse, 2000). At the moment, membrane modules are offered on the market at costs considerably lower than 40 US$$\cdot m^{-2}$. On the other hand however, household modules are relatively small which would

result in an increase of the price per surface area. Therefore, the assumed price of 40 US$·m^2 seems to be realistic.
As Table 1 shows, the required capacity for drinking water is approx. 10 - 40 L·day^{-1} per family. Assuming a stable flux of 4 - 10 L·h^{-1}·m^{-2}, the membrane area needed is 0.17 - 0.42 m^2. The costs of such a membrane area itself are estimated to be about 0.7 - 1.7 $ per person and year (Table 1). As such, a system would not require pumps or other auxiliary equipment, and the estimated total costs would not be much higher. Thus, the costs do not exceed the affordability limit of 10 $ per person and year, defined by the WHO for the poorest part of the world's population (Sobsey, 2002). The application on a community scale would result in estimated membrane costs of 0.8 - 2.1 $ per person and year for the coverage of basic domestic water needs (Table 1). Thus, the running costs of the system will be affordable for an average slum dweller or villager, and surely are lower than the costs for buying bottled water in most of the countries.

Table 1 - Estimation of membrane costs for point-of-use and small scale decentralized water treatment

Water Treatment System	Point-of-use (family)	Small Scale (community)
Purpose of water treatment	drinking/cooking 2-8 L·person^{-1}·day^{-1}	basic domestic needs 20 L·person^{-1}·day^{-1}
Capacity	Family of 5 people ≤ 0.04 m^3·day^{-1}	Community of 250 people 5 m^3·day^{-1}
Membrane area required assuming flux of 4-10 L·h^{-1}·m^{-2}	0.17-0.42 m^2	21-52 m^2
Membrane lifetime expectancy	2 years	4 years
Membrane costs	3.4-8.4 $· family^{-1} ·year^{-1} 0.68-1.68 $·person^{-1}·year^{-1}	208-521 $·community^{-1}·year^{-1} 0.83-2.08 $·person^{-1}·year^{-1}

However, the initial investment costs could represent a significant barrier to adoption. The approaches adopted by many NGOs in developing countries include free distribution or subsidizing of the household drinking water treatment systems. However, this approach is difficult to maintain sustainably. Instead, market-based approaches should be explored (Heierly, 2008). Households in developing countries spend a significant proportion of their income on water collection and treatment, as well as managing the impacts of water-borne disease. If communities and consumers are made aware of these costs, and accept that household water treatment systems can in part substitute for them, an economic demand can be created (Sobsey, 2002). Alternate financing mechanisms should be explored to increase accessibility of the household systems for the poor. This includes rental or leasing options, and possibly extension of microcredit loans, which allow users to make payments in small increments over time.

The development of a system

The prior research on ULP UF has been made in a laboratory setting, using flat membrane modules in configurations which allowed easy control of operating conditions, but are not appropriate for application in households or communities. In collaboration with KometenzZentrum Wasser Berlin, Veolia and Opalium, a pilot plant based on the principle of ULP UF has been designed and built (Figure 4). The pilot plant has a capacity of around 3 m^3 d^{-1}. Biological sand filtration (BSF) is used as a pre-treatment and is introduced into the system in order to increase biological stability of water and decrease the surface load of the membrane. It was shown (see Appendix A) that BSF removes 60-80% of the bioploymers and 40-60% of the humic acids which results in an overall increase of flux of the ultra-low pressure UF and a decrease of the required membrane surface. Thus, for community scale

systems, the use of sand filtration as a pretreatment leads to lower total investment costs and improved water stability, and therefore can be recommended.
The pilot plant has been tested with and without BSF first on the river Marne in France, and now is in operation in South Africa, where tests are carried out to provide drinking water from river for the rural settlement of Ogunjeni (Kwazulu-Natal region).

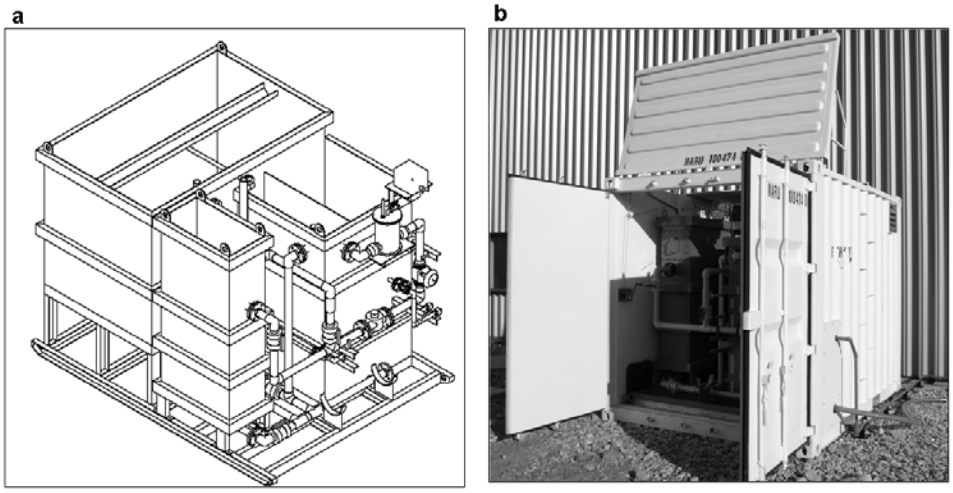


Fig. 4 - Pilot plant based on biological sand filtration and ultra-low pressure ultrafiltration

ULP UF system has been also implemented for drinking water treatment and grey water recycling in the "self-sufficient house" within the project "self". In this project, rainwater is collected in a reservoir on the roof of the house and is filtered by gravity through an UF membrane with an area of 0.7 m^2. The system is designed to provide 30 l/day of drinking water for a period of 14 days without a rainfall. Grey water is treated in a membrane bioreactor operated similar to the drinking water system. In total, "self" provides 100 L of water daily.

The next step will be to study the potential of application of ULP UF on a household scale. For this, a robust system designed for the use at household scale should be developed and the system evaluated in the field. The efficiency and capacity of the system should be studied as a function of the water quality parameters, such as concentration of NOM fractions, turbidity, dissolved oxygen content and microbial load. Although the broad range of water qualities was simulated in laboratory to access the impact and limitations of water quality parameters (chapter 3), the only tests done with real waters outside Switzerland are ongoing tests in South Africa and tests done in France (see above). Actual waters from tropical regions should be studied in more detail to confirm the impact of water quality parameters on the capacity and efficiency of the ULP UF system. A project focusing on the investigation of ULP UF systems for application in households in slums and rural areas of Kenya is planned.

The choice of the membrane module is expected to have a major impact on important aspects such as productivity, maintenance and economics. Up till now, most of the experiments were conducted with flat sheet membranes. Capillary modules are often used for ultrafiltration of drinking water due to lower price and compactness of the module. However, in preliminary experiments, capillary modules were not suitable for the long-term operation due to clogging of the entire capillaries. Further investigations are needed in order to assess the potential of capillary modules for operation without cleaning under ultra-low pressure conditions. Tubular membranes or capillary modules operated in "outside-in" mode were not studied but can be

explored. The optimal membrane module configuration should be evaluated in close cooperation with membrane producers.
Another critical point which should be addressed is the quality assurance of decentralized application of the technology. Finally, the household and community systems should be evaluated in a number of case studies. In addition to the evaluation of the technological efficiency of the system, the users' preferences, namely affordability, reliability, low maintenance requirements, robustness, easy handling and aesthetic appeal have to be addressed. The implementation of the ULP UF technology or any household or community water treatment system should be combined with the capacity building initiatives for local partners, including private sector producers and distributors, NGOs, and universities.

The phenomenon of flux stabilization in other fields of membrane technology

This thesis shows that biofouling which is usually regarded as a major limitation of membrane processes can in fact provide beneficial effects resulting in formation of more heterogeneous biofouling layer with low resistance. These beneficial effects can be explored also in other fields of the membrane technology where formation of a biofilm or a biofouling layer is an issue.

The formation of biofilms on membranes has been studied in membrane processes for waste water treatment. As mentioned in chapter 3, there are some similarities between a membrane bioreactor and an ULP-UF system. For MBR's it is important to derive which fraction of NOM contributes most to fouling and how the biological activity in the reactor and in the fouling layer influences the fouling process. The heterogeneous structures were observed in fouling layers in ULP-UF and MBRs and the factors affecting the membrane fouling mechanisms can be similar in both systems, although the hydrodynamic conditions are different.
In chapter 3 the primary wastewater effluent was used to increase the TOC of the river water and simulate the impact of high biopolymer and nutrient loads. It was shown that stabilization of flux occurred also in case of filtration of primary effluent diluted to 30% in aerobic conditions. This result indicates that in principle, the phenomenon of flux stabilization can be applied for treatment of wastewaters with low organic load, such as for recycling of grey water.
Also, this technology can be interesting when disinfection of wastewater is needed, such as during wastewater re-use for agriculture used in developing countries. In this case, primary effluent can be diluted to the required concentration with untreated surface water and after ULP UF directly used for irrigation.

In nanofiltration (NF) and reverse osmosis (RO), biofouling leads to reduced performance and increases the costs of these technologies (Flemming et al, 1997). Biofouling is specially a problem in spiral-wound modules used for NF and RO membranes. It was shown that a feed water spacer between the membranes functions as attachment base for biomass (Baker and Dudley, 1998). The nutrients are partly or completely rejected by the NF and RO membranes, which results in relatively high concentrations of nutrients near the membrane surface (Kim, et al., 2006; Vrouwenvelder, et al., 2009a) and intensifies biological growth. Due to relatively high nutrient concentrations and high transmembrane pressure used in these processes, compact fouling layers are formed on the membrane (Ivnitsky et al., 2007) resulting in increase of resistance.

Membrane biofouling is typically controlled by the measures which aim at preventing biofilm growth, namely disinfection, pre-treatment and cleaning (Al-Amoudi and Lovitt, 2007). A lot of research is currently done on the development of new "anti-fouling" membranes by incorporating disinfectants or other active substances into the membrane materials or by reducing adsorption properties of the membranes.

Another approach can be used to control biofilm growth instead of preventing it once the biological processes leading to the formation of heterogeneous structures in biofilms and biofouling layers are understood. By doing so, the biofilms with high heterogeneity can be "designed" on the membranes and the resistance due to biofilm formation reduced.

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Appendix A

Operation and maintenance of decentralized drinking water treatment systems based on ultra-low pressure ultrafiltration

Maryna Peter-Varbanets, Rostyslav Mudryk, Wouter Pronk

presented at WISA Membrane Technology Conference, 13-15. May, 2009, Stellenbosch, South Africa

Operation and maintenance of decentralized drinking water treatment systems based on ultra-low pressure ultrafiltration

Maryna Peter-Varbanets[1,2], Rostyslav Mudryk[1], Wouter Pronk[1]
[1]*Eawag, Swiss Federal Institute of Aquatic Science and Technology, Ueberlandstrasse 133, 8600 Duebendorf, Switzerland*
[2]*Institute of Environmental Engineering, ETH Zurich, 8093 Zurich, Switzerland*

Abstract
Inadequate access to safe drinking water threatens the health of over a billion people in developing countries. Decentralized systems can be an effective solution to reduce water-borne illnesses.
Ultra-low pressure ultrafiltration (UF) is a technology developed for decentralized drinking water disinfection using gravity as a driving force. It is based on phenomenon of the flux stabilization on a level of 4-10 $L \cdot h^{-1} \cdot m^{-2}$ under ultra-low pressure. The flux can be maintained for extended periods of time during dead-end operation, without chemical cleaning or flushing. Operation and maintenance limit the application of decentralized systems in developing countries. Our results show that ultra-low pressure UF requires virtually no maintenance. Although no flushing is required our results show that a periodical forward flushing increases the performace of the system. The flux may be further increased if intermittent operation is combined with flushing and done after the standstill period.
High concentrations of natural organic matter (NOM) decrease the level of flux stabilization for ultra-low pressure UF. In such cases, a pre-treatment may be required to reduce the impact of NOM and variability of water quality. We explored slow sand filtration (SSF) as a pre-treatment. Our results show that SSF increases the average flux due to the removal of biopolymers and humics. For community-scale systems, the application of SSF as pre-treatment decreases the required membrane surface area, reducing the costs of the system.

1 Introduction
Global assessments by the WHO and UNICEF have shown that one-sixth of the world population did not have access to safe water for drinking at the beginning of 2000 (1). Most problems occur in developing countries (DC) and countries in transition (TC), where centralized water treatment systems often are non-existent or malfunctioning. It has been shown that in many situations decentralized systems can be much more effective than centralized systems in reducing the risk of illnesses (2).

In principle, membrane technology is attractive for such applications. Ultrafiltration provides an absolute barrier for controlling hygienic hazards and its modular construction allows implementation on all possible scales. Furthermore, the costs of the membranes itself have decreased significantly in the last decades (3). However, the application of UF technology in DC and TC is limited by other factors. A critical aspect of membrane based small-scale systems (SSS) and point-of-use systems (POU) is the operation, maintenance and control (4). Most of the currently available membrane systems need regular flushing, cleaning and/or chemical treatment. This makes them less suitable for use in DC and TC. In addition, for

application in rural areas of DC, systems should be able to operate with untreated surface water, and should be independent on electricity or tap pressure (4).

Ultra-low pressure ultrafiltration is a technology developed for decentralized drinking water disinfection using gravity as a driving force (5). The technology uses the phenomenon of flux stabilization on a level of 4 -10 $L \cdot h^{-1} \cdot m^{-2}$ under ultra-low pressure. The flux can be maintained on a constant level for extended periods of time with dead-end operation, without chemical cleaning or flushing. While the daily requirement of drinking water for a family amounts to 20 L/day, 0.5 m^2 of membrane would be sufficient to provide this amount of water with the flux mentioned above. The costs of the membranes have decreased significantly in the last decades and UF membranes for a price below 40 $\$/m^2$ are available on the market. Thus, ultra-low pressure ultrafiltration may be explored for decentralized drinking water disinfection in developing countries (5).

Operation and maintenance requirements of this technology are significantly lower comparing to the conventional UF based systems (5). However, some maintenance may still be required to provide stable operation of the system on a long term. For applications in households (POU) it can be assumed that standstill periods occur (e.g. during the night), and therefore the performance during intermittent operation should be studied. High concentrations of some NOM fractions decrease the level of flux stabilization for ultra-low pressure UF. Thus, a pre-treatment may be required to reduce the impact of NOM and variability of water quality. However, pretreatment processes increase the costs and chance of failure of the systems, and the whole system finally should meet the low-costs and low-maintenance criteria (4).
Here we examine operation and maintenance requirements for POU and SS systems based on ultra-low pressure ultrafiltration. The focus of the paper is on the impact of intermittent operation, flushing options and long-term flux recovery. Pre-treatment by slow sand filtration is evaluated with different feed water qualities.

2 Material and Methods

2.1 Feed water

River water was pumped directly from River Chriesbach (Duebendorf, Switzerland) to the storage tank or collected every 1-2 days and stored. The basic composition of the water was: TOC = 1.5-3 mgL^{-1}; Turbidity = 0.2-2 NTU. During rain events, which typically lasted 0.5-1 day, the turbidity and TOC reached values around 30 NTU and 4 mg C/L respectively.

2.2 UF membranes and membrane test units

For each experiment we used a new flat sheet polyethersulfone membrane (PBHK, Biomax) with a nominal cutoff of 100 kDa. The clean water permeability of the membrane was 1200 ± 100 $L \cdot h^{-1} \cdot m^{-2}$bar (at 20°C).
The membrane test units were standard polycarbonate filter holders of 48 mm inner diameter purchased from Whatman. For the experiments with forward flushing we used two-part plexi-glass membrane modules of our own design. The membrane (25 cm^2) was placed on a spacer on one part of the module and sealed with a silicon O-ring and a second part. The retentate volume of the module was 25 cm^3.
To remove conservation agents, the new membranes were stored for at least 24 h in de-ionized water and filtered with 1 L of de-ionized water under pressure used in the system. The efficiency of this procedure was assessed by DOC measurements of the de-ionized water permeate according to the method described below.

Potential leakage was checked by mounting a Teflon film instead of the membrane and applying a pressure of 1.5 bar.

2.3 Long term ultrafiltration experiments

We used hydrostatic pressure as a driving force for the membrane filtration. A water level difference of 0.4-1.1 m (38-108 mbar) was used. A schematic presentation of the experimental set-up is shown in Fig. 1.

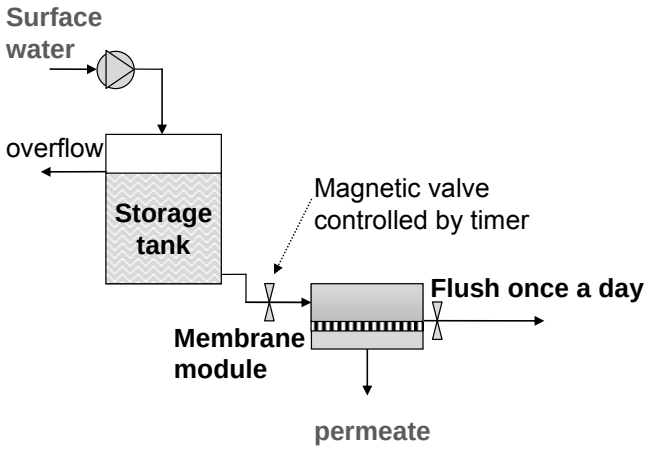


Fig. 1 - Schematic presentation of a laboratory scale system set-up with flushing

A feed water tank (1.1 L) was placed on the required level difference over the membrane module and connected to it with flexible tubing. River water was pumped into the feed water tank through a thermostated vessel, where it was pre-heated to 20^0C. The pressure in the system was maintained constant by an overflow in the storage tank. Feed water was also used for forward flushing after the standstill period (as shown on Fig.1). When the impact of flushing was studied, flushing was carried out every day manually by opening a tap of the module to achieve a flow-rate of approx. 10 ml/min during 10 minutes. The amount of flushing water thus represents about 25% of the water produced. The flow-rate of 10 ml/min corresponding to a Reynolds number of 6.8. This implies laminar, non-turbulent flow, and therefore only the particles loosely attached to the membrane surface will be removed. Turbulent flow rates (Re > 1000) can not be achieved in a POU system without the use of powerful pumps and therefore, these conditions were not studied.
The permeate flux was measured and logged with the Ohaus Adventure Pro scale with a maximum failure of 0.1 g. Data were logged every 2-5 min in the beginning of the cycle (up to 1 day) and 1 h afterwards.

2.4 SSF/UF experimental set-up

The schematic presentation of the SSF/UF set-up is shown in Fig. 2. River water (river Chriesbach, Duebendorf) was heated to 20^0C and pumped to two similar thermostated Slow Sand Filters (SSFs) and to an intermediate tank feeding the reference UF module. The level of water in SSFs was kept constant by an overflow. The flow-rate was regulated by needle valves installed on the outflow side of the filters. One filter was operated continuously, while the other SSF was in operation for 5 hours per day and remained wet during the standstill period.

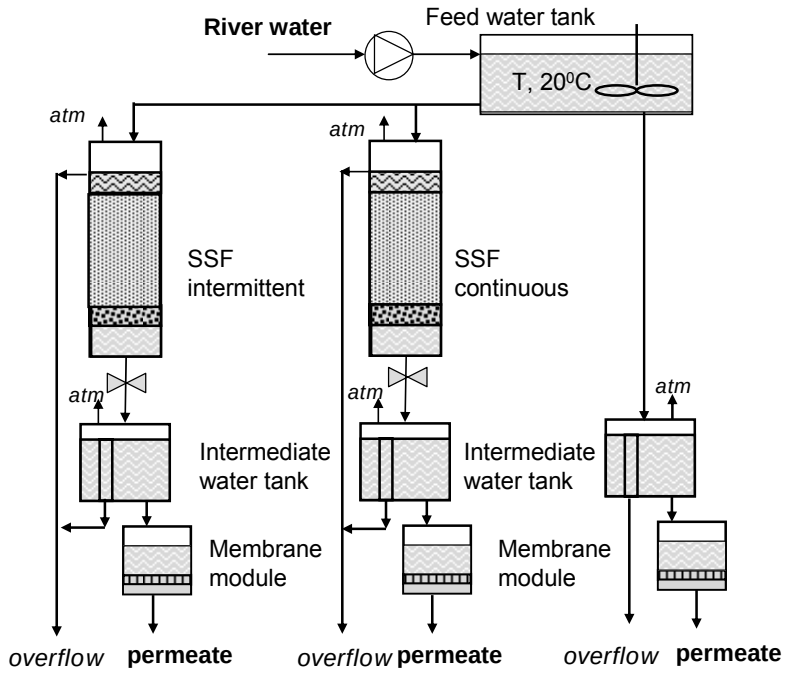


Fig. 2 - Schematic presentation of a laboratory scale SSF/UF system set-up

Water treated in SSF was directed to the intermediate tank, operated under atmospheric pressure and after directed to the UF unit installed under the tank on a height necessary to assure 60 mbar hydrostatic pressure. Membrane flux was controlled as described above.

2.5 Operational parameters of SSF/UF experimental set-up

The operational parameters of SSF/UF experimental set-up are shown in Table 1.

Table 1- Operational parameters of the SSF/UF experimental set-up

Parameter	**value**	**unit**
SSF parameters		
Filter diameter	15	cm
Filtration Area	175	cm^2
Sand bed height (0.25 mm sand fraction)	30	cm
Height of support gravel layers	8	cm
Supernatant height	15	cm
Slow sand filtration		
Flow rate	0.9	L/h
Linear flow	0.05	m/h
Residence time in sand:		
Continuous operation	2.2	h
Standstill period	21.2	
Residence time in supernatant	3.2	h
Residence time in underdrain volume	2.2	h
Ultrafiltration		
Membrane area	16.6	cm^2
Membrane module volume	15	cm^3

2.6 NOM characterization

The different NOM fractions, including dissolved organic carbon (DOC), biopolymers, humics, low molecular weight (LMW) humics, organic acids and neutrals, and hydrophobic organic carbon were characterized by liquid chromatography coupled to an organic carbon detector (LC-OCD). The system was described in detail in (6). The detection limit of the method was 10 µgC/L.

2.7 Assimilable organic carbon (AOC)

AOC was measured using a batch growth bioassay with a natural microbial community, followed by staining and cell enumeration by flow cytometry. The method was described in detail in (7). The method had a detection limit of 10 µgC/L.

3 Results and Discussion

3.1 Operation and maintenance of the ultra-low pressure ultrafiltration

Ultralow pressure UF uses the phenomenon of flux stabilization on a level of 4-10 $L \cdot h^{-1} \cdot m^{-2}$ under pressure of 40-150 mbar (5). Stabilization of flux occurs after 2-5 days and the stabilized flux value depends on the TOC of the feed water. No back-flushing, chemical cleaning or forward flushing is used, and a dead-end filtration mode is applied. Maintenance of the system is limited to the delivery of water to the feed storage tank and collection of the permeate. However, some maintenance may still be required to extend the service life of the system.

The daily requirement of drinking water for a family of 5 people amounts to about 20 L/day. The POU systems are designed to treat this amount of water. In most available POU systems the treatment is usually done once or twice a day, depending on the flow-rate of the filter or a batch size and local customs (8). Therefore, the system should be suitable for intermittent operation. Here the influence of the standstill times of 4 to 24 h was studied.

Fig. 3 shows that the flux of the UF membrane increases after the standstill period (A) and depends on the duration of the standstill period (B). The increase of the flux with the increase of the standstill period can be described by a second order polynomial regression for the studied period up to 24 h.

One of the plausible explanations of this effect is a relaxation of the fouling layer due to reduction of transmembrane pressure (TMP). Increase of TMP to the initial value after a standstill period results in a slow decrease of the flux. For the experiment shown in Fig. 3 (A), flux stabilized only approx. 40 h after the beginning of the operation. Moreover, the level of flux stabilization after the standstill period was similar to the level before the standstill period, which shows that the relaxation/compression of the fouling layer is reversible.

Fig. 4 shows the increase of the flux with the increase of the duration of the standstill period compared to the absolute values of the decrease of flux with the duration of operation. The results indicate that the relaxation of the fouling layer during standstill period occurs faster than its compression. Thus, at equal operation and standstill periods the initial flux after

standstill will be higher than the stabilized flux value. Therefore, the average flux can be expected to be higher than the flux during continuous operation.

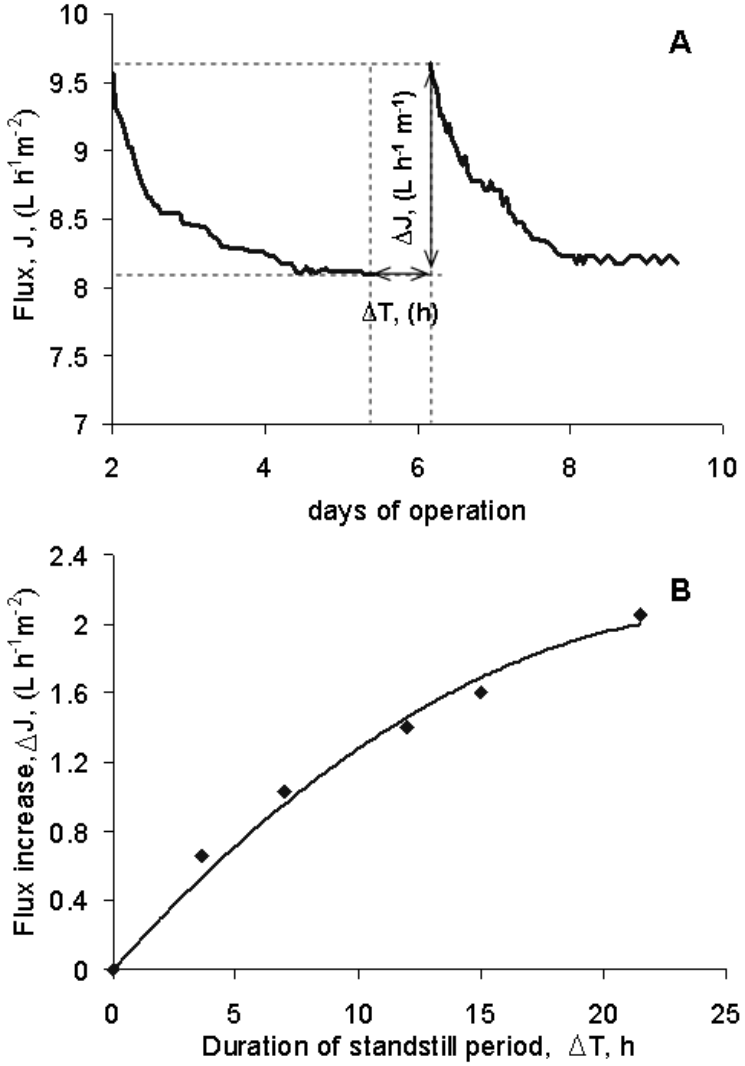


Fig. 3 - Increase of flux after the standstill period (A) and its dependence on the duration of the standstill period (B)

This is illustrated in Fig. 5, which shows the flux of the system operated intermittently (5 h operation, 19h standstill), compared to the flux of the system operated continuously under similar conditions. The duration of operation is too short to reach re-stabilization of flux. The increase of flux after the standstill period remains approximately the same for the studied period of 30 days. Thus, intermittent operation of the system results in an increase of the average flux.

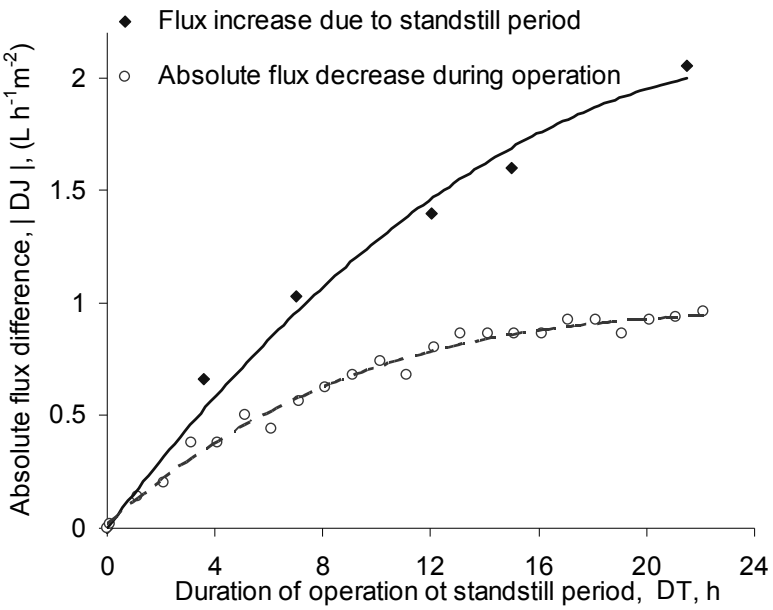


Fig. 4 - The increase of flux with the increase of the duration of the standstill period compared to the absolute decrease of flux during operation

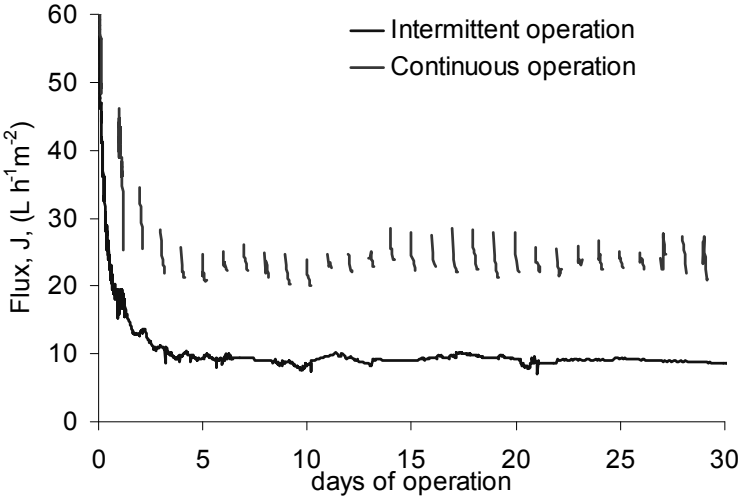


Fig. 5 - Flux stabilization during intermittent and continuous operation of ultrafiltration

Assuming that the average flux value linearly depends on the duration of the standstill period we can estimate the dependence of the daily water production of the system on the duration of operation (Fig. 6). Figure 6 shows that the maximal production capacity of the system is achieved if the system is operated intermittently and the standstill period is approx. 6 h. Thus, continuous operation of the system does not result in the highest capacity.

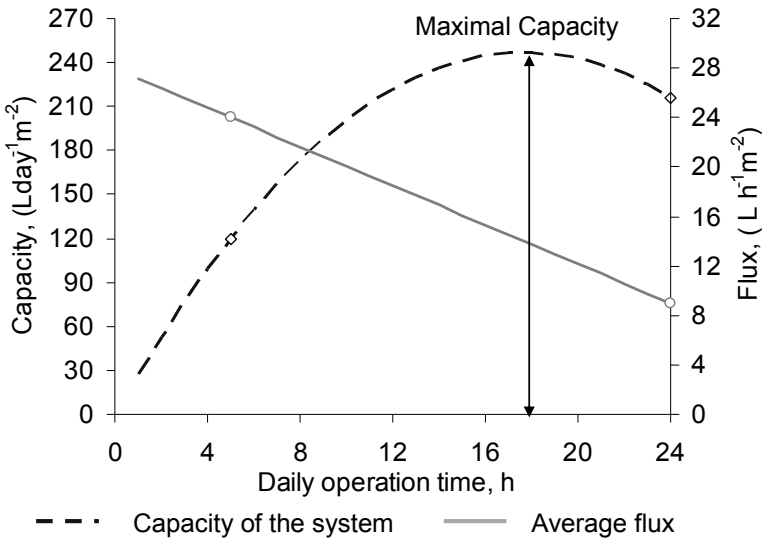


Fig. 6 - Dependence of average flux and capacity of the system from the period of daily operation of the ultra-low pressure UF system

3.2 Flushing the membrane surface

It is evident that dead-end operation of ultrafiltration without backflushing and cross-flow results in accumulation of the retained material on the membrane surface. The structure of the fouling layer remains open to sustain a stable flux of 4-10 $L \cdot h^{-1} \cdot m^{-2}$ for at least 5 months of operation (9). However, on a long term it might be necessary to remove part of the fouling layer to prevent increase of its thickness and stabilize the flux for a virtually unlimited period of time. Flushing the membrane surface with feed water may be sufficient to remove loosely attached particles and prevent further growth of the layer. We expect that combination of forward flushing with intermittent operation will have the highest impact on the stability of the flux.

To study the impact of forward flushing, we operated 5 systems in parallel for a period of 120 days. The flushing was done directly after the standstill period. Table 2 shows the average flux estimated for the period of operation of 30 days (starting with the day 5) and the daily capacity of the system calculated for the average flux values. The results indicate that the stabilization of flux occurs on a higher level for the system operated with the longest standstill period (12 h) and with flushing. Flushing itself seems to be efficient only in combination with intermittent operation. The average value of stabilized flux, observed for the system operated continuously with flushing, does not exceed the typical average flux value observed for the systems operated without flushing, fed with similar water (6-8 $L \cdot h^{-1} \cdot m^{-2}$) (9).

We suppose that the synergistic effect of intermittent operation and flushing on the flux stabilization is caused by a decrease of stability of the fouling layer. The decrease of stability of the layer may be induced by regular changes in TMP due to intermittent operation. The structure of the layer remains more open compared to the fouling layer formed under continuous operation, resulting in easier detachment of the accumulated particles and biomass. Removal of such excess fouling material results in a decrease of fouling layer thickness, thus decreasing its resistance. For the system operated continuously, the structure of the fouling layer remains more compact. Flushing under laminar flow conditions (Re = 6.7) removes only loosely and non-attached particles from the layer, and it can be expected that

this does not affect its structure. Thus, the resistance of the fouling layer remains similar to the layer formed in the system operated without flushing.

Table 2 shows that the average capacity of the system is higher for all of the studied systems operated intermittently with flushing (150 - 171 $L \cdot day^{-1} \cdot m^{-2}$) compared to the systems operated continuously (138 $L \cdot day^{-1} \cdot m^{-2}$). This result is in agreement with the data shown in Fig. 6 for the intermittent operation without flushing.

Table 2 - Main parameters of the surface flushing experiment

Standstill time, h	Operation time, h	Average flux, (days 5-35), $L \cdot h^{-1} \cdot m^{-2}$	Average capacity, $L \cdot day^{-1} \cdot m^{-2}$	Flush volume, % of produced water
0	24	5.76	138	29
3	21	8.13	171	23
6	18	8.68	156	26
12	12	12.52	150	27
12	12	10.58	127	no flush

3.3 Pre-treatment

There are two main reasons to consider pre-treatment of the feed water for ultra-low pressure UF:

- Reduction of particulate and NOM loads on the membrane increasing the flux and extending the service life of the membrane;
- Decrease of variability of the water quality due to e.g. storm events resulting in more stable operation.

For decentralized applications, in principle, all pre-treatment technologies can be applied in the same way as in the centralized treatment of drinking water. Besides efficiency in improving certain water quality parameter and the system costs, the requirements to the systems include ease of use, low maintenance, environmental sustainability and independence of electricity (4). Slow sand filtration (SSF) is a possible pretreatment process, but is also used in DC as a stand-alone water treatment technology on different scales (8, 10). However, if not maintained correctly, slow sand filtration alone does not provide complete protection against pathogens. In contrary to rapid sand filtration, slow sand filtration does not require backflushing. The maintenance of a SSF is limited to the removal of the schmuzdecke (once in 3-6 month depending on water quality), which however would require a certain level of training (10, 11). Besides turbidity removal and disinfection, the degradation of some fractions of NOM is expected to take place in the slow sand filter. Thus, slow sand filtration seems to be a promising technology for pre-treatment of the feed water with high NOM concentrations. Here we explore its impact on the efficiency of the ultra-low pressure ultrafiltration and discuss its impact on the maintenance of the household and community scale systems.

3.4 NOM removal by slow sand filtration

Fig. 7 shows concentrations of different NOM fractions in feed and outflow of SSFs. Approx. 20-50 % of the TOC is removed in the intermittently operated SSF while the TOC removal is 0-30% in continuously operated SSF. During first 50 days of operation, approx. 60% removal of humics is observed in the intermittent SSF and approx. 40% in the continuous system. The

efficiency of humics removal decreases in time in both filters, which can be explained by the decreasing adsorption capacity for humics on the sand. In contrary, the removal efficiency of biopolymer fraction increases with time to 60-80% at the end of the experiment. This can be explained by the development of biomass in the SSF. There is no clear trend for the removal efficiency of building block fraction of NOM. The differences in the other fractions of NOM are less significant (data not shown).

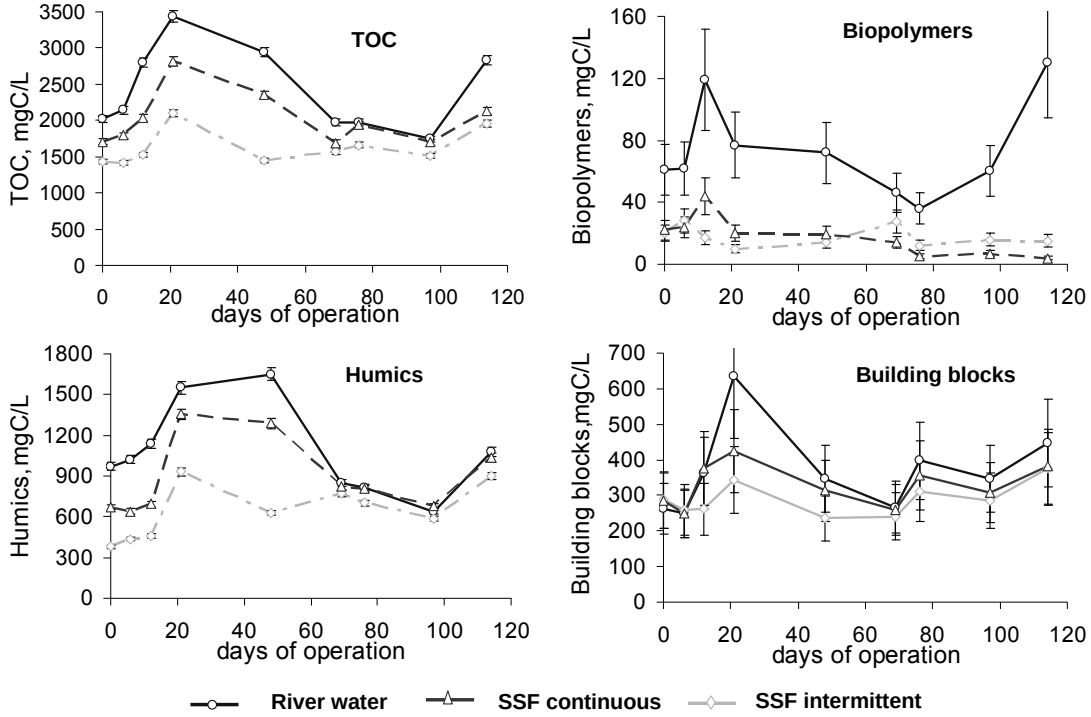


Fig. 7 - Concentrations of some fractions of NOM in feed water and in outflow of intermittent and continuous slow sand filters

3.5 Influence of slow sand filtration on the flux

The filtrate of both sand filters was used to feed two UF modules, as described in the Material and Methods section. The UF module fed by filtrate of the intermittent sand filter was operated also intermittently during 5 h/day similar to the SSF.

Flux values of the UF modules are shown in Fig. 8 and compared to a reference system, fed with untreated river water. The stabilization of flux of the continuously operated SSF/UF system occurred on a level of 10-12 $L \cdot h^{-1} \cdot m^{-2}$ – about two times higher than the flux of the reference system (about 6 $L \cdot h^{-1} \cdot m^{-2}$). The flux of the intermittently operated system fluctuated from 15 to 40 $L \cdot h^{-1} \cdot m^{-2}$. An increase of flux after the standstill period was observed in each cycle.

The higher flux of the continuously operated SSF/UF system in comparison to the direct UF system can be explained by degradation and adsorption of biopolymers and humics in the SSF. This result is in agreement with literature reporting reduced biofouling and NOM fouling of the UF membranes after biological pre-treatment (12, 13, 14).
The average flux in the intermittently operated SSF/UF system is approx. a factor 4.5 higher compared to direct UF. According to the flux data for continuous operation (Fig. 8), the reduction of TOC due to SSF results in an increase of flux by a factor 1.83. Furthermore, the

discontinuous operation during 5 h per day, results in an increase of average flux by a factor 2.52, as shown in Fig. 5. Addition of both effects gives an increase of flux by a factor 1.83•2.52=4.6, which is comparable to the observed increase of the flux by a factor 4.5.
In can be concluded that the effects of intermittent operation and pretreatment on flux are additive. Thus, operating ultra-low pressure ultrafiltration with slow sand pre-filtration under intermittent conditions allows increasing the capacity of the system and decreasing the required membrane surface area.

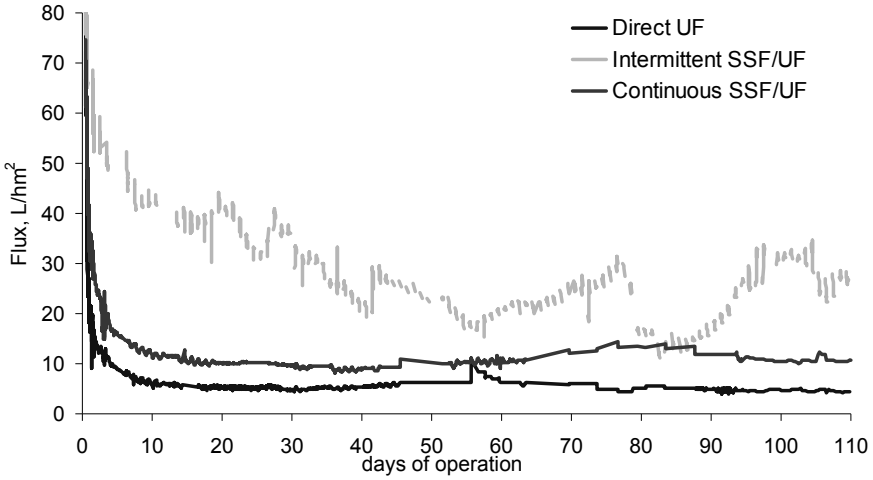


Fig. 8 - Flux of intermittently and continuously operated systems combining SSF and UF and a reference direct UF system

Fig. 8 shows that the values of flux for the intermittent SSF/UF do not only vary within each cycle but also that flux variations occur on a longer time scale (in the order of weeks). The changes in TOC or different NOM fractions do not correlate with the fluctuations of the flux (Figs. 7 and 8). Besides, the fluctuations occur only in intermittently operated systems, which also indicates that water quality is not the main reason of these flux variations. We suppose that the fluctuations of the flux are caused by changes in the fouling layer structure, which is intensified by intermittent operation. We mentioned above that the increase of flux after the standstill period may lead to relaxation and destabilization of the structure of the fouling layer. In the extreme case, destabilization of the structure can lead to aggregation of particles and biomass, accumulated in the layer. Aggregation could be observed on the membrane surface at operated times over 30 days. In general, the fluctuations of flux started simultaneously with the beginning of the aggregation. Fig. 9 illustrates the fouling layer of the systems operated under continuous and intermittent conditions for 48 days. These pictures show clearly that aggregation was more intense in the system operated intermittently. Also elevated TOC values of the feed water seemed to intensify this process (data not shown).

3.6 Biological stability of water

Ultrafiltration of natural water reduces its biological stability. Although pathogenic microorganisms do not grow in the natural water environment (15), re-growth may affect the taste and odor and reduce acceptance of the water. Moreover, households may try to clean the biofilms appearing on their water storage tanks due to re-growth, increasing the risk of contamination.
Assimilable organic carbon (AOC) is a parameter indicating biostability of water (16). It is generally accepted that water is biostable if AOC is lower than 20 µg/L (17). We measured

AOC concentrations in raw water, SSF outflow and UF permeates and the results are shown in Fig.10.

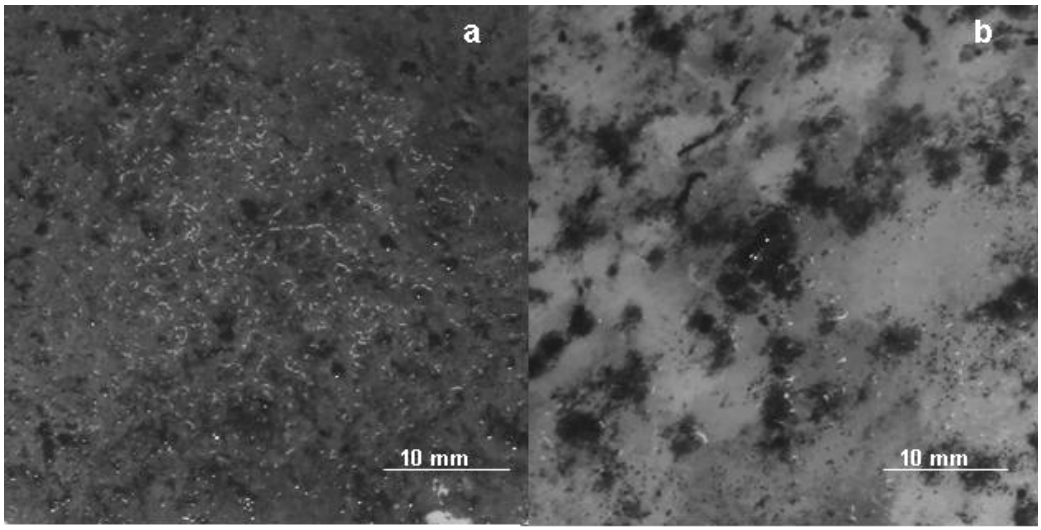


Fig. 9 - Fouling layer formed in the systems operated continuously (a) and intermittently (b) for 48 days

This figure shows that the river water sampled on days 69 and 90 is already biostable and the changes in water quality after slow sand filtration are not significant. The results for days 97 and 104 indicate that slow sand filtration improves the biostability to a level below 20 µg/L. Direct UF reduces the AOC value of the high-AOC river water (days 97 and 104), however not below the limit of 20 µg/L. This reduction may be due to biological processes in the biofouling layer on the membrane.

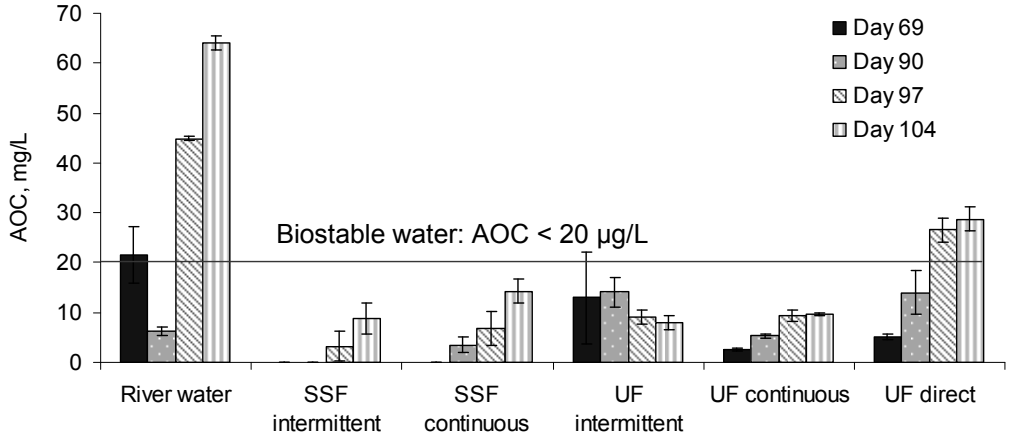


Fig. 10 - Assimilable organic carbon concentrations in in feed water and in water treated by intermittent and continuous slow sand filters

3.7 Evaluation of the operation and maintenance of the decentralized systems with and without pre-treatment

Ultra-low pressure ultrafiltration requires virtually no maintenance. For dead-end operated POU systems, maintenance is limited to filling of the feed water tank. Maintenance

requirements increase if flushing of the system is carried out to extend its service life or if system is operated intermittently.

Gravity-driven UF can be operated with our without SSF as a pre-treatment. The following three parameters influence the choice to operate with or without SSF:

a) SSF leads to increase of the flux of the UF (see Fig. 8);
b) SSF decreases the impact of the variability of water quality due to e.g. storm events;
c) SSF requires qualified maintenance once the filter is clogged.

The impact of these parameters on the performance, costs and maintenance will be discussed below for POU systems and community water systems separately.

3.7.1 POU systems

For the POU systems, it can be assumed that the system is not continuously filled with water, so that standstill times occur, e.g. during the night. Our results confirm that operating the UF membrane intermittently improves its performance. The system should be designed to keep membrane wet independently of the duration of the standstill period. A household may be advised or trained to do surface flushing regularly to further increase the performance of the system and extend its service-life. If this is not carried out, it will not cause any irreversible consequences for the system. Decrease of the flux on a long term may force the household to react and start flushing the system.

Our results showed that slow sand filtration reduces the re-growth potential of water. Re-growth itself cannot directly cause any harm, but it influences taste and smell negatively and can result in a decreased acceptance or even rejection of the system. Furthermore, it could force a household to wash his storage tank (e.g. with untreated water or hands) and contaminate it.
Water treated in POU system is usually consumed directly after treatment and the problem of post-contamination or deterioration of taste is less severe. Contamination may still occur if the overall hygiene of the households is low (18). Post-chlorination in this case will not solve the problem: chlorine requires reaction time of approx. 30 min. which is too long if water was contaminated directly before consumption (e.g. by use of contaminated cups or bottle used for drinking).

Besides low costs, one of the main prerequisites for application of POU systems in developing countries is to assure stable performance without maintenance (2, 4). Any additional pre-treatment will increase operation and maintenance requirements for the POU system and should be avoided wherever possible. To treat enough water for one family (20 L/day), assuming an average flux of 5 L/h/m^2 and an effective runtime of 8 hours per day, a membrane area of 0.5 m^2 would be required. The costs of such system will be determined as a sum of the costs of the membrane itself, its housing and storage tanks. While 0.5 m^2 of the membrane may be already packed in relatively small module and membrane costs are relatively low (below 40 US$/$m^2$ (3)), the decrease of the required membrane surface due to pre-treatment will not reduce the total costs of the system to a large extent. The costs to construct a household slow sand filter in DC are estimated to 20 US$ $L \cdot day^{-1} \cdot m^{-2}$ (4), and therefore, the total costs of the system will increase considerably when a sand filter is installed. Thus, we may conclude that for the POU applications SSF is not recommended for pre-treatment due to maintenance difficulties and increase of the costs of the system.

3.7.2 Community water treatment systems

The problem of the maintenance discussed above for POU systems is less severe for a community water supply, because usually a person responsible for the maintenance of the system is available who is trained to maintain the system. Usually, community water treatment systems are operated continuously and water produced during the night is stored. For ultra-low pressure UF it was shown however that the maximal system capacity is achieved if water is filtered intermittently (Fig. 6). The optimal duration of the standstill period in the cases studied was 3-9 h. However, intermittently operated systems require an operator or control equipment, increasing its maintenance and costs. Thus, the decision to operate the system intermittently or not, will depend on local conditions.

Assuming a community of 250 people, water used for basic domestic needs only (20 L/day per person) and a flux of 5-7 $L \cdot day^{-1} \cdot m^{-2}$ results in a required membrane area of about 35 m^2. Assuming the price of 1 m^2 of UF membrane is 40 $ (3), the investment costs for the membrane will result in 1400 $. In contrary to POU systems, it can be assumed that these costs are a significant part of the total investment costs of the system. Increase of flux due to pre-treatment reduces the membrane area required and thus the costs of the membranes by a factor 1.8 (resulting in 770 $ membrane costs).
In contrary to the UF, SSF may be built from locally available materials. The costs of the SSF strongly depend on the local prices for the materials, transport and labor. On average, the construction of a SSF in developing countries costs approx. 80-120 $ per m^2 of filtration area (19). Assuming the recommended flux of 100 $L \cdot day^{-1} \cdot m^{-2}$, the investment costs of SSF will amount to approx. 208 $ for the community system described above. Thus, if the SSF is built from locally available materials, investment costs are lower than investment costs required for the additional membranes. In addition to the cost benefit, SSF leads to an improved water quality, especially with regard to biostability. Thus, it can be concluded that application of SSF as a pretreatment provides important advantages for community water supply.

The maintenance of the SSF - monitoring the water flow and scrubbing of the “schmutzdeke” when filter is clogged - should be done by a trained operator.
If the turbidity of raw water is over 20 NTU, up-flow roughing filters may be considered to use instead of SSF or in addition to it (depending on the NOM concentrations) (20). Roughing filters are known to be effective in reducing turbidities from 200-2000 NTU to <20 NTU (11, 20). The maintenance requirements for roughing filters are limited to a regular drainage of the filter under hydrostatic pressure. If constructed from locally available materials, the costs of the filter may be kept low.

Post-contamination may cause severe health risks if water has to be carried for a long distances after treatment or if the water is stored during longer periods of time in the households (21). In this case, chlorination of water should be considered. However, the difficulties of handling chlorine have to be taken into account and the operator has to be trained to use it. Besides, the acceptance of chlorinated water is generally low due to taste and odor issues (21).

Based on the discussion above, table 3 summarizes the operation and maintenance requirements and suitability of pre-treatment for ultra-low pressure UF depending on scale of the system.

Table 3 - Operation, maintenance and pre-treatment requirements for POU and Community scale systems based on ultra-low pressure UF

	POU system	**Community scale**
Intermittent operation	unavoidable, results in increase of flux	depending on water quality may result in higher daily water production, not recommended if operator is not available daily
Flushing	recommended once a day before operation	once a day or when visited by operator (minimum once per week)
Pre-treatment	not recommended, screen may be used to protect membrane	SSF is recommended for high DOC waters: if built locally, reduces required membrane surface Roughing filter may be used for turbid waters (>20 NTU)
Post-treatment	not recommended	Post-chlorination: recommended if water has to be delivered on a long distance after treatment

4 Conclusions

The systems based on ultra-low pressure ultrafiltration require virtually no maintenance, which increases the suitability for decentralized drinking water treatment in developing and transition countries. Maintenance requirements increase if the system is flushed to extend its service life or if pre-treatement is applied to increase the average flux and reduce the membrane surface.

An increase of flux after a standstill period occurs, probably due to relaxation of the fouling layer. Afterwards, the flux decreases again to the original value, but this takes a relatively long time. Therefore, intermittent operation with relatively short standstill periods (3-9 hours) results in an elevated average flux in comparison to continuous operation. The flux may be further increased if the membrane surface is flushed with the feed water after the standstill period. Due to these effects, the maximal capacity of the system can be achieved if the system is operated intermittently with a standstill period of approx. 3-9 h, followed by a forward flush.

Slow sand filtration removes 60-80% of the bioploymer fraction and 40-60% of the humics fraction of NOM. This results in an overall increase of flux of the ultra-low pressure UF and a decrease of the required membrane surface. Furthermore, SSF results in a decrease of re-growth potential of water (AOC). With the water quality tested here, the water pre-treated by SSF can be considered as biostable. The combination of SSF and UF operated intermittently will further increase the flux. However, intermittent operation may intensify aggregation of the fouling layer and cause fluctuations in flux.

For community scale systems, the use of sand filtration as a pretreatment leads to lower total investment costs and improved water stability, and therefore is highly recommended.

For POU applications, any additional pre- and post-treatment will increase operation and maintenance requirements for the system and thus increase the risk of failure.

Acknowledgements

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Appendix B

Low-pressure ultrafiltration and membrane fouling by polysaccharides

Maryna Peter-Varbanets, Karin Borkmann, Wouter Pronk

in "Techneau: Safe Drinking Water from Source to Tap. State of the Art and Perspectives", ed. T. van den Hoven, C. Kazner, IWA Publishing, London, 2009.

Low-pressure ultrafiltration and membrane fouling by polysaccharides

M. Peter-Varbanets[1,2], K. Borkmann[1], W. Pronk[1]

[1]*Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, 8600 Dübendorf, Switzerland*
[2]*Institute of Environmental Engineering, ETH Zürich, 8093 Zürich, Switzerland*

Abstract

Low-pressure membrane systems have good perspectives for application in decentralized drinking water treatment. Fouling takes place but can be stabilized in dead-end mode at low pressures without membrane flushing or cleaning. In order to optimize such systems, it is important to investigate the fouling mechanisms. Polysaccharides are known to be relevant to fouling, but not much is known about the influence of polysaccharide structure and properties on fouling. Therefore, we systematically investigated the impact of polysaccharide and solution properties on UF membrane fouling. Regarding the initial stage of flux decline the polysaccharide structure, and particularly the availability of carboxyl groups, has a major impact on membrane fouling, while the molecular weights of polysaccharides does not play a significant role (in the studied range of Mw 5-250 kDa). The presence of metal ions and ionic strength also influences the fouling, which can be explained by the fact that both metal ions and ionic strength stabilize gel structure, and increasing the possibility of water trapping by hydrogen bonding, which leads to the higher permeability. However, independently of the initial solution conditions, flux stabilization on the level of approximately 10 $L.h^{-1}.m^{-2}$ was observed at higher permeate volumes. 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 permeability on the constant level, determined by the water retention properties of the gel structure.

1 Introduction

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 (WHO, 2004). 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 alternatives to centralized treatment concepts. In an extensive literature review (Peter-Varbanets et al., 2009a) we showed that the choice of reliable and affordable systems for decentralized application is limited, and that membrane-based treatment systems provide opportunities. Furthermore, experiments were carried out with low-pressure, dead-end ultrafiltration without pretreatment and without using pumps, backflushing or cleaning (Peter-Varbanets et al., 2009b). It was shown that such systems can be operated during extended periods of time (up to 5 months) with stable flux values using untreated river water and even using diluted wastewater. However, also in these systems the flux is limited by membrane fouling and therefore, it is important to investigate the basic mechanisms of membrane fouling. Besides humic substances (Clark and Lucas, 1998), polysaccharides are recognized to be an important component of natural waters which cause membrane fouling (Kimura et al., 2004), and it has

been found that electrochemical interactions play an important role in the fouling process (Amy and Cho, 1999). However, relatively little knowledge is available on the influence of polysaccharide structure, composition and properties on fouling. In this paper, UF fouling by polysaccharides with different molecular weights and functional groups is investigated at varying water matrix compositions (ionic strength, metal ions). The data are interpreted and the consequences for decentralized water treatment are discussed.

2 Methods

2.1 Polysaccharides

Several polysaccharides have been used in the study. Their main properties are shown in Table 1. The selection of these polysaccharides was based on the molecular structure of the polysaccharide, availability of the specific functional groups and the molecular weight. 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.

Table 1 - Characteristics of the polysaccharides

Polysaccharide	Specific groups	Molecular weights of polymer, kDa	Approx. molecular weight of single unit, Da
Alginate	-COONa	12-80	175
Hyaluronate	-COONa $-NH-CO-CH_3$	68-340	189
Pectin	-COONa $-COOCH_3$	30-100	158.5
Heparin	$-NH-SO_3Na$ $-O-SO_3Na$	4-6	195
N-acetylated-de-O-sulphated heparin	$-NH-CO-CH_3$ $-NH-SO_3Na$	12-15	184
Carboxymethylcellulose	$-O-CH_2-COONa$	250	189
Dextran	-	5 50 670	162
Starch	-		162

In order to find a comparable concentration unit for polasaccharides with different chain lengths and different compositions, the same concentration of sugar-subunits was used for all solutions (0.002 mM). When a polasaccharide contained different types of sugars, the average molar mass of these sugars was taken. 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), $NaHCO_3$ (0.125 mM) and a buffer solution of 3-(N-Morpholino)-propanesulfonic acid (MOPS, 0.5 mM). The pH was adjusted by addition of HCl (0.1 M) or NaOH (0.1 M) and was kept constant at pH 7.6 - 7.8. The ionic strength was controlled by conductivity measurements and when necessary adjusted with NaCl.

2.2 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 at a transmembrane pressure of 150 mbar. 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.

2.3 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 flow was measured by a scale, which was connected to a PC. Data were logged every 2 min.

2.4 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 1 L 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. At least 2 L of solution was filtered through the membrane and the flux was monitored as described above.

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 in Fig.1. As shown in Fig.1a, the flux decreased much more severely during filtration of alginate, Hyaluronate (HA) and Carboxymethylcellulose (CMC) in comparison to Dextran independently of its MW. Relatively small differences in flux decline can be observed for Dextrans with different molecular weights. 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 similar flux decline patterns were observed. 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 can be see from 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. 1b, 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. 1c, 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 a 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.

3.2 The role of metal ions

As we can see from the Fig. 1b and 1c, Ca plays an important role, and 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, thus achieving organized structures. With increasing concentrations of polysaccharide and metals, gel structures may be formed. Alginate shows specific ion binding characteristics and the affinity for alkaline earth metals increases in the order Mg << Ca < Sr < Ba.

Thibault (Thibault and Rinaudo, 1985) found that under Na and Mg salt forms, the polymers behave as single chain polyelectrolytes, 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 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).

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

As shown in Figure 2, the fouling is more severe in the presence of Mg and Na than in the presence of Ca and Ba, which are able to form gels. It was mentioned before that in the presence of Mg and Na, alginate has the behavior of a single chain polysaccharide and therefore is not able to form organized networks and gels, while in the presence of Ca and Ba gels are formed. This can be explained by the fact that Ca/Ba containing gel layers are more hydrated, with water molecules trapped by hydrogen bonding in the gel matrix (de Kerchove and Elimelech, 2006). The higher rate of hydration leads to a higher permeability of the gel layer, and therefore to a 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 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 (Xia et al., 2004; Choo et al., 2005). Therefore, it is necessary to consider the role of Fe ions in membrane fouling by polysaccharides.

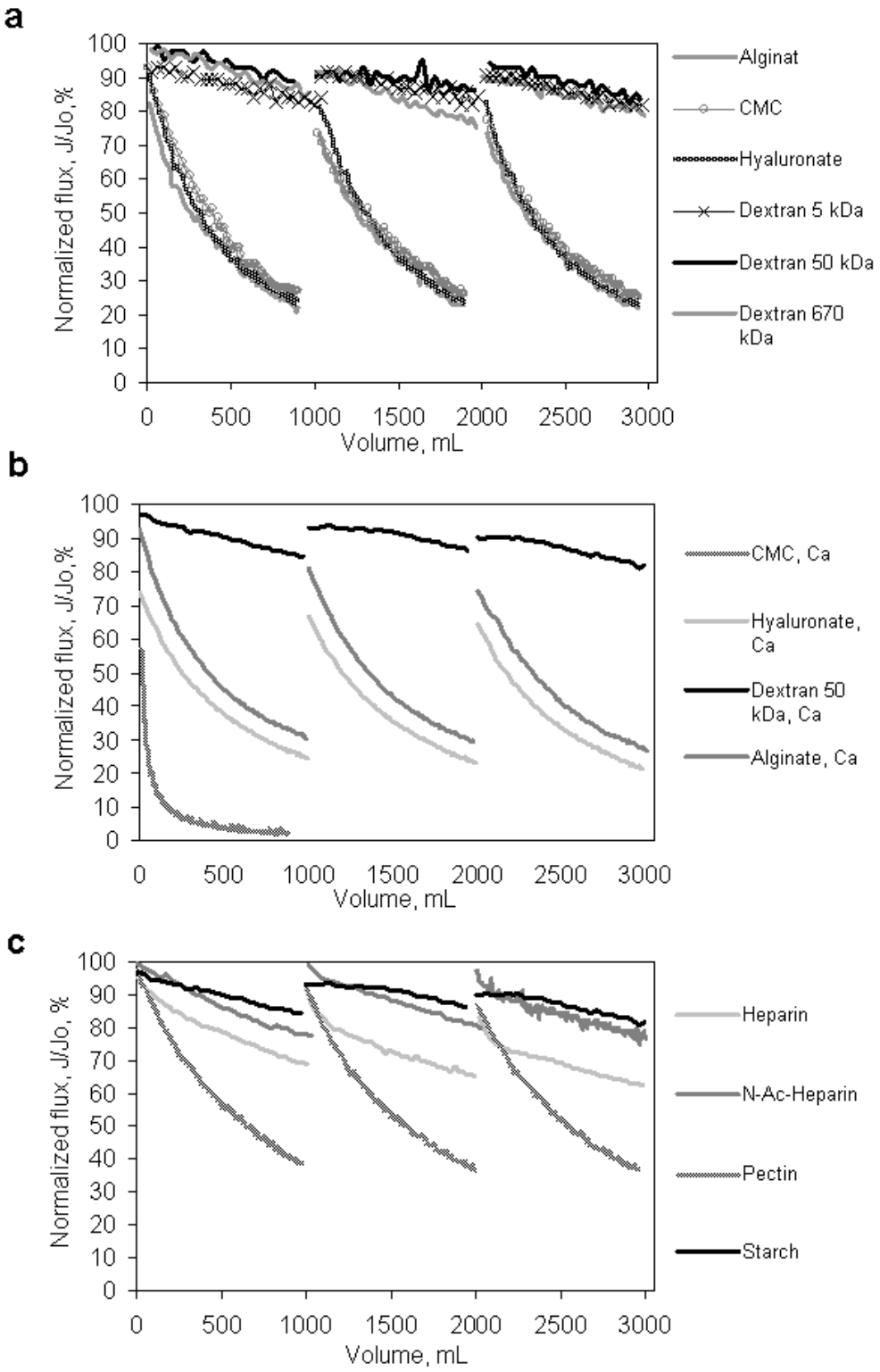


Figure 1 - Impact of different polysaccharides on the flux decline: (a) polysaccharides in solutions without Ca; (b, c) in solutions with Ca; Polysaccharide/Ca = 1/1.

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, also the impact of Fe(III) without alginate was investigated. The solutions were prepared in two different ways: preparing an acidic Fe(III) solutions and adding this to the alginate 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 $Fe(OH)_3$ rather than to formation of Fe-alginate complexes, because 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 an excess of Fe, and therefore, except of the Fe-alginate compound, colloidal iron hydroxides were also formed in the system.

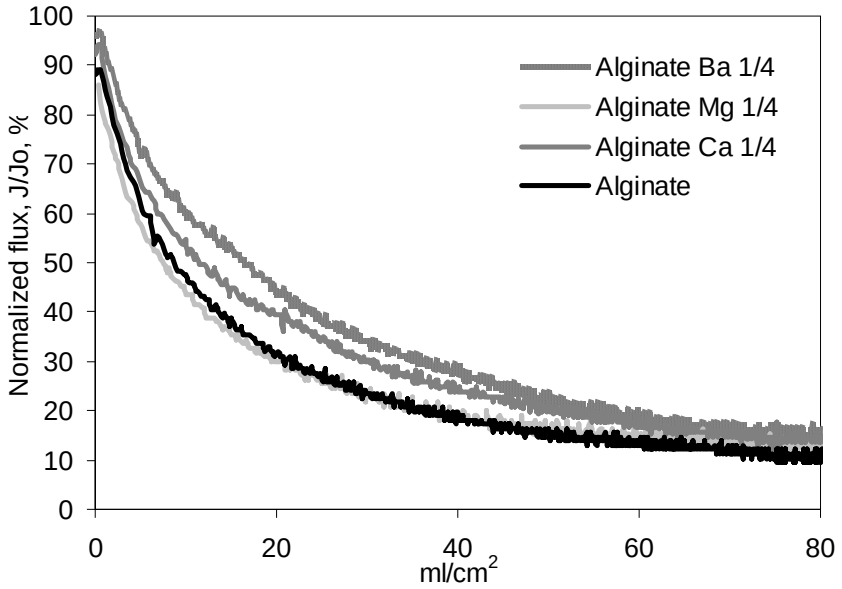


Figure 2- Impact of Ca, Mg, Ba and Na on flux in the presence of alginate

Fig. 3 represents the flux values of the experiments with Fe (III), with and without alginate. As shown in 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 way the Fe(III) was prepared. There was no iron detected in the permeate in both cases, which meant that all iron was retained by the membrane, independently from the way the Fe(III) colloids have been obtained. Both systems containing alginate and Fe(III) showed significant flux decline, comparable to the system containing alginate and Ca. This indicates a similar mechanisms of fouling with Fe(III) as with Ca and Ba, suggesting that in the presence of Fe(III) structured polysaccharides complexes are formed.
Furthermore, it can be concluded that the presence of (Fe-)colloids in the system does not influence the flux. 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. Apparently, both structures do not influence flux decline in the presence of alginate significantly.

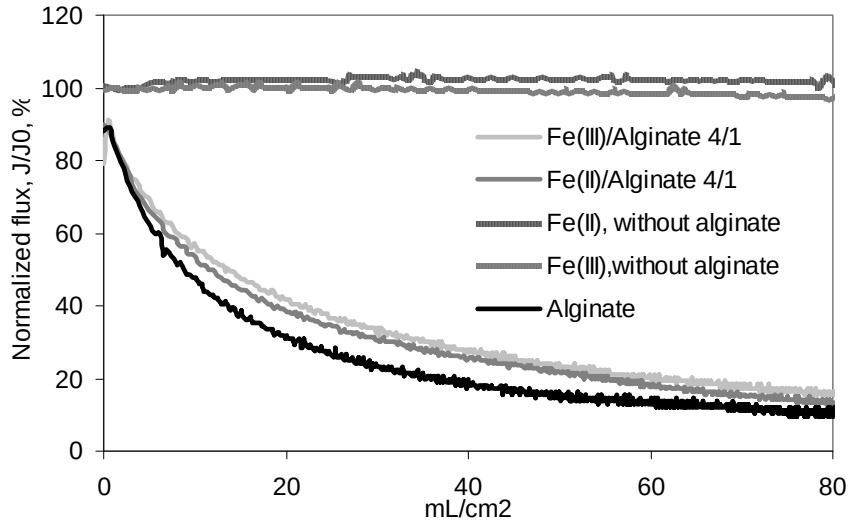


Figure 3 - Impact of Fe(III) on flux in systems with and without alginate. Fe(III) was directly added to alginate solutions, while in the experiments marked "Fe(II)", the Fe(II) was added initially, and than slowly oxidized to Fe(III). The ionic strength of all solutions was adjusted by NaCl

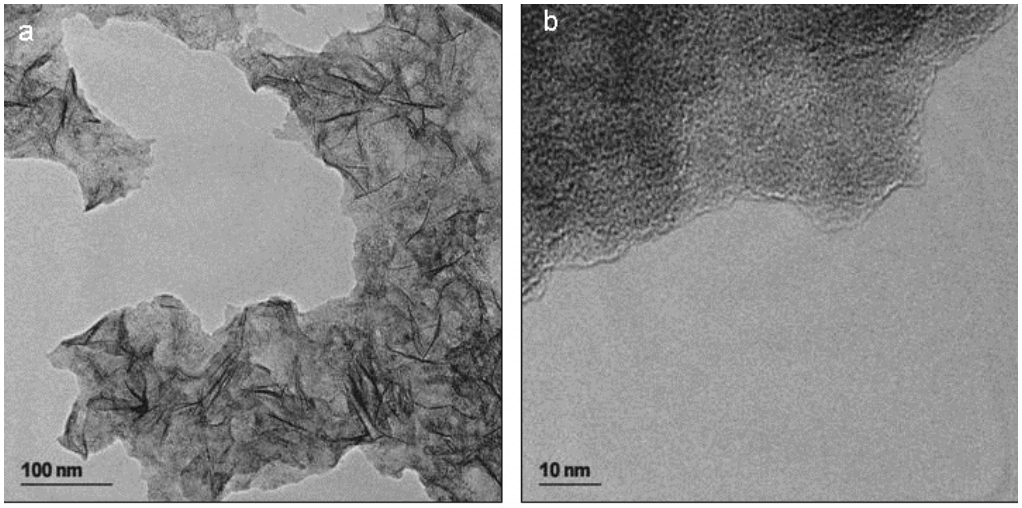


Figure 4 - TEM pictures of particles obtained from Fe-alginate solution, where (a) $Fe(OH)_3$ was made by oxidation of Fe(II)-alginate solution with air and pH increase, (b) - $Fe(OH)_3$ was obtained by precipitation from Fe(III)-alginate solution

3.4 The influence 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.

In Fig.5, the impact of ionic strength on the flux decline caused by Hyaluronate is shown. As we can see from the flux decrease graphs in Fig. 5, increase of the salt concentration 0.1 M leads to less fouling and higher flux values, and at higher concentrations the degree of fouling remains the same.

The impact of the ionic strength on the fouling by NOM has been considered in some studies before (Frank and Belfort, 2003). It is known that the cations of added salt neutralize the

anionic carboxylic group of NOM by a charge shielding effect (Ise and Sogami, 2005; Berriaud, 1998). The charge shielding induces van der Waals interactions and formation of inter- and intra-molecular hydrogen bonds, stabilizing a certain structure of a macromolecule and increasing the water content of the gel formed. Thus, the gel acts as a looser and more fluid structure, resulting in an increase of flux.
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 this theory: once the hydrogen bonds are formed, a further increase of the concentration of NaCl should not have an impact on the structure, and thus on the flux.

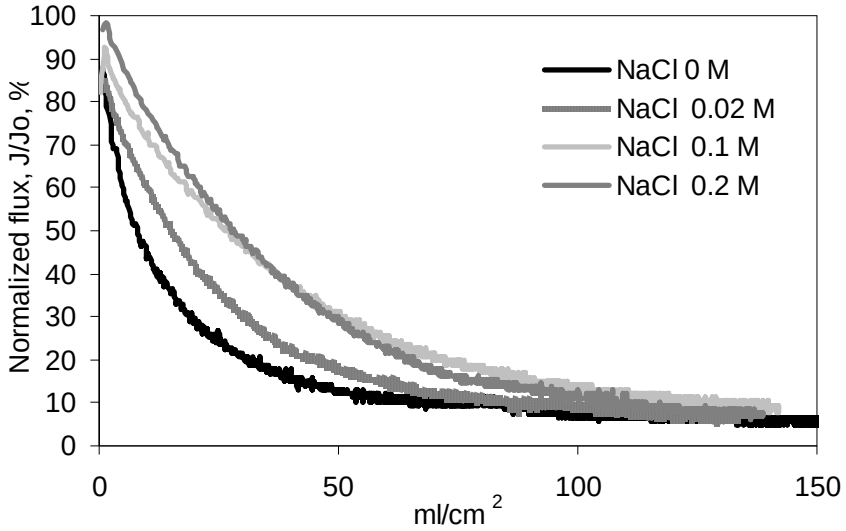


Figure 5 - Impact of the ionic strength on the flux decline caused by hyaluronic acid.

However, another theory states that 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). This theory is based on the reduction of the size of macromolecules with the increase of the ionic strength (Schaefer, 2001). Apparently, this effect is less significant for hyaluronate and the theory is not valid in the case of hyaluronic acid / NaCl.

3.5 Long-term experiments and flux stabilization

Fig. 5 (and also Fig. 2, 3) shows the flux behavior during the long-term filtration without backflushing. In the initial period of the flux curves (volume of the polysaccharide solution filtered through the membrane up to 80 mL/cm^2 or 800 L/m^2), a strong flux decline occurred, but 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 different polysaccharides and the impact of solution conditions cannot be noticed anymore during this stage of ultrafiltration. These flux decline patterns indicate that the mechanisms of fouling layer formation at the beginning of the cycle differ from the situation where substantial fouling layer should already have been formed.
In this paragraph we will focus on phenomena of flux stabilization (the impact of different parameters on the first part of the cycle has been discussed before). As mentioned above, the stabilization of the flux curve is being observed after approx. 80 mL of solution passed through 1 cm^2 of the membrane. This corresponds to the accumulation about 0.03 mg of alginate over 1 cm^2 of the membrane. Assuming an average polysaccharide concentration occurring in the gel structure of 2.9 g/L (Rolin et al., 1998), the layer thickness can be calculated to be around 100 μm, which is a realistic value as seen by visual observation, but

not confirmed by measurements. Being a network of randomly distributed chains, the gel can be expected to act as a filter for transport of other macromolecules (Laurent, 1995). This network, as any filter, can be characterized by a porosity and water permeability (Beeriaud et al., 1998; Rolin, 1998). Therefore, the fouling layer formed on the membrane surface can be considered as a semi permeable membrane itself. Actually, alginate has been used for production of membranes in different fields of separation (Patil et al., 2007). In order to investigate the structure of alginate gels, AFM pictures were made of an alginate gel obtained by centrifugation of an alginate solution of 0.365 µg/L, and compared to an UF membrane used in our investigations (Figs. 6a and 6b). As shown, indeed membrane-like structures are observed in the case of alginate, with a similar surface-roughness as the UF membrane.

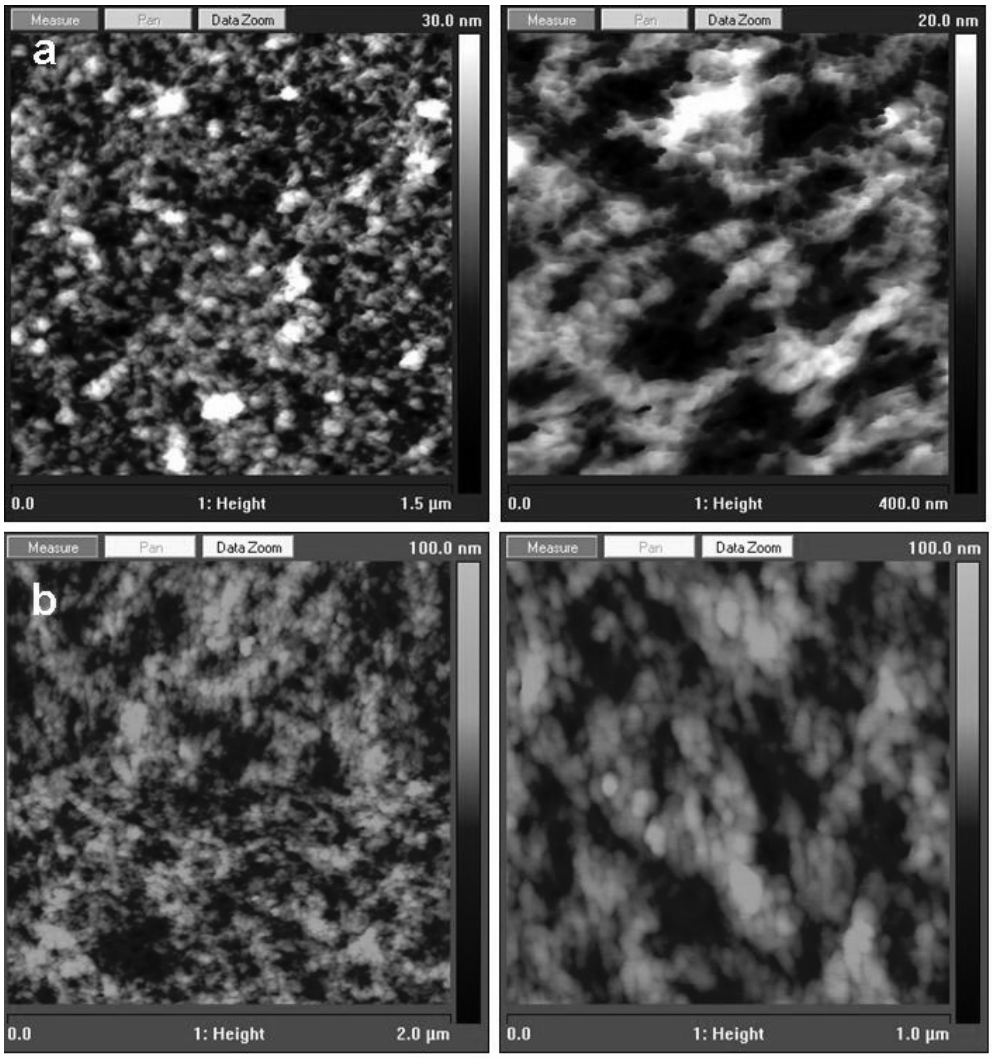


Figure 6 - AFM Pictures: (a) centrifuged alginate gel; (b) clean UF membrane (PES)

3.6 Relevance for practice

Stabilization of the flux on a level of around 7 $L.h^{-1}.m^{-2}$ has been observed in dead-end UF systems without backflushing operated during extended periods of time (Peter-Varbanets et al., 2009b). As reported here, flux stabilization occurs with polysaccharide solutions at a level of around 10 $L.h^{-1}.m^{-2}$, which is in the upper range of the flux with natural waters. The difference between these values can probably be explained by the presence of more hydrophobic, smaller components in natural waters (e.g. humic substances) which can lead to pore blocking.

As shown in Fig. 6, deposition of polysaccharides on the membrane can lead to the formation of a secondary membrane. It can be expected that the separation properties of this layer depends on the type of polysaccharide and the matrix composition. Also in the case of dead-end UF systems, stationary fouling layers are formed which are expected to contain bulk polysaccharides and EPS (Peter-Varbanets et al., 2009b). Such may improve the separation characteristics of the membrane.
While biological activity exists in the systems operated with natural water, it can be assumed that a fraction of the polysaccharides present in natural waters is enzymatically hydrolysed when trapped in the fouling layer. Thus, the role of polysaccharides in dead-end low-pressure UF systems is considered less detrimental than in conventional membrane filtration. Actually, the hydrolysis of polysaccharides in such fouling layers can have a positive effect in creating channels which facilitate flow and contribute to reducing the resistance in biologically active fouling layers.

4 Conclusions

We have systematically investigated the impact of polysaccharide structure, availability of functional groups and molecular weight on membrane fouling at conditions suitable for POU systems (hydrostatic pressure of 120-150 mbar and no backflushing). Our experimental results lead us to the following conclusions:
Regarding the initial stage of flux decline (0-800 L/m^2) 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).
The presence of metal ions has a strong impact on the fouling: 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 a higher permeability of these metal containing gels. At elevated ionic strength the permeability is increased. This may be explained by the formation of hydrogen bonds, which can contribute to swelling of polysaccharides in the solution and on the surface in looser and more fluid gel structures.
Independently of the initial solution conditions, after approx. 800 L/m^2 has been filtered, the flux stabilizes on a level of approx. 10 $L.h^{-1}.m^{-2}$. 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 permeability on a certain level, determined by the water retention properties of the gel structure.

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Curriculum Vitae

Surname		Peter
Name		Maryna
Personal Details:	Maiden name	Varbanets
	Date of birth	15.12.1981
	Place of birth	Pripjat, Ukraine
Education		
	01/2006 - 06/2010	PhD student at Eawag: Swiss Federal Institute of Aquatic Science and Technology, Department of Process Engineering
	05/1999 - 07/2005	Bachelor and Master studies at National Technical University of Ukraine NTUU “KPI” in Chemical Technology and Engineering
	08/1987 - 06/1998	Secondary School and Gymnasium in Kyiv, Ukraine
Practical experience and projects		
	07/2010-present	Postdoctoral researcher at Eawag: Swiss Federal Institute of Aquatic Science and Technology, Departments of Process Engineering and Water and Sanitation in Developing Countries
	01/2006-06/2010	EU Project TECHNEAU, WP2.5: Compact units for decentralized supply
	01/2006 - 06/2006	EU Project TECHNEAU, WA1: Rethink the system: Global trends affecting the water cycle
	09/2004 - 06/2005 03/2002 - 06/2003	Undergraduate teaching assistant at National Technical University of Ukraine NTUU “KPI” , Kyiv, Ukraine
	07/2003 - 06/2004	Internship at Clariant AG, Muttenz, Switzerland: Synthesis of polymers
	07/2002 - 06/2005	Undergraduate research assistant at NTUU “KPI”, Kyiv Ukraine: Solvent sublation for industrial wastewater treatment
	02/2002 - 08/2002	Internship at Ukrwodbezpeka AG., Kyiv Ukraine: Bactericidal polymers for drinking water disinfection