



Ultrafiltration to reuse laundering wash water: evaluation of membranes and permeate flux

Mattia Giagnorio^{a,b,*}, Lene Fjerbæk Søtoft^a, Alberto Tiraferri^b, Henrik Grüttner^a

^aDepartment of Chemical Engineering, Biotechnology and Environmental Technology, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark, Tel. +39 0110907670; email: mattia.giagnorio@polito.it (M. Giagnorio); Tel. +45 65507479; email: lfj@kbm.sdu.dk (L.F. Søtoft); Tel. +45 20585076; email: hegru@kbm.sdu.dk (H. Grüttner)

^bDepartment of Environment, Land and Infrastructure Engineering (DIATI), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy, Tel. +39 0110907628; email: alberto.tiraferri@polito.it

Received 1 April 2016; Accepted 25 July 2016

ABSTRACT

Laundering industry consumes and discharges large amounts of water and surfactants, and the demand of surface active agents used for washing is increasing worldwide. Some of these substances are considered contaminants of emerging concern, as they persist in the environment. This work aimed at evaluating the feasibility of ultrafiltration as a method to treat the wash wastewater and possibly reuse the surfactant-rich permeate stream in laundry facilities. In particular, evaluation of surfactant recovery was performed through analysis of the permeate flux and properties obtained through polymeric and ceramic membranes. Wash water samples were collected at an industrial laundering facility for hospital linen and filtered through different ultrafiltration membranes with varying molecular weight cut-off. The critical micelle concentration of the detergent was quantified, and capillarity measurements were used to determine the concentration of free surfactants in water. The system was designed to comprise two filtration steps in series: a pre-filtration step did not allow recovery of surfactant or the production of a high quality permeate, but it was necessary to remove large contaminants and to minimize the amount of foulants in the feed water of the second filtration, from which reusable permeates were finally produced. Recovery of 43% and 39% of reusable surfactants were achieved using polymeric and ceramic membranes, respectively. Results suggest the existence of an optimal molecular weight cut-off, which for this work was equal to approximately 6 kDa. Since the operation temperature may have significant impact on the energy requirements of the washing process, the influence of feed water temperature on surfactant recovery was also preliminary investigated. Results suggested the possibility to recover water and surfactants by directly treating wastewater streams of high temperature and the potential of integrating an ultrafiltration system in large laundering facilities.

Keywords: Ultrafiltration; Laundering industry; Surfactants; Critical micelle concentration; Molecular weight cut-off; Wastewater

1. Introduction

The laundering industry utilizes a large quantity of fresh water and chemical products [1,2], among which surfactants are the most important [3]. Washing 1 kg of textiles requires,

on average, 15 L of water, and the average industrial washing facility discharges a total amount of 400 m³ of wastewater per day [4]. Furthermore, feed water entering washing machines needs to be of relatively high purity (e.g., low level of calcium and magnesium) to maximize the cleaning efficacy of detergents and to avoid textile deterioration [5]. Wastewater produced by laundries contains diverse organic and inorganic substances, such as proteins, salts and metal ion, mineral oils,

* Corresponding author.

dangerous substances and, above all, high concentrations of surfactants [4].

The efficiency of surface active agents is strictly dependent on the length of their hydrophobic tails at the liquid–solid interface [6], which has the ability to lower the surface tension of the washing liquid, thus improving its wetting capability [7,8]. The decrease of liquid surface tension is directly proportional to the increase of surfactant concentration until the critical micelle concentration point (CMC) is reached [6]. Beyond the CMC, further addition of surfactant in solution simply translates into an increase in the number of micelles without affecting the quantity of surface active agents available for contaminant removal [9–11]. The efficiency of cleaning processes is thus solely related to the portion of surfactants present as individual free molecules [11]. As a safety factor in the laundering industry, it is common practice to add a higher dose of detergents compared with that strictly necessary for entrapping the contaminants. However, the concentration always remains below the CMC. The extra-dose may be recovered and reused in the system.

From an economic standpoint, 56% of the total amount of surfactants produced worldwide in 2014 was used in laundering processes, with an overall profit of more than US \$18 billion. An average increase in surfactant demand of 2.6% per year is expected at least up to 2022 [12]. The substantial amounts of both water and surfactants utilized by the laundering industry suggest the development of more environmentally friendly systems based on the recovery of these resources to reduce the overall environmental footprint of this widespread business. In addition, washing systems require a large quantity of energy within the so-called Sinner's circle, which comprises interrelated mechanical, thermal, and chemical energies, together with target contact times [13]. In devising a technology to recover resources within a laundering facility, it is necessary to maintain a process approach, that is, studying a method that can be integrated directly into a laundering facility.

Membrane filtration systems offer more flexibility compared with conventional treatment technologies, such as precipitation, activated carbon, or ozonation [14,15]. Numerous research studies have been conducted on the application of membrane technology in processes involving surfactants. 96% and 87% of surfactants rejection were achieved using regenerated cellulose ultrafiltration (UF) membranes with molecular weight cut-off (MWCO) of 5 and 10 kDa, respectively [16]. High rejection of micelles was obtained with UF hollow fibers modules characterized by an MWCO between 0.5 and 4 kDa [17]. Other authors recommended to use ceramic materials to prevent damage due to chemicals presented in wash water [13]. The application of ceramic ultrafiltration membranes was proven to be a successful technology to recover surfactants from contaminated aqueous solutions at high operating temperature (above 90°C) [18,19]. Thanks to the ability of surfactant to sequester other molecules in water, micellar-enhanced UF (MEUF) systems were developed in recent decades. This technology is applied to remove organic compounds from water through the addition of surfactants. The obtained solution is then filtered through UF membranes that reject micelles entrapping the organic material [20]. Several studies have demonstrated the effectiveness of this process to reject high quantity of micelles and organic material with

polymeric membranes characterized by MWCO in the range 5–10 kDa [21,22]. It is also known that polysulfone membranes with MWCO between 30 and 500 kDa can be applied to separate surfactants from oily solutions [23]. An overview of membrane-based processes applied to surfactant solutions was compiled by Suárez et al. [24]. However, no studies so far have focused on evaluating the recovery of free surfactants from wash water produced by laundering facilities.

In this paper, the treatment of laundering wash wastewater in UF is studied with the goal to evaluate the possibility to recover water and free surface active agents in the permeate stream. Wastewater of a continuous batch washing (CBW) machine of a hospital laundry is treated using polymeric and ceramic membranes with different MWCO, thus investigating the influence of these parameters on permeate flux and properties. A dual filtering step is discussed, which allows foulant removal prior to detergent recovery, thus maximizing the efficacy of this latter step. Different analytical procedures are applied to describe the behavior of surfactants in water. In particular, a capillarity-based technique is deployed as a method to determine the CMC point as well as the free surfactant concentration in water. Since laundering facilities are working with temperatures up to 80°C, experiments are also carried out using feed water and permeate streams at high temperature, thus suggesting the potential for also recovering energy within the system.

2. Materials and methods

2.1. CBW machine and wash wastewater samples

Wash wastewater samples were collected at the University Hospital laundry of Odense (OUH laundry) from the most efficient CBW machine, which performs 75% of the total daily batches. This system comprises four main washing steps: pre-wash, main wash, rinsing, and finishing zone. Textiles and some detergents are introduced in the pre-wash zone where the temperature is between 30°C and 40°C; further detergents are added in the main wash zone where the temperature reaches 80°C. Wastewater is discharged during these two initial steps. Fresh water is introduced in the rinse and finishing zones, in such a way to create a counter-current process within the machine. The objective of the pre-wash and the main wash steps is to remove contaminants from linens at high temperature without requiring the same water purity of the rinsing steps. Since the composition of the produced wash wastewater changes from batch to batch depending on the type of linens treated, samples used for the experiments in this study were the assortment of exhaust water from a number of cycles.

2.2. Detergent and membranes

The detergent, Silex Emulsion M, was obtained from the OUH laundry. On average, 1.75 g of Silex Emulsion M is used per kilogram of textile. The detergent comprises 15–30 wt% of non-ionic surfactant. The composition of surface active agent mixture was not provided by the manufacturer.

The main characteristics of the membranes used for experiments are reported in Table 1. Four different polymeric and two different ceramic membranes were employed.

Polymeric membranes with MWCO of 100, 50, 20, and 6 kDa were purchased from Alfa Laval (Denmark) as round flat sheets with diameter of 20 cm. All membranes were fabricated with a polypropylene support and then cast with a polysulfone (GR series) or fluoropolymer (FS series) separation layer. Ceramic membranes were delivered in single tubular modules with length of 1,200 and 500 mm for the 300 kDa (titanium, Tami Industries, France) and for the 7.5 kDa (aluminium, Inopor GmbH, Germany) MWCO, respectively. All these membranes perform in the UF range and size exclusion is their main separation process.

2.3. Filtration tests

As suggested by the manufacturer, all membranes were rinsed with sodium hydroxide solution (pH 10) for 30 min prior to their use for filtration. At the end of each filtration process, the membranes were treated with citric acid (pH 3) and then NaOH to restore neutral pH in the system. Filtrations were performed with a stainless steel setup provided by Alfa Laval, LabStak® M20. Two online pressure gauges monitored the inlet and outlet pressures continuously; see scheme of the filtration setup in Fig. 1(c). Permeate fluxes were calculated

as $J_p = \frac{V}{A \cdot t}$, where J_p is the permeate flux ($\text{L m}^{-2} \text{h}^{-1}$), obtained as the change in permeate volume, V , over time, t , divided by the total membrane area, A . Deionized water (DI) was filtered through the system before and after the filtration tests, and the resulting DI permeate fluxes were measured.

The sequence and conditions of filtration were different using polymeric and ceramic membranes; see Figs. 1(a) and (b). In all cases, a pre-filtration process was followed by a recovery filtration step. Pre-filtration was necessary to remove most of the large contaminants that would have rapidly fouled the tighter membranes used in the second filtration step aimed at producing recoverable permeates. Ideally, wash wastewater should be treated and reused at high temperature coming directly from the main wash stage, which would allow recovery of heat as well as surfactants. Ceramic materials withstand these conditions but not polymeric membranes, which were deployed with the rationale of reusing wastewater coming from the pre-wash step at lower temperature.

2.3.1. Tests with polymeric membranes

The filtration tests conducted with polymeric membranes consisted of two steps:

- Pre-filtration was carried out with 100 kDa MWCO membranes at the same temperature (approximately 45°C) of collection of the wash water from pre-wash of the OUH laundry CBW machine. Wash water (25 L) was filtered by four FS40PP membranes in parallel, by constantly recovering the retentate stream, which was reintroduced into the feed water container. An efficiency of 85% was achieved after 3 h of operation, collecting almost 22 L of permeate, which was then used as feed water for the filtration step aimed at surfactant recovery.
- Part of the permeate from pre-filtration was treated using 50 kDa MWCO membranes (GR51PP), part using 20 kDa MWCO membranes (GR61PP), and the remaining sample

Table 1

Membranes used for recovery test and their properties. The reported values of permeability are average values, and they were measured under different applied pressures and using a feed solution of deionized water

Membrane	Material	MWCO (kDa)	Area (m^2)	Permeability ($\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$)
GR51PP	Polysulfone	50	0.018	50
GR61PP	Polysulfone	20	0.018	40
FS40PP	Fluoro polymer	100	0.018	180
FS81PP	Fluoro polymer	6	0.018	100
Tami	TiO_2	300	0.02	120
Inopor	$\gamma\text{-Al}_2\text{O}_3$	7.5	0.011	86

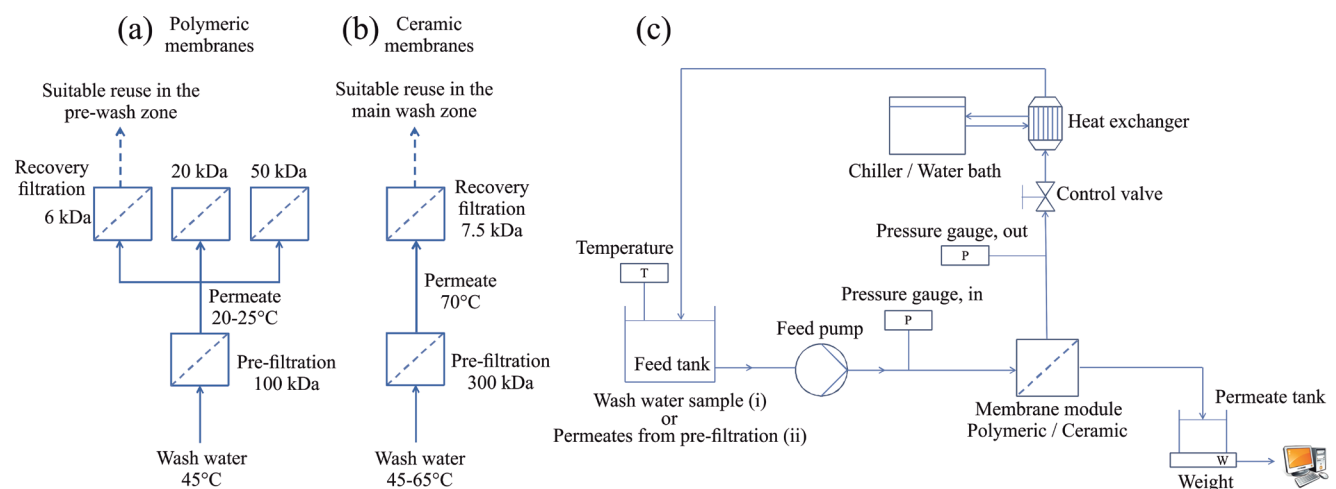


Fig. 1. Schematic and conceptual diagrams of the filtration tests and of the lab setup. Treatment train with (a) polymeric and (b) ceramic membranes. (c) Laboratory setup used for filtration tests.

was filtered through membranes with a MWCO of 6 kDa (FS81PP). These recovery filtrations were performed in 1 h at ambient temperature (20°C–25°C).

Permeate fluxes were monitored at different applied inlet pressures between 2 bar (29 psi) and 6 bar (87 psi) in both the pre-filtration and the recovery filtration processes.

2.3.2. Tests with ceramic membranes

A specific setup was installed for ceramic membranes, which included a water bath to increase the temperature during filtration (Fig. 1(c)), thus evaluating the possibility to recover both heat and free surfactant molecules directly from the main wash step of the CBW machine. As mentioned above, filtration was divided in two steps: a pre-filtration and a filtration phase. The wash water sample collected at OUH laundry (20 L) was (i) pre-filtered using 300 kDa MWCO ceramic membranes, thus collecting 10 L of permeate after 3 h of operation. The temperature varied from approximately 45°C to 65°C. (ii) The permeate from the first step was then used as feed water for a 1-h recovery filtration through 7.5 kDa ceramic membranes, conducted at 70°C. Permeate fluxes were monitored at different applied inlet pressures ranging between 1.5 bar (22 psi) and 4.5 bar (65 psi) in both the pre-filtration and the recovery filtration processes.

2.4. Measurement of the CMC point

The measurement of the CMC for the non-ionic surfactants present in Silex Emulsion M was performed following two analytical procedures, one based on conductivity and the other on capillarity. Solutions of varying concentration of detergent were prepared in DI, ranging from 50 to 36,000 mg/L. Capillarity measurements were carried out by filling a specific container equipped with five capillary tubes with 2.3 mL of solution. A dial gauge was used to measure the level reached by the solution inside the tubes, and the five values were averaged. The procedure was repeated for DI and for each concentration of detergent. The surface tension, ST , was thus calculated as $ST = C \cdot K$, where C is the average capillary level reached by the solution and K is a coefficient of proportionality, computed by imposing a value of the surface tension for DI equal to 72.8 dyn/cm. The CMC point is the value of surfactant concentration above which the surface tension remains constant, even following addition of further surfactant in solution. Below the CMC point, the obtained curve was used to convert values of capillarity to amount of free surfactant for all the permeate samples.

For the same solutions of known surfactant concentration, conductivity was measured with a conductivity meter (Brand HACH, Hach Lange ApS, Denmark). Since the linear increase of conductivity depends only on monomers in the solution (i.e., the free surfactants), once the CMC is reached, a clear break can be observed in conductivity trend [25,26]. This method based on conductivity was also used to measure the CMC. Each test was repeated three times taking the average as the final value.

2.5. Measurement of the total amount of surfactant

LCK 433 Hach Lange cuvettes (Hach Lange S.r.l., Italy) were used to determine the total amount of surfactant (i.e., both free agents and agents bound with contaminants) in the wash water samples collected at the OUH laundry and in each of the permeate samples obtained by filtration. Chemicals contained in the cuvette render all the surface active agents free. The amount of free molecules was then measured by light absorption with a UV-Vis spectrophotometer (DR3900 Benchtop, Hach Lange ApS, Denmark) in the UV range. Three measurements were performed for each sample, and their results were averaged.

2.6. Characterization and evaluation of the permeate physicochemical properties

Conductivity, pH, and COD values were measured for each of the permeate samples in addition to the surfactants content. In the CBW machine, water with usable surfactants may be recycled in the pre-wash and in the main wash stages of the cycle, in which detergent is added and high temperature is required (between 45°C and 85°C). Therefore, the permeates must respect the limits for water reuse in these washing zones, set based on company practice and on the typical needs related to the treated linens; these values are reported in Table 2.

3. Results and discussion

3.1. Behavior of surfactant in aqueous solution

Fig. 2 presents results obtained by capillarity and conductivity tests on solutions of varying detergent concentration. Capillarity measurements showed a decrease in surface tension at increasing amount of Silex Emulsion M, for concentrations lower than 2 g/L; see Fig. 1(a). Further increase in detergent concentration above this point did not affect the value of surface tension, which remained constant. Fig. 2(b) shows that conductivity increased linearly with two different slopes, revealing a clear break at 2 g/L. Based on both capillarity and conductivity measurements, the CMC of this solution was assumed to be 2 g/L. Above this point, further increase in detergent concentration only results in formation of micelles [25], whereby hydrophobic tails are associated with each other and are incapable of producing the desired decrease of surface tension.

The two analytical procedures adopted in this study, based respectively on capillarity and on conductivity, produced equivalent results in terms of CMC. This observation implies that capillarity may be used as a stand-alone method to determine the CMC point of detergent solutions.

Table 2
Limits for water reuse in two different stages of the washing cycle

Stage	pH	Conductivity (mS/cm)	COD (mg/l)
Pre-wash	6–10	2	–
Main-wash	6–10	2	1,000

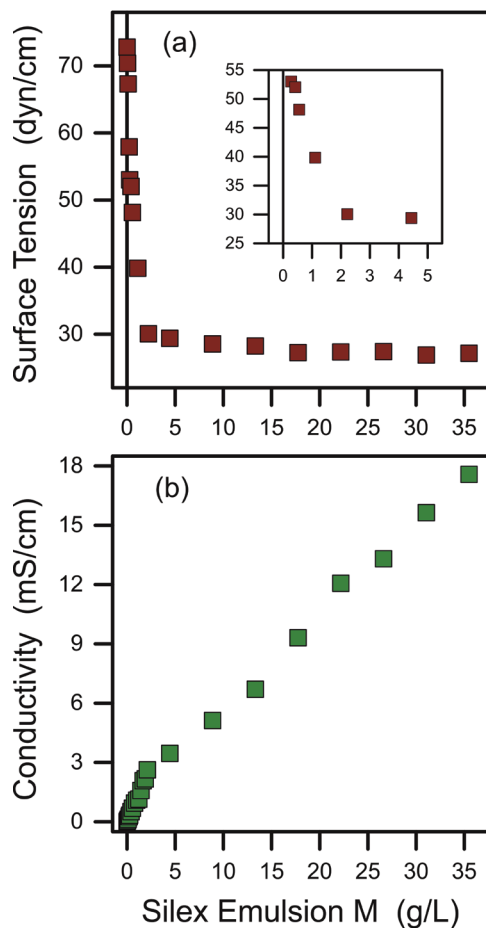


Fig. 2. Identification of the CMC point of Silex Emulsion M through the application of (a) the capillarity method, with the consequent calculation of the surface tension, as described in 2.3.1, and (b) conductivity. Data points refer to averages of three measurements at each emulsion concentration. All experiments were conducted at room temperature ($21^{\circ}\text{C} \pm 2^{\circ}\text{C}$).

Performing a capillarity test is a reliable and facile way to measure the free surfactant concentration in water as a function of the solution surface tension. The results obtained with capillarity tests further indicate that the surface tension of the washing liquid may be significantly lowered by addition of small amounts of Silex Emulsion M. While a small dosage is ideally required for effective washing, the large quantity of textiles treated every day, and the high quality of cleaning to be achieved obliges the laundering industry to over-dose the detergent.

3.2. Recovery and process efficiency

3.2.1. Fluxes measured during wash water filtration

Fig. 3 shows the permeate fluxes measured in the pre-filtration tests carried out with 100 kDa polymeric membrane, FS40PP (Fig. 3(a)), and 300 kDa ceramic membrane, Tami (Fig. 3(b)). Fluxes were measured at four intervals (time 1 through 4), distanced 45 min from each other. For both polymeric and ceramic membranes, fluxes were similar at values

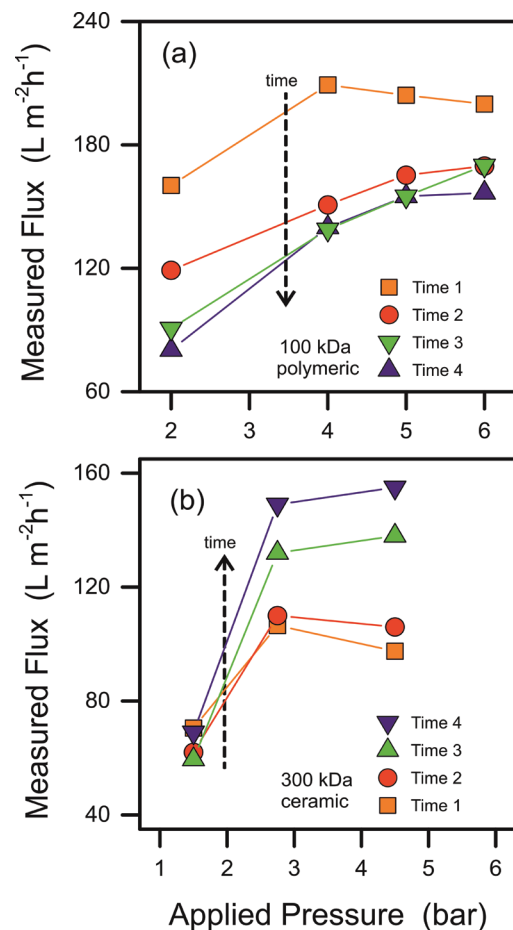


Fig. 3. Flux measurements of wash water as a function of applied pressure through (a) 100 kDa polymeric membranes and (b) 300 kDa ceramic membranes. For each applied pressure, four flux measurements were performed at intervals of 45 min, referred to as time 1 through 4 in the graphs. Fluxes were found to decrease in time for polymeric membranes and to increase for ceramic membranes. Lines are intended to be used as guide for the eyes only.

of applied pressure above 3–4 bar. This result implies that both types of membrane were subjected to fouling [27], which became more important as transmembrane pressure increased. Analogous results were observed by previous studies [28]. Laundering wash water comprises a large amount of organic matter [29], considered to be one of the main foulants in membrane application [30,31], together with suspended materials coming from fabrics. Past studies investigated treatment of laundry wash water using membrane bioreactor (MBR) systems, in which organic components are degraded while being retained [32,33]. Other reports demonstrated the feasibility of MBR also from an economic viewpoint [34]. Data presented in Fig. 3 indicate that the permeate flux increased in time for ceramic membranes, while it decreased when polymeric membranes were applied. Fouling was present in both cases. However, the increase of operating temperature during the tests with ceramic membranes offset the flux loss due to fouling.

Fig. 4 presents the permeate fluxes for the actual recovery filtration steps with 6 kDa polymeric membranes, FS81PP (Fig. 4(a)), and 7.5 kDa ceramic membranes, Inopor (Fig. 4(b)). Data points referring to wash water permeate flux (green triangles) reveal higher values than those shown in Fig. 3. This result is rationalized with the better quality of the feed solution, coming already purified from organic foulants and fabric material following the pre-filtration steps. The flux obtained through the ceramic membrane increased almost linearly with applied pressure. This trend was less pronounced for the tests carried out using polymeric membranes. Again, the influence of temperature may explain this difference: higher temperature has been shown to result in reduced fouling [35,36].

Overall, high permeate fluxes were measured during all tests, suggesting the feasibility of this process to filter pre-treated wash wastewater. Values of flux obtained by filtering DI water before and after treatment of wash water (blue squares and red circles, respectively) suggest that the flux decline observed during the tests was due to reversible fouling,

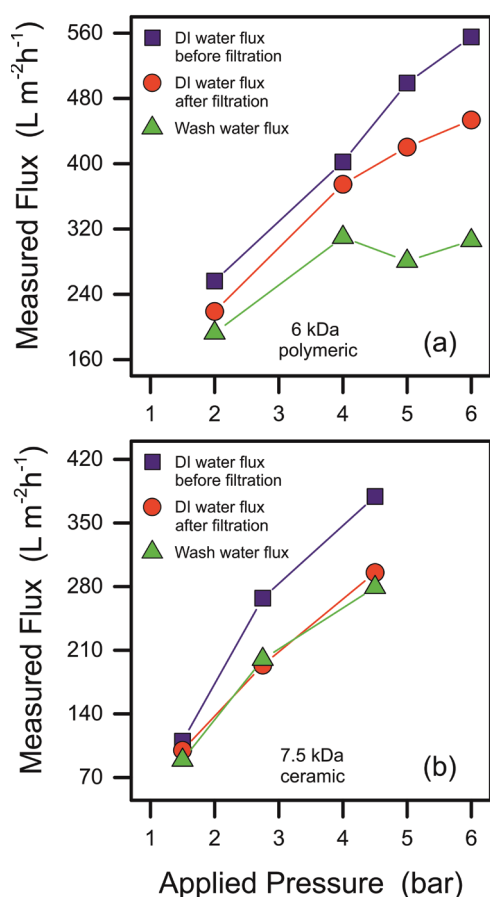


Fig. 4. Measured fluxes for both DI water and wash water at different applied pressures for (a) 6 kDa polymeric membranes and (b) 7.5 kDa ceramic membranes. Experiments using wash water (green triangles) followed a UF pre-treatment step through 100 kDa polymeric membranes or 300 kDa ceramic membranes, respectively. The flux of DI water was measured (blue squares) before and (red circles) after wash water filtration. Lines are intended to be used as guide for the eyes only.

mostly related to the formation of a cake at the membrane/solution interface. Simple periodic physical cleanings would thus maximize the process efficiency.

3.2.2. Recovery of surfactant and assessment of potential permeate reuse

Tests using Hach Lange cuvettes were performed on the wash water samples and on the permeates obtained after pre-filtration using FS40PP and Tami membranes. In both cases, a concentration of 66 mg/L of surfactants was measured, which is well below the CMC of the detergent. Therefore, detergent was not rejected by pre-filtration. This observation suggests that the size of the surfactant molecules and of micelles entrapping contaminants is smaller than 100 kDa, thus passing freely through the membranes, and that the fouling mechanism in these tests was not related to the adsorption of surfactant molecules within the membrane pores or to concentration polarization. Pre-filtration does not allow recovery of surfactants and, as shown in Table 3, the permeate stream obtained from pre-filtration does not respect the limits imposed by the company to reuse it in the pre-wash or in the main wash zone of the CBW machine. However, this pre-treatment is useful to produce a relatively clean solution to feed the actual recovery steps, performed at lower MWCO.

Concentration of non-ionic surfactants in feed water and permeates obtained by the recovery filtration steps was also measured with Hach Lange cuvettes; see results in Fig. 5(a). Data indicate that 43% and 39% of the total amount of surfactants in the feed solution were recovered in the permeate after filtration through the polymeric and ceramic membranes, respectively. The results obtained by the application of Hach Lange cuvettes and of capillarity measurements were the same; see Fig. 5(b). It must be reminded that while the cuvette method measures the total amount of surfactant in water, capillarity tests yield the value of free surface active agents. Therefore, the recovered surfactant in our experiments was present as free molecules, which would be available to decrease the surface tension of the solution and to entrap the contaminants in the case of reutilization of this treated stream. The remaining portion of surfactants, rejected during filtration, was hence bound in micelles entrapping contaminants. Moreover, the permeate properties (Table 3) suggest that the permeate obtained from the recovery filtration stages with 6 and 7.5 kDa membranes may be suitable for reuse inside the CBW machine. The values achieved are in fact below the limits suggested to be able to recycle the treated stream in the pre-wash or in the main wash stage of a cycle (limits are summarized in Table 2).

Analogous results were achieved through the utilization of polymeric and ceramic membranes with similar MCWO, although during filtration at different temperature. This result suggests that the extent recovery of free surfactants is not significantly dependent on the filtration temperature. In a hypothetical application of an integrated membrane treatment applied to the CBW machine, the treatment and recovery of water coming at high temperature from the main wash stage of the washing cycle would result in savings of both detergent and energy supply.

Table 3
Permeate physicochemical parameters

Membrane MWCO (kDa)	pH	Conductivity (mS/cm)	COD (mg/l)
100	11.98	2.36	1,031
50	10.54	1.382	751
20	8.98	1.375	624
6	8.77	1.22	623
7.5	8.63	1.24	657

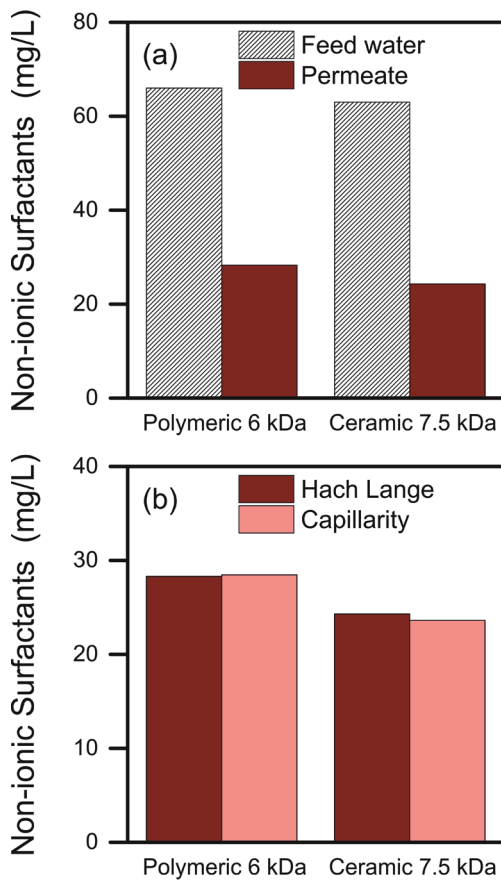


Fig. 5. Summary of the recovery of non-ionic surfactants. (a) Concentration of surfactants in (patterned bars) feed water and (solid red bars) permeate water following UF filtration using 6 kDa polymeric membranes and 7.5 kDa ceramic membranes. Approximately 40% of surfactant was recovered in both cases. (b) Surfactant concentrations in the permeate measured through the application of (dark red bars) Hach Lange cuvettes and (light red bars) capillarity, demonstrating the uniformity between results obtained by applying different methods.

3.2.3. Influence of membrane properties on process performance

Additional surfactant recovery tests were carried out using 50 and 20 kDa polymeric membranes on the wash water solutions following pre-filtration. Permeate fluxes (not shown) were almost negligible, initially around $15 \text{ L m}^{-2} \text{ h}^{-1}$, one order of magnitude lower than fluxes through 6 kDa

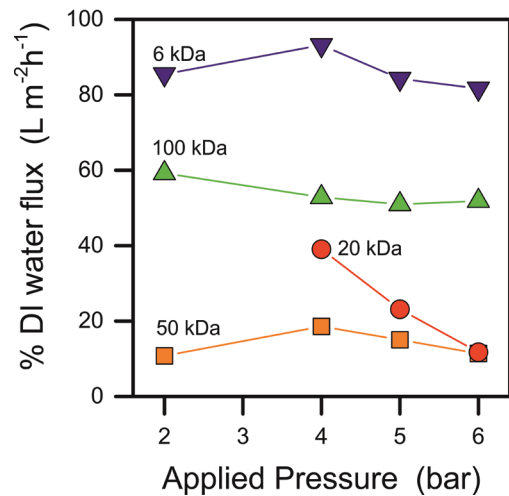


Fig. 6. The percentage ratio of DI water flux measured after wash water filtration with respect to the flux measured before treatment, as a function of applied pressure. Results are presented for each of the polymeric membranes tested, as labeled in the graph. The feed solution through 100 kDa membrane coincided with wash water coming directly from the laundry facility. The permeate from this pre-filtration process was used to feed all the other membranes specified in the graph. Lines are intended to be used as guide for the eyes only. Experiments were conducted at room temperature ($21^\circ\text{C} \pm 2^\circ\text{C}$).

membranes. Furthermore, fluxes showed a 70% decrease in less than 1 h of operation at the constant applied pressure of 8 bar. We hypothesize that polymeric membranes characterized by intermediate MWCO are not suitable to treat wash water from the laundering industry, even if the permeate obtained from filtration with 20 kDa polymeric membranes respected the limits imposed for water reuse. The main reason of the low performance achieved in these tests may be the presence of surfactant micelles entrapping contaminants. The application of Hach Lange cuvettes and capillarity method to the feed and permeate solutions showed that only a small quantity of free surfactants were filtered through the 50 and 20 kDa membranes and that micelles entrapping contaminants were rejected. Around the 70% of the total amount of surfactants in wash water were rejected by each type of membranes. Therefore, the low fluxes observed are partly rationalized with clogging due to blocking the membrane pores by micelles entrapping contaminants. Indeed, the micelle average size should be in the range 30–60 kDa, comparable with the pore size of these membranes [28]. Previous studies also stated that clogging is a characteristic phenomenon of membranes with intermediate pore sizes [37].

The influence of membrane pore size on the process efficiency is summarized in Fig. 6, where we present the ratio of DI flux measured before and after each filtration step with polymeric membranes of different MWCO. The 6 kDa polymeric membranes were affected mostly by reversible fouling; DI flux after filtration was around 80% the value measured prior to wash water filtration, regardless of the applied pressure [38]. On the other hand, membranes with intermediate MWCO presented irreversible fouling. Here, the DI flux after

membrane usage was significantly lower compared with that measured for clean membranes [39].

A reduction in membrane fouling was previously achieved through addition of coagulants in laundry wash wastewater [40,41], causing formation of large flocules in the feed water, thus avoiding membrane clogging. However, free surfactants may be entrapped in the coagulation-precipitation process. It should be noted that a variable pressure system (i.e., increasing the transmembrane pressure over the time to maintain constant flux) should produce more reversible fouling than a constant pressure system [42]. Previous studies suggest that while hydrophobic membranes generally retain free surfactant more efficiently than hydrophilic membranes [43], they are more subjected to fouling [44,45]. Moreover, non-ionic surfactants adsorb more readily on hydrophobic membrane surfaces compared with anionic surfactants, thus impairing the efficiency of the filtration process [46]. Therefore, membranes fabricated with different materials than polysulfone or fluoropolymers (e.g., PES membranes modified with polyvinylpyrrolidone [47]) may show better performances than the Alfa Laval series used in our experiments. These mechanisms may be taken into account to optimize a UF process to recover detergents from laundering wash water solutions.

4. Concluding remarks

UF was applied to treat laundering wash water and to evaluate the capability of polymeric and ceramic membranes to produce an adequate flux of good-quality permeate. A recovery of approximately 40% of usable non-ionic surfactants was achieved using a pre-filtration step through high MWCO membranes and a final filtration through membranes characterized by small pores. The pre-filtration process helped in removing foulants from the wash water solution coming directly from a laundry facility. Similar results were obtained with polymeric and ceramic membranes. The properties of the permeate sample were within the requirements suggested to ensure safe reuse of the treated water within the first two washing steps of the CBW machine. Our research also suggests that there exists an optimal range of MWCO to prevent membrane clogging and to maximize the efficiency of the process. The high flux observed during filtration and the significant amounts of surfactant recycled at the end of the treatment train suggest that UF may be a valid method to reduce the environmental impact of laundering operations.

In a hypothetical industrial application, these results should be considered as the very first step to design an integrated UF system. The characteristics of wash water vary significantly depending on the type of textiles treated [13,48] (i.e., different composition and amount of organic matters). Research should therefore progress to investigate the efficiency of surfactant recovery treating wash waters from different laundering facilities or from diverse types of linens. The best configurations to recover energy should also be evaluated carefully. We demonstrated that ceramic membranes allow operating the treatments at high temperature, suggesting the possibility to recover energy in large laundering facilities. While the recovery of energy and surfactants would reduce waste and potentially translate into direct economic benefits for the facility, an assessment of capital and operational costs vs. economic benefit should be carried out

taking into account the possible schemes of integrating the UF system to the washing machines.

Acknowledgments

This study was funded by the University of Southern Denmark and by Politecnico di Torino. We thank collaboration at the University Hospital Laundry of Odense, which delivered the water samples and detergents.

References

- [1] C. Pakula, R. Stamminger, Electricity and water consumption for laundry washing by washing machine worldwide, *Energy Effic.*, 3 (2010) 365–382.
- [2] Y.X. Yu, J. Zhao, A.E. Bayly, Development of surfactants and builders in detergent formulations, *Chin. J. Chem. Eng.*, 16 (2008) 517–527.
- [3] J.J. Scheibel, The evolution of anionic surfactant technology to meet the requirements of the laundry detergent industry, *J. Surfactants Deterg.*, 7 (2004) 319–328.
- [4] I. Ciabatti, F. Cesaro, L. Faralli, E. Fatarella, F. Tognotti, Demonstration of a treatment system for purification and reuse of laundry wastewater, *Desalination*, 245 (2009) 451–459.
- [5] A. Tímár Balázsy, Wet cleaning of historical textiles: surfactants and other wash bath additives, *Stud. Conserv.*, 45 (2000) 46–64.
- [6] M.J. Rosen, Relationship of structure to properties in surfactants. II. Efficiency in surface or interfacial tension reduction, *J. Am. Oil Chem. Soc.*, 51 (1974) 461–465.
- [7] T. Corey Arthur, *Mechanics of Immiscible Fluids in Porous Media*, Water Resources Publications, LLC, Highlands Ranch, Colorado, 1994.
- [8] R. Varadaraj, J. Bock, S. Zushma, N. Brons, Relationships between dynamic contact angle and dynamic surface tension properties for linear and branched ethoxylate, ethoxysulfate, and sulfate surfactants, *J. Colloid Interface Sci.*, 147 (1991) 403–406.
- [9] R. Gruden, O. Kanoun, Fast and Low-Cost Online Detection of Critical Micelle Concentration Based on Impedance Spectroscopy, Seventh International Conference on Sensing Technology (ICST), Wellington, New Zealand, 2013, pp. 135–140.
- [10] M.J. Rosen, *Surfactants and Interfacial Phenomena*, 3rd ed., John Wiley & Sons, Hoboken, New Jersey, 2004.
- [11] E. Smulders, W. von Rybinski, E. Sung, W. Rähse, J. Steber, F. Wiebel, A. Nordskog, *Laundry Detergents*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2002.
- [12] Ceresana, *Market Study: Surfactants*, 2nd ed., Ceresana, Constance, Germany, 2015.
- [13] S. Sostar-Turk, I. Petrinic, M. Simoncic, Laundry wastewater treatment using coagulation and membrane filtration, *Resour. Conserv. Recycl.*, 44 (2005) 185–196.
- [14] A. Cipollina, G. Micale, L. Rizzuti, *Seawater Desalination – Conventional and Renewable Energy Processes*, 1st ed., Springer, Berlin, Germany, 2009.
- [15] B. Milan, *Membrane Processes in Industry and Biomedicine*, 1st ed., Springer, New York, USA, 1971.
- [16] A. Drews, H. Arellano-Garcia, R. Schomacker, M. Kraume, G. Wozny, Ultrafiltration of surfactant micelles: cross-flow experiments and flux modelling, *Comput. Aided Chem. Eng.*, 28 (2010) 787–792.
- [17] I. Kowalska, M. Kabsch-Korbutowicz, K. Majewska-Nowak, M. Pietraszek, Removal of detergents from industrial wastewater in ultrafiltration process, *Environ. Prot. Eng.*, 31 (2005) 207–219.
- [18] M.S. Dahanayake, Y.B. Yang, M.E. Ventura, Recovery and Reuse of Amphoteric Surfactants from Aqueous Solutions, US Patent No. 5919980, 1999.
- [19] M.E. Ventura, M.S. Dahanayake, Recovery and Reuse of Nonionic Surfactants from Aqueous Solutions, US Patent No. 6207058, 2001.
- [20] J.S. Yang, K. Baek, J.W. Yang, Crossflow ultrafiltration of surfactant solutions, *Desalination*, 184 (2005) 385–394.

- [21] S.V. Jadhav, K.V. Marathe, Micellar enhanced ultrafiltration: a comparative study, *Can. J. Chem. Eng.*, 91 (2013) 311–317.
- [22] R. Urbanski, E. Goralska, H.J. Bart, J. Szymanowski, Ultrafiltration of surfactant solutions, *J. Colloid Interface Sci.*, 253 (2002) 419–426.
- [23] J.R. Sweet, Pressure Induced Surfactant Recovery during Ultrafiltration of Water-Oil Emulsion, US Patent No. 4892660, 1990.
- [24] L. Suárez, M.A. Diez, R. Garcia, F.A. Riera, Membrane technology for the recovery of detergent compounds: a review, *J. Ind. Eng. Chem.*, 18 (2012) 1859–1873.
- [25] K. Boussu, C. Kindts, C. Vandecasteele, B. Van der Bruggen, Surfactant fouling of nanofiltration membranes: measurements and mechanisms, *ChemPhysChem*, 8 (2007) 1836–1845.
- [26] A.M. Khan, S.S. Shah, Determination of critical micelle concentration (Cmc) of sodium dodecyl sulfate (SDS) and the effect of low concentration of pyrene on its Cmc using ORIGIN software, *J. Chem. Soc. Pak.*, 30 (2008) 186–191.
- [27] R.W. Baker, *Membrane Technology and Applications*, 2nd ed., John Wiley & Sons, Chichester, England, 2004.
- [28] B. Van der Bruggen, G. Cornelis, C. Vandecasteele, I. Devreese, Fouling of nanofiltration and ultrafiltration membranes applied for wastewater regeneration in the textile industry, *Desalination*, 175 (2005) 111–119.
- [29] A. Brik, P. Schoeberl, B. Chamam, R. Braun, W. Fuchs, Advanced treatment of textile wastewater towards reuse using a membrane bioreactor, *Process Biochem.*, 41 (2006) 1751–1757.
- [30] Q.L. Li, M. Elimelech, Organic fouling and chemical cleaning of nanofiltration membranes: measurements and mechanisms, *Environ. Sci. Technol.*, 38 (2004) 4683–4693.
- [31] H.C. Kim, B.A. Dempsey, Effects of wastewater effluent organic materials on fouling in ultrafiltration, *Water Res.*, 42 (2008) 3379–3384.
- [32] I. Petrinic, M. Curlin, J. Racyte, M. Simonic, Textile wastewater treatment with membrane bioreactor and water re-use, *Tekstil*, 58 (2009) 11–19.
- [33] Z. Badani, H. Ait-Amar, A. Si-Salah, M. Brik, W. Fuchs, Treatment of textile waste water by membrane bioreactor and reuse, *Desalination*, 185 (2005) 411–417.
- [34] C. Nicolaidis, I. Vyrides, Closing the water cycle for industrial laundries: an operational performance and techno-economic evaluation of a full-scale membrane bioreactor system, *Resour. Conserv. Recy.*, 92 (2014) 128–135.
- [35] A. Al-Amoudi, R.W. Lovitt, Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency, *J. Membr. Sci.*, 303 (2007) 6–28.
- [36] W.S. Ang, S.Y. Lee, M. Elimelech, Chemical and physical aspects of cleaning of organic-fouled reverse osmosis membranes, *J. Membr. Sci.*, 272 (2006) 198–210.
- [37] B.Q. Liao, D.M. Bagley, H.E. Kraemer, G.G. Leppard, S.N. Liss, A review of biofouling and its control in membrane separation bioreactors, *Water Environ. Res.*, 76 (2004) 425–436.
- [38] A.Y. Zahrim, C. Tizaoui, N. Hilal, Coagulation with polymers for nanofiltration pre-treatment of highly concentrated dyes: a review, *Desalination*, 266 (2011) 1–16.
- [39] B. Tansel, W.Y. Bao, I.N. Tansel, Characterization of fouling kinetics in ultrafiltration systems by resistances in series model, *Desalination*, 129 (2000) 7–14.
- [40] X. Shang, H.C. Kim, J.H. Huang, B.A. Dempsey, Coagulation strategies to decrease fouling and increase critical flux and contaminant removal in microfiltration of laundry wastewater, *Sep. Purif. Technol.*, 147 (2015) 44–50.
- [41] H.C. Kim, X. Shang, J.H. Huang, B.A. Dempsey, Treating laundry waste water: cationic polymers for removal of contaminants and decreased fouling in microfiltration, *J. Membr. Sci.*, 456 (2014) 167–174.
- [42] H.C. Kim, B.A. Dempsey, Membrane fouling due to alginate, SMP, EfOM, humic acid, and NOM, *J. Membr. Sci.*, 428 (2013) 190–197.
- [43] I. Kowalska, Dead-end and cross-flow ultrafiltration of ionic and non-ionic surfactants, *Desal. Wat. Treat.*, 50 (2012) 397–410.
- [44] A. Abdelrasoul, H. Doan, A. Lohi, Fouling in Membrane Filtration and Remediation Methods, H. Nakajima, Ed., *Mass Transfer - Advances in Sustainable Energy and Environment Oriented Numerical Modeling*, InTech, Rijeka, Croatia, 2013.
- [45] A.S. Jonsson, B. Jonsson, The influence of nonionic and ionic surfactants on hydrophobic and hydrophilic ultrafiltration membranes, *J. Membr. Sci.*, 56 (1991) 49–76.
- [46] M. MietttonPeuchot, O. Ranisio, C. Peuchot, Study of behaviour of membranes in the presence of anionic or nonionic surfactants, *Filtr. Sep.*, 34 (1997) 883–886.
- [47] A. Sumisha, G. Arthanareeswaran, Y.L. Thuyavan, A.F. Ismail, S. Chakraborty, Treatment of laundry wastewater using polyethersulfone/polyvinylpyrrolidone ultrafiltration membranes, *Ecotoxicol. Environ. Saf.*, 121 (2015) 174–179.
- [48] C.T. Wang, W.L. Chou, Y.M. Kuo, Removal of COD from laundry wastewater by electrocoagulation/electroflotation, *J. Hazard. Mater.*, 164 (2009) 81–86.