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Abstract: The hydrophilicity of regenerated cellulose (RC) ultrafiltration (UF) membranes could be utilized in industrial processes even more than today if there was more information on their thermal stability. Therefore, in this study two different RC UF membranes were used in a temperature range from 15 to 70°C in order to evaluate their performance stability at high temperature. The experiments were performed in neutral, alkaline, and acidic conditions. The influence of temperature on pure water permeability, observed Dextran retention, and membrane structure were used as evaluation criteria. According to the results the tested membranes could be used at 70°C in the tested conditions for several days. The results, however, indicated also that the use in acidic and alkaline conditions at 70°C might shorten the operational life of the membranes.

Keywords: Ultrafiltration, permeability, observed retention, membrane structure

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INTRODUCTION

Regenerated cellulose (RC) ultrafiltration (UF) membranes are optimal membranes because of their hydrophilicity, for instance, for the purification of paper mill process water and for the filtration of protein solutions (1)–(4). However, the hydrophilicity of RC membranes could be utilised in industry, for example in the sugar industry (5), even more than today if there was more information on temperature resistance of these membranes. Manufacturers recommend 50–55°C (6, 7) to be the maximum operating temperature for some RC membranes, while the temperatures of the filtered process fluids can often be above that. For instance, the temperature of process streams in the dairy industry can be above 50°C (8), in the sugar industry between 70 and 98°C (9, 10), in the pulp and paper industry between 60 and 70°C (11, 12), and in the textile industry between 50 and 90°C (13, 14).

A process stream having a high temperature can be pre-cooled to the temperature a membrane is known to stand before filtration. However, filtration at high temperature (in aqueous solutions 50–90°C) (15) might offer several advantages in UF applications. A high temperature leads to a high flux, because the increase in temperature causes a decrease in the viscosity and the density of the process fluid and an increase in the diffusivity of the fluid content (16, 17). Also, pumping of a process fluid is cheaper at a higher temperature due to the lowered fluid viscosity (17) and energy and time is saved, if a process fluid having a high temperature can be filtered without pre-cooling. Thus, filtration at high temperature is often economical. Furthermore, high temperatures up to 90°C used at least periodically prevent microbial growth in food industry applications (15).

A disadvantage is that a high filtration temperature might cause changes in the polymeric membrane matrix and, thus, change the membrane performance and its properties. When a high temperature has no detrimental effect on the membrane and no fouling occurs, the flux increases linearly with increasing temperature. A linear relation between temperature and flux is found for instance in the nanofiltration experiments of Schaep et al. (18) (temperature range 10–30°C) and Jian et al. (19) (20–70°C), and in the micro- and ultrafiltration experiments of Benítez et al. (20) (20–55°C) and Kowalska et al. (21) (25–55°C). Thus, the effect of temperature on a membrane might be detected for instance as a deviation in the linear increase of flux with increasing temperature. Kowalska et al. (22), for example, discovered in their UF experiments with polyethersulphone (PES) membranes a non-linear increase of flux with increasing temperature from 25 to 55°C. They explained that the non-linear flux increase was attributed to the thermal expansion of the membrane material. Vázquez et al. (23) reported a change in flux performance of two different RC UF membranes when temperature was increased above 40°C. At temperatures below 40°C flux increased with increasing temperature while at temperatures above 40°C flux decreased with increasing temperature.

According to these authors this change in flux performance was caused by the changes in the polymer matrix occurring around 40°C.

The change in membrane morphology due to the filtration at high temperature might also be observed as a hysteresis behavior of the water flux and the solute retention: the flux and retention do not recover when the temperature is decreased again after periodic filtration at high temperature. This was found for instance both in the experiments of Mänttäri et al. (9) and Yao et al. (24). The reason for hysteresis could, according to Yao et al. (24), be a permanent reorientation of the polymer chains at high temperature.

In addition to flux values, filtration at high temperature might also change the rejection properties of a membrane. However, when the rejection properties of a membrane are compared at two different temperatures, it has to be noted that temperature affects both the solute and the membrane characteristics. For instance, Kowalska et al. (21) filtered sodium dodecyl sulphate (SDS) solution with UF membranes made from RC, PES, polysulphone (PS), cellulose acetate (CA), and polyamide (PA) with a cut-off value equal to 5, 10, and 30 kg/mol. According to their results the retention of SDS was slightly decreased with an increased temperature (from 25 to 55°C). The temperature increase affected the membranes having higher cut-off values more. The authors explained the phenomenon with temperature dependent changes of SDS and with a thermal expansion of the membrane material with increasing temperature. Schlesinger et al. (25) measured a lower hemicellulose retention at 49°C than at room temperature in the filtration of alkaline process liquor with nanofiltration membranes made from PES and PS. In alkaline conditions the membranes were swelled which lead to an increase in effective pore size of the membranes. This and the elevated temperature were, according to the authors, the reasons for the lowered retention values.

Accordingly, the use of RC membranes at higher temperatures than 50°C could be advantageous if the membrane characteristics were not changed due to high temperature. Thus, the usability of two different RC UF membranes in the temperature range from 15 to 70°C was examined in this study. The aim was to evaluate if an alteration to a high temperature changes the performance and the characteristics of these membranes. The evaluation criteria were the stability of membrane permeability, structure, and observed Dextran retention after filtration at high temperature in neutral, acidic, and alkaline conditions.

MATERIALS AND METHODS

Filtration Module

In the filtration experiments a flat sheet type laboratory filter was used. The laboratory filter contains three flat sheet modules in parallel and the

combined membrane area of this apparatus is $3 \times 0.0046\,m^2$. More information on this filtration apparatus can be found in a paper by Mänttäri et al. (26).

Experimental Methods

Before all the experiments the membrane sheets were rinsed with RO treated water in an ultrasound bath 3 times for 10 min in order to remove the membrane preservation agents. The influence of a short-time exposure to high temperature on the membranes was tested in an experiment, where temperature was increased and decreased stepwise. This experiment was performed with RO treated water at a constant 100 kPa pressure.

The observed retention of the membranes was determined both at 70°C and at 50°C in order to evaluate if the membranes had similar rejection characteristics at both temperatures. In these experiments the flux was maintained at the same level by controlling the pressure. The permeate was recirculated to the feed tank in all experiments.

The thermal resistance of the membranes was also tested in experiments, where the membranes were periodically used at 20°C and at 70°C at 100 kPa. The filtration steps at high temperature were long, from 16 to 89 hours. In the filtration steps performed at 20°C the pure water fluxes and the observed Dextran retentions of the membranes were measured in order to see the influence of the high temperature filtration steps on the membranes. For the evaluation of the effect of temperature on the membranes in alkaline conditions the pH in the filtration steps performed at high temperature was adjusted with NaOH to a value of 10. Correspondingly, the influence of temperature on the membranes in acidic conditions was examined by adjusting the pH of the steps done at high temperature with HCl to a value of 3. The low temperature filtration steps were always performed in neutral conditions.

Dextran T40 (Pharmacosmos A/S) having a molar mass of 41 kg/mol was used as the model compound for the determination of retention. The Dextran concentration in the feed was 130–150 mg/L. The feed and the permeate samples taken during the retention experiments were analyzed with a Shimadzu TOC 5050-A total organic carbon analyzer.

Calculations

The observed retention was determined, because it indicates how the membrane usability in a separation process might change due to filtration at high temperature. The observed retention, R_{obs}, of Dextran was calculated by using the measured total organic carbon (TOC) content of the permeate

and the feed samples as shown below.

$$R_{obs} = 1 - \frac{c_p(TOC)}{c_f\,(TOC)} \tag{1}$$

R_{obs}: observed retention of total organic carbon; $c_p(TOC)$: concentration of total organic carbon in permeate (mg/L); $c_f(TOC)$: concentration of total organic carbon in feed (mg/L).

Membrane Analysis

The chemical structure of the membrane samples was analyzed with attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) by using a Perkin-Elmer 2000 FTIR spectrometer with the wire coil operating at 1350 K as a radiation source, triglycine sulphate (TGS) as a detector and optical KBr as a beamsplitter. A KRS-5 crystal (thallous bromide iodide) was used as an internal reflection element. The effective incident angle of the IR radiation was 51°.

The membrane structure was analyzed with a JEOL JSM-5800 scanning electron microscope (SEM) with 10 kV accelerating voltage and 12 mm working distance. Before the imaging, the samples were dried at room temperature and pre-coated with a 45 nm gold layer. The analyses of the C2 sheets used in the experiments could not be performed with SEM, because the layers of the C2 membrane disjoined from each other during membrane drying.

UF Membranes

The membranes tested were the commercial C 30FM membrane (Microdyn Nadir) and a test membrane C2, which is in a developing stage. According to Microdyn Nadir (6), the skin layer of the C 30FM is made from regenerated cellulose and the support layer is made from polyethylene terephthalate (PET). The maximum operating temperature given in the membrane data sheet is 55°C. The cut-off value of the C 30FM is according to Microdyn-Nadir 30 kg/mol. The skin layer material of the C2 membrane is regenerated cellulose and its support layer is made from a blend of polypropylene (PP) and polyethylene (PE). The cut-off value of the C2 membrane is in the same range as that of the C 30FM. In the experiments C2 membrane sheets from different batches were used.

Although the skin layers of both of the tested membranes were made from regenerated cellulose according to the manufacturers, ATR-FTIR analysis revealed differences in their chemical structure. Regenerated cellulose can be produced by hydrolyzing cellulose acetate in alkaline conditions. In the spectra of the C 30FM membrane residues of cellulose acetate could be

seen (Fig. 1) (carbonyl absorption (C═O) at 1746 cm^{-1} and C-O ester band at 1235 cm^{-1} (27, 28)). These bands are lacking in the spectrum of the C2 membrane. Earlier studies have also shown that the morphology of the C2 and the C 30FM membranes is different. The C 30FM contains macrovoids in the layer between the skin and the support layer while the corresponding layer in the C2 membrane is thinner and sponge-like. (5)

RESULTS AND DISCUSSION

Effect of High Temperature in Neutral Conditions

As expected based on theory and earlier studies (16, 17), the pure water flux of the tested membranes increased with increasing temperature and decreasing water viscosity in the temperature range from 15 to 70°C (Fig. 2). The flux of the C2 membrane recovered when temperature was increased and decreased stepwise. Furthermore, the measured flux of the C2 increased with increasing temperature and decreasing viscosity as it was expected based on the Darcy's law (17, 29). This indicates that the C2 membrane was not influenced by short filtrations at 70°C. In the flux values of the C 30FM a slight hysteresis was found (Fig. 2) and the measured flux values were lower than the expected flux based on Darcy's law at temperatures higher than 60°C. Thus, the results demonstrate

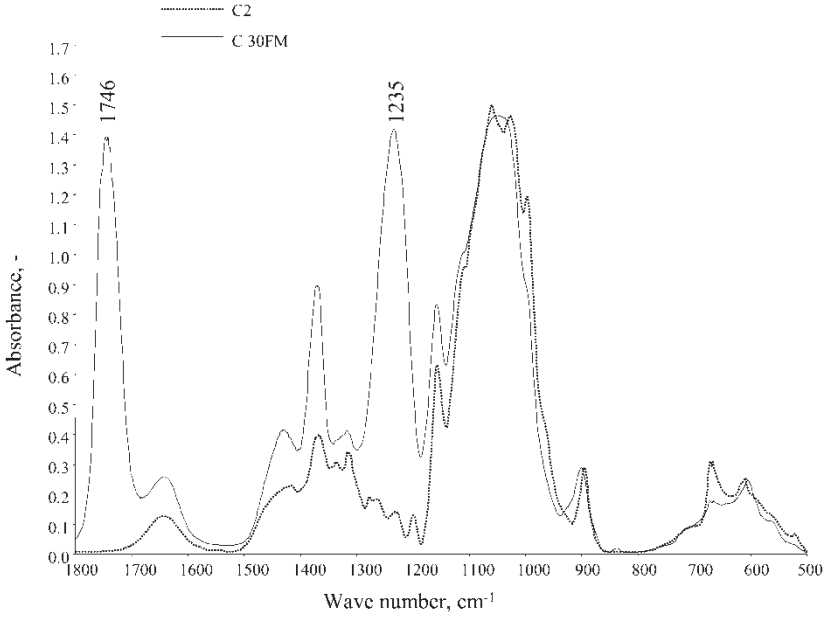

Figure 1. ATR-FTIR spectra of the C2 and the C 30FM membranes.

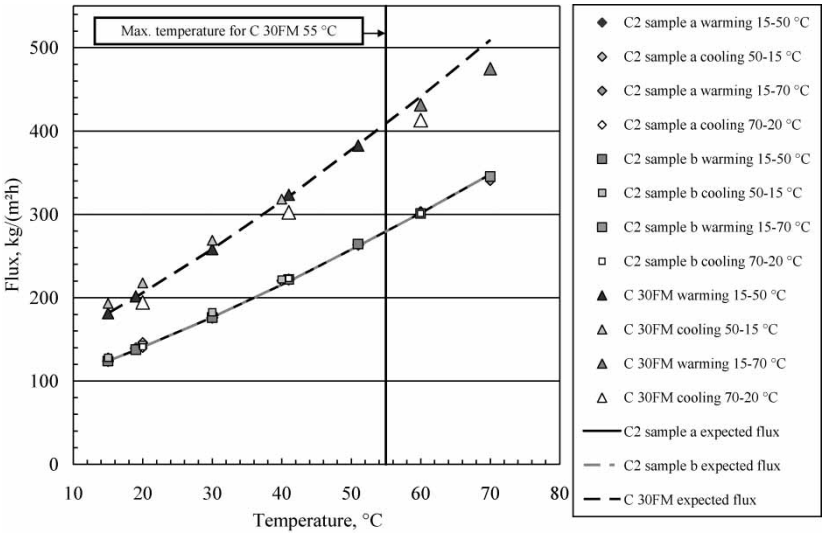

Figure 2. The relation of pure water flux and temperature in the experiments and the expected flux curves. The expected flux was based on the correction of the flux values in the beginning of the experiment (15°C) with the ratio of the water viscosity values at different temperatures (based on Darcy's law). The experiment was done with RO treated water at constant 100 kPa pressure with a laboratory scale flat sheet filtration apparatus. The C2 membrane used in these experiments was from batch 1.

that the C 30FM membrane might somehow change already during a short filtration at 70°C. Vàzquez et al. (23) observed that the flux performance of RC membranes changed clearly in the temperature range 35–40°C due to the change occurring in the polymer matrix in that range. With the RC membranes C2 and C 30FM, however, a phenomenon of this kind was not observed.

The flux of the C2 membrane was lower than the flux of the C 30FM through the whole examined temperature range (Fig. 2). This was most probably due to the differences in membrane structures. In the C2 membrane the layer just under the skin layer is thin and sponge-like while the corresponding layer in the C 30FM membrane contains macrovoids (5). This structure difference might also cause the difference in the stability of the membranes during the stepwise increase and decrease of temperature (Fig. 2). At temperatures above 60°C the susceptibility of the structure of the C 30FM (containing macrovoids) to compact under pressure might be increased. Furthermore, the slight membrane compaction could prevent the flux to increase to the level, which was expected based on Darcy's law (17, 29). After the filtration at 70°C the water flux of the C 30FM was lower than before the filtration at 70°C at the whole temperature range. This could also derive from the irreversible membrane compaction. The sponge-like membrane structure of the C2 is not as susceptible to compaction under pressure as the more porous membrane structure in the C 30FM (5).

The pure water fluxes of the membranes C2 and C 30FM were at 50°C and at 100 kPa 264 kg/(m^2 h) and 383 kg/(m^2 h), respectively. At 70°C and at 100 kPa the pure water fluxes were 345 kg/(m^2 h) (C2) and 475 kg/(m^2 h) (C 30FM). (Fig. 2) Therefore, if the capacity of the membrane process was the most important factor in choosing the filtration temperature, a higher temperature would be used. The quality of the produced permeate is, however, often at least as crucial factor as high capacity, and thus, the observed Dextran (41 kg/mol) retention was also measured at first at 70°C and after that at 50°C (Table 1). Flux was controlled to be at the same level at both temperatures. According to earlier studies (21, 22, 25) retention was expected to be lower at a higher temperature but the results showed that the observed Dextran retention of the C2 membrane was the same both at 70°C and at 50°C and the retention of the C 30FM membrane was slightly higher at 70°C than at 50°C. The results indicate that the C2 has similar rejection characteristics at 50 as at 70°C while the C 30FM might be tighter at 70°C than at 50°C due to some alterations in the membrane material. On the other hand the results might also derive from temperature dependent changes in the Dextran molecules.

The differences in the influence of temperature on the C2 and C 30FM membranes were also noted in the experiments, where the filtration was in turns performed at 20°C and at 70°C in neutral conditions. Two experiments of this kind were done and Fig. 3 shows the pure water permeabilities measured at 20°C in neutral conditions between the filtration steps performed at 70°C in the other of those experiments. The results of both of the experiments were similar. The pure water permeability of the C2 at 20°C was at the same level before and after the steps done at 70°C. The permeability of the C 30FM was slightly lower (about 12%) after the first filtration step performed at 70°C but remained after the further steps done at 70°C at that level. SEM images (Fig. 4) did not reveal a clear compaction of the C 30FM membrane after these experiments. However, earlier studies (5) have shown that the C 30FM containing macrovoids in its inner

Table 1. Observed Dextran (41 kg/mol) retentions and fluxes of Dextran solution at 70 and 50°C in two parallel experiments A and B

Membrane	Retention 70°C, %	Flux 70°C, kg/(m^2 h)	Retention 50°C, %	Flux 50°C, kg/(m^2 h)
Experiment A				
C2 sample a (batch 3)	95	300	94	300
C 30FM sample a	96	504	92	483
C 30FM sample b	94	504	90	476
Experiment B				
C2 sample b (batch 3)	85	375	86	358
C 30FM sample c	94	540	87	527
C 30FM sample d	94	551	85	529

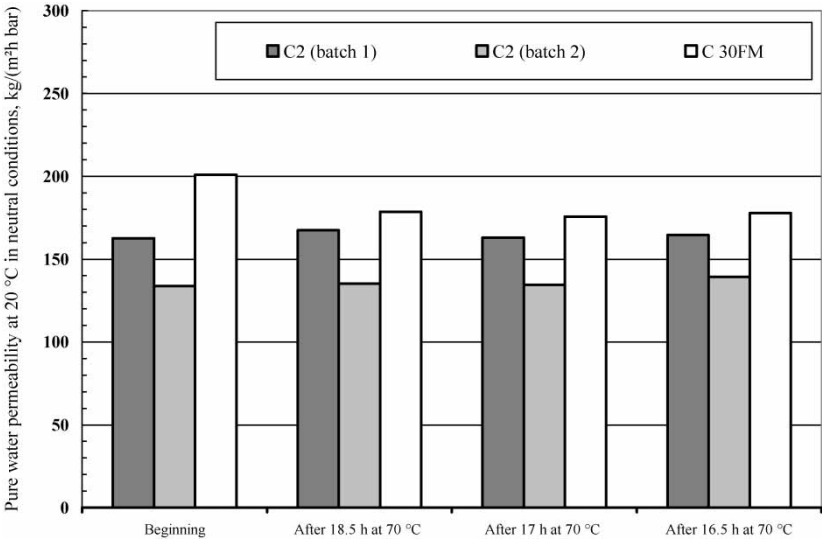

Figure 3. Pure water permeabilities measured at 20°C in neutral conditions between filtration steps having neutral conditions and high temperature (70°C).

structure is more susceptible to compaction under pressure than the C2 membrane having a sponge-like inner structure and that the C 30FM membrane could be slightly compacted already at 100 kPa even though the thickness decrease is not detectable from SEM images. Thus, it could be that the permeability decrease noticed in the experiments was due to membrane compaction. It is possible that also the hysteresis of the permeability values of the C 30FM observed in the experiment concerning the stepwise increase and decrease of temperature derived from slight membrane compaction (Fig. 2).

The filtration at 70°C and the compaction of the membrane did not, however, affect the observed Dextran (41 kg/mol) retention of the C 30FM (90%) (measured at 20°C). Also the observed retention of the C2 remained unchanged despite the long filtration steps at 70°C. The retention of the C2 membrane was 80% (from batch 1) and 90% (from batch 2). According to the FTIR results, the use at high temperature did not alter the chemical structures of the C2 and the C 30FM membranes.

Effect of High Temperature in Alkaline Conditions

In alkaline conditions a membrane might swell (25) and its temperature resistance might thus differ from that in neutral conditions. Thus, the membranes were tested in three experiments, where they were used in turns at 20°C in

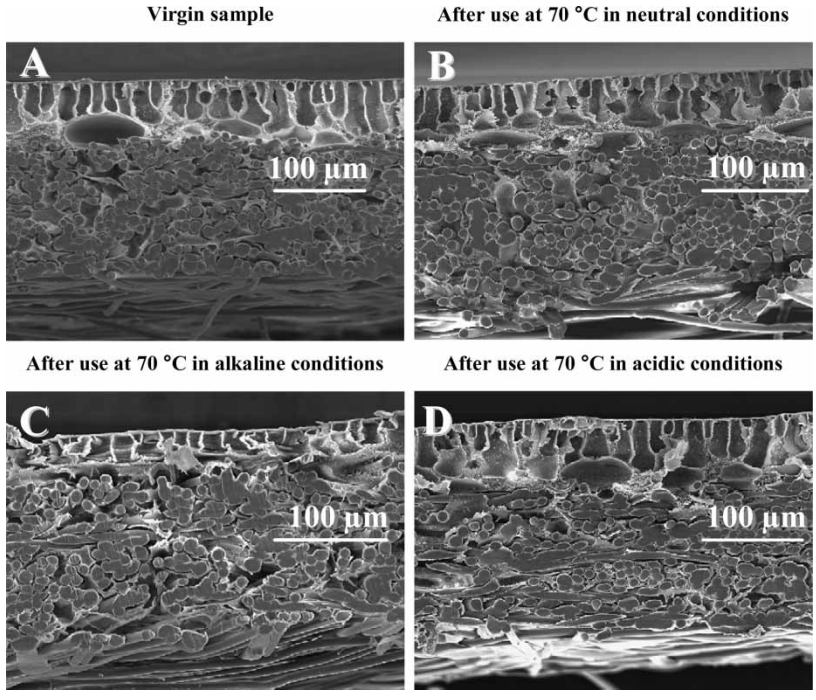

Figure 4. The effect of filtration temperature on the structure of the C 30FM membrane in neutral, alkaline and acidic conditions. a) virgin membrane sample, b) membrane sample after filtration at 70°C in neutral conditions, c) membrane sample after filtration at 70°C in alkaline conditions and d) membrane sample after filtration at 70°C in acidic conditions.

neutral conditions and at 70°C in alkaline conditions (pH 10). The trends of pure water permeability values measured at filtration steps at 20°C were similar in all the experiments and Fig. 5 presents the permeability values from one of these experiments.

The alkaline conditions at high temperature produced changes in the pure water permeabilities (measured at 20°C) for both the C2 and the C 30FM membranes (Fig. 5) already after the first filtration step performed at 70°C and at pH 10. After the further alkaline high temperature filtration steps the permeabilities remained at that changed level. However, the permeability changes after alkaline conditions at high temperature were different for the C2 and for the C 30FM membranes.

The permeability of the C2 decreased on an average 15% (calculated from the results of four different membrane sheets). However, no FTIR detectable changes in the chemical structure of the C2 were found and the observed Dextran retention of the C2 (90%) remained unchanged despite the alteration in the extreme conditions. Thus, the permeability decrease could derive from

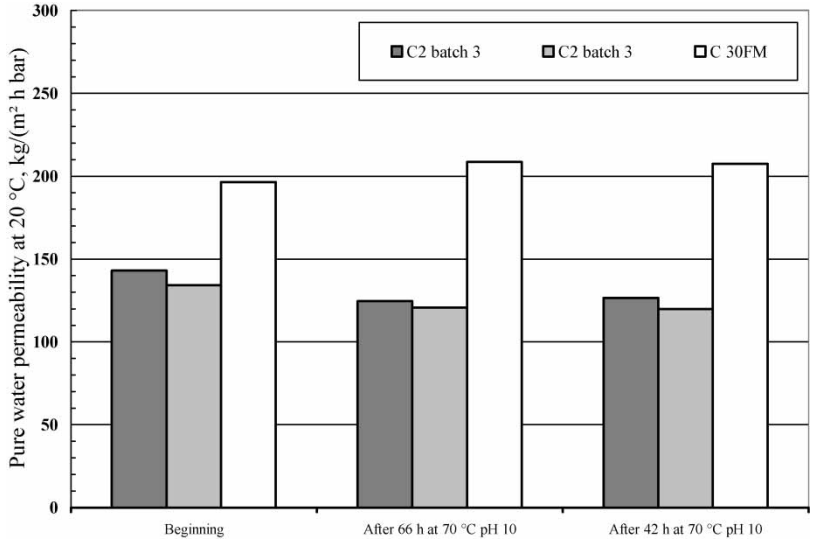

Figure 5. Pure water permeabilities measured at 20°C in neutral conditions between high temperature filtration steps which were performed in alkaline conditions (pH 10).

the change in the membrane physical structure but that could not be analyzed due to the disjoining of the membrane layers from each other during membrane drying.

The permeability of the C 30FM membrane, on the contrary, increased on an average 8% (calculated from the results of four different membrane sheets). Thus, the influence of high temperature on the pure water permeability was opposite in alkaline conditions to neutral conditions although the SEM images (Fig. 4) clearly revealed that the C 30FM was compacted during the filtration in alkaline conditions at 70°C. The reason for this could be the changes in the chemical structure of the C 30FM membrane. The comparison of the ATR-FTIR spectra of the virgin C 30FM sample and the samples used in alkaline conditions at 70°C (Fig. 6) showed that the bands at 1746 cm^{-1} and at 1234 cm^{-1} presenting the carbonyl group and the C-O ester band deriving from cellulose acetate (27, 28, 30) decreased clearly and there was a new band at 1335 cm^{-1} interpreted as an -OH group (30, 31) after filtration at 70°C at pH 10. This might indicate that the acetyl groups in the C 30FM membrane material were hydrolysed during the filtration (32). The increase of hydroxyl groups in the membrane material might increase the membrane hydrophilicity, which could be the reason for the increase of pure water permeability after alkaline conditions.

According to Rosa et al. (32), a hydrolysis of acetyl groups in the membrane material could also lead to an increase in pore radius. The observed Dextran (41 kg/mol) retention of the C 30FM, however, remained

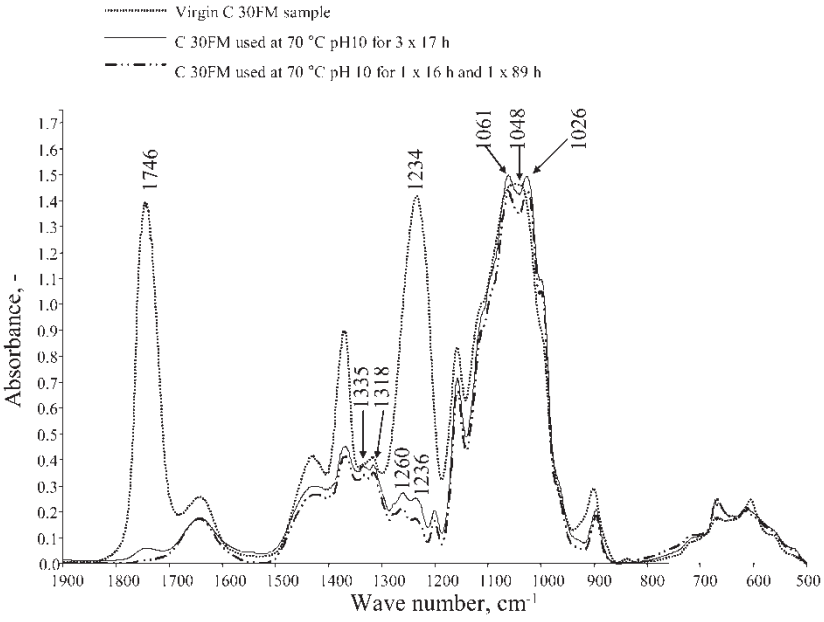

Figure 6. ATR-FTIR spectra of C 30FM samples: virgin and used in alkaline conditions (pH 10) at high temperature (70°C).

unchanged (90%) after several filtration steps in alkaline conditions at 70°C. On the other hand, the membrane compaction (SEM images, Fig. 4) might have been causing membrane tightening to some extent and as a result from the two contrary phenomena retention remained unchanged.

The manufacturer of the C 30FM membrane announced the applicable pH range of the membrane to be 1-11 with a maximum temperature of 55°C (6). Thus, 70°C and pH 10 are extreme conditions to the membrane. However, in this study the use of the C 30FM in those extreme conditions over several days did not affect significantly the pure water permeability and the observed Dextran retention although clear changes in the membranes chemical and physical structure were noticed. Thus, the C 30FM could, based on these results, be applied in alkaline conditions at 70°C at least for some time.

Effect of High Temperature in Acidic Conditions

The thermal resistance of the membranes was examined also in acidic conditions by performing two different experiments where pH of 3 for the feed water at the high temperature filtration steps was used. The trends of the pure water permeabilities of the membranes during the two experiments were similar and the results of the other experiment are shown in Fig. 7.

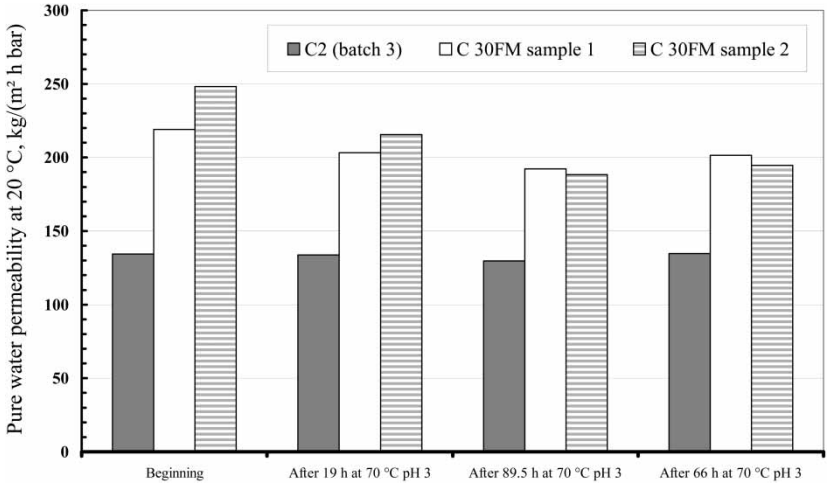

Figure 7. Pure water permeabilities measured at 20°C in neutral conditions between filtration steps having acidic conditions (pH 3) and high temperature (70°C).

As in neutral and alkaline conditions also in acidic conditions the performance of the C2 and the C 30FM differed from each other. The results showed that the use of the C2 at 70°C and pH 3 did not have an influence on its pure water permeability at 20°C (Fig. 7) and the observed Dextran (41 kg/mol) retention of the C2 membrane remained unchanged (90%). The permeability of the C 30FM decreased on an average by 11% (calculated from the results of four different membrane sheets). The decrease was strongest after the first acidic step and after the following steps the permeability level at 20°C became more stable. The observed Dextran (41 kg/mol) retention of the C 30FM membrane sheets (measured at 20°C) used in the experiments concerning thermal stability in acidic conditions were for some reason in the beginning of the experiments lower (84%) than the observed retention of the sheets used in experiments concerning thermal stability in neutral and alkaline conditions. The retention of the C 30FM sheets increased to 90% after several acidic high temperature filtration steps. SEM images (Fig. 4) did not reveal a clear compaction of the C 30FM after the filtration in acidic conditions at 70°C. However, the permeability decrease and the retention increase could result from a slight compaction, which is not detectable with SEM.

Although acetyl groups might be hydrolyzed to hydroxyl groups also in acidic conditions (32) based on the ATR-FTIR results hydrolysis did not take place during the use of the C 30FM at 70°C at pH 3. Also the permeability decrease indicated that hydrolysis was not occurring. Actually, the acidic conditions at 70°C did not produce any FTIR detectable changes in the chemical structure of the C 30FM membrane but the FTIR spectra (Fig. 8)

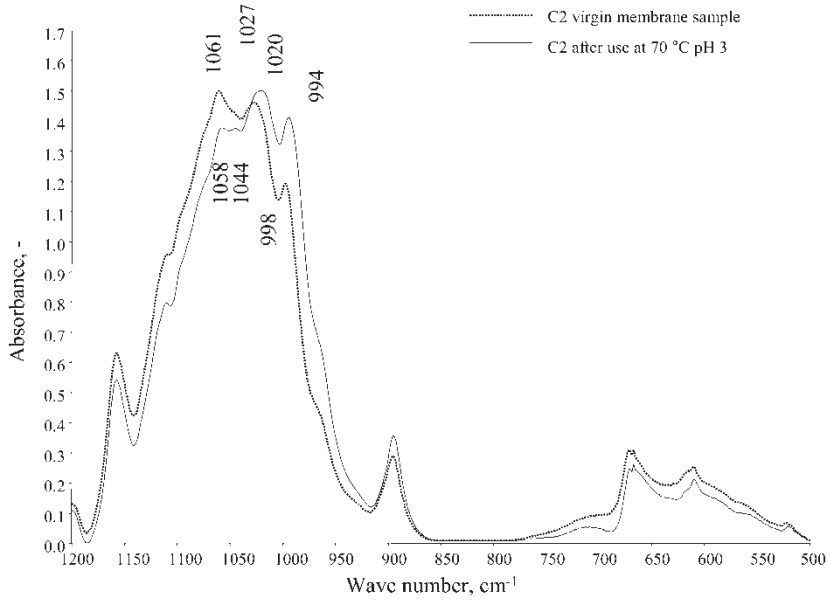

Figure 8. ATR-FTIR spectra of virgin and used (70°C, pH 3) C2 membrane samples.

demonstrated changes in the membrane material of the C2 membrane. The changes occurred in the wave number range $995-1065\ cm^{-1}$ and they concerned C-C and C-O bonds (30, 31, 33). These changes did not, however, affect the water permeability and the observed Dextran retention of the C2 membrane.

CONCLUSIONS

Regenerated cellulose membranes have been found to be very applicable in aqueous based UF separation processes due to their remarkable hydrophilic properties. They could, however, be used in even more applications than today, if there was more information on their high temperature resistance. Thus, this study aimed to evaluate the influence of high temperature (70°C) on two RC UF membranes, the C 30FM and the C2, in neutral, alkaline, and acidic conditions. The evaluation criteria were the influence of the test conditions on their pure water permeability, on the observed Dextran (41 kg/mol) retention (measured at 20°C in neutral conditions) and on the membrane structure. The results revealed that temperature affected differently the performances of the C2 and the C 30FM membranes. This was most probably due to the differences in the chemical and physical structures of the membranes.

In neutral conditions the filtration at 70°C did not cause changes in the performance of the C2 membrane while a slight decrease was found in the pure water permeability of the C 30FM membrane after the filtration at 70°C. The observed Dextran retention of the C 30FM remained stable. The filtration in alkaline conditions at 70°C produced a slight decrease in the water permeability of the C2 membrane but did not influence its observed Dextran retention or chemical structure. On the contrary, the use of the C 30FM in alkaline (pH 10) conditions at 70°C caused hydrolysis of the acetate groups in its membrane material, which might have been the reason for a slight increase in the pure water permeability. The observed Dextran retention of the C 30FM membrane remained unchanged, which might be due to the influence of membrane compaction. The performance of the C2 membrane remained stable also after several days in acidic conditions at high temperature. However, the test conditions produced some changes in the membrane matrix of the C2 membrane seen with FTIR (C-C and C-O bonds). As in neutral conditions so also in acidic conditions the high temperature filtration steps caused a decrease in the pure water permeability of the C 30FM membrane. The observed Dextran retention of the C 30FM membrane increased due to filtration at acidic conditions at high temperature and thus, it might be that the membrane was slightly compacted.

The results of the study indicated that despite the slight changes of the membranes after the use in the extreme conditions they could be applied in these conditions at least for several days. However, in industrial applications membranes should withstand extreme conditions for months or years. The slight changes noted in the membranes and their performances might indicate that although the membranes stand the tested conditions, the filtration in those conditions might shorten membrane lifetime. The situation in industrial applications is also more demanding than in laboratory experiments, because in industrial applications not only temperature and pH, but also the interaction between the compounds in the process streams and the membrane surface affects the membrane performance and its stability. Therefore, longer experiments using real process streams are needed to ensure the applicability of the C 30FM and the C2 membranes in neutral, acidic and alkaline conditions at 70°C even though the results here show that the regenerated cellulose membranes could be used much more extensively in industry than what is the case today, especially, in applications where hydrophilic membranes are demanded.

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