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Graphical abstract

Illustration prepared by Xavier Pita, Scientific illustrator at KAUST.

Membrane backwash cleaning using CO₂ nucleation

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Abstract

Low pressure membranes, such as ultrafiltration (UF), are widely used in water treatment applications, including the pretreatment of reverse osmosis desalination. UF membranes produce a water of superior quality, in addition to reducing the footprint and the use of chemicals, compared to conventional methods. However, membrane fouling remains a major drawback, and frequent membrane cleanings are required to maintain the flux of water and its quality. Typically, after a series of backwashes using an UF permeate, a chemical cleaning process is applied to fully recover the membrane's permeability. However, frequent chemical cleanings negatively affect the lifetime of the membrane, the environment, and increase operational costs. Here, we introduce a novel cleaning method that uses a solution saturated with CO₂ to clean the membranes through the backwash step. As the pressure drops, the CO₂ solution becomes supersaturated, and bubbles start to nucleate within the membrane pores and on its surface, resulting in the effective removal of the deposited fouling material. These foulants are further helping the nucleation process as they are considered as imperfection sites with high creation and growth of bubbles. Investigations performed for different synthetic feed solutions of organic compounds (sodium alginate), colloidal matter (silica) and sea salts, at different concentrations, show that our new physical cleaning process using CO₂ is more performant than the regular backwash using Milli-Q water. We obtain a 100% flux

recovery, in a short time, even under severe irreversible fouling conditions. Based on these results, we conclude that replacing water by a solution saturated with CO₂ for the backwash cleaning of filtration membranes provides significant benefits to existing cleaning processes, and represent a promising alternative for improving and lowering the frequency of conventional chemical cleaning methods.

Keywords: Membrane cleaning, backwash, fouling, carbon dioxide nucleation, RO pretreatment, desalination.

1. Introduction

The rapid growth of the global population and the phenomenon of urbanization has led to a rapid increase of the demand for consumable water, resulting in a 5% annual growth of the desalination market, with a total capacity currently reaching about 100 million m³/day (GWI, 2018). Membrane-based desalination, mainly via reverse osmosis (RO) process, has been shown to be a better choice, economically, than most other conventional methods (Ghaffour et al., 2013; Amy et al., 2017). As a result, the capacity of RO desalination plants has increased more rapidly over the past decade (GWI, 2018). Because the performance of these plants highly depends on the quality of the feed water, an extensive pretreatment of the water is necessary in order to optimize the overall process, enhance the plant's performance, and reduce the total cost of water (Voutchkov, 2008; Missimer et al., 2013; Rahmawati et al., 2012).

Ultrafiltration (UF) membranes provide a physical barrier, based on the size of their pores and the effective rejection of any colloidal matter larger than these pores. Over the last decade, the use of UF membranes has grown rapidly and is expected to accelerate in the near future, as more and more plants are being built (GWI, 2014; Wolf et al., 2005). UF

membranes are widely used in the desalination industry, mostly because of the high quality of water they produce, in a consistent manner, regardless of the quality of the feed water. An UF pretreatment uses fewer chemicals than conventional methods, and, as a result, offers a higher operating flux and a longer life for the RO membrane (Kim et al., 2009; Prihasto et al., 2009; Al-Mashharawi et al., 2013). However, it does have a significant drawback: the accumulation of undesirable substances, called ‘foulants’, on the surface of the membrane. These foulants are responsible for partially or fully blocking the pores of the membrane. There are different types of fouling: particulate fouling, organic fouling, biofouling, and a combination of those (Voutchkov, 2008; Dhakal et al., 2018; Ghaffour, 2004). The rate at which the foulants accumulate on the surface of the membrane depends on the quality of the feed water. A rapid decrease in the permeate flux generally occurs (at constant feed pressure), under harsh conditions. Therefore, frequent cleaning of these membranes is necessary to maintain a sufficient flux of good quality water; this includes a backwash step to restore the permeability of the membrane, using an UF permeate. However, irreversible fouling generally occurs after a series of backwashes (depending on the membrane and types of foulants), requiring an extra chemical cleaning step e.g. ‘cleaning in place’ (CIP) or ‘chemical-enhanced backwash’ (CEB). In addition to its high cost, chemical cleaning is an aggressive process that has negative effects on the lifetime of the membrane and the environment.

Finding better alternative membrane cleaning methods to maintain the effectiveness of the UF process is essential to follow the rapidly increasing capacity and development of the process. The alternative techniques presented here are expected to elongate the lifetime of the membranes, including RO, be friendly to the environment and lower operational costs.

Lowering the frequency of chemical cleanings generally requires the use of a two-phase cleaning methods. By sparging air to the feed stream, air bubbles are able to mechanically

remove the foulants from the surface of the membrane (Cui & Taha, 2003; Guigui et al., 2003; Ndinisa et al., 2006; Serra et al., 1999; Willems et al., 2009). However, the efficiency of this technique suffers from: i) the need for modules to be vertically positioned, ii) possible channeling, iii) inefficient removal of sticky foulants, and iv) incapacity to remove foulants from inside the pores.

The CO₂ nucleation cleaning method, still to be a new procedure, uses the nucleation of bubbles formed on the membrane surface to effectively remove all foulants physically (from the membrane) (Ngene et al., 2010). By dissolving CO₂ in water, carbonic acid is produced, resulting in a shift of the pH. H₂CO₃ is dominant at pH 4, and therefore, a water saturated with CO₂ is expected to have a pH value of approx. 4 (Fig. S1). The carbonic acid acts as a low- pH cleaning agent (Moreno et al., 2017).

The main reason for selecting CO₂, rather than any other gas, is because CO₂ is one of the most soluble gases in water (Fig. S2), mainly due to its polarity (Bauget & Lenormand, 2002; Jones et al., 1999). It has also been reported that air scouring, or the use of other gases such as nitrogen or oxygen, during the cleaning process does not significantly improve the cleaning performance due to the formation of stagnant bubbles or bubbles travelling in the flow channel, blocking the flow and reducing the ability of scouring (Ngene et al., 2010). More details are provided in the supplementary information (Figs S1 and S2).

There are four different types of nucleation: I) classical homogeneous nucleation, II) classical heterogeneous nucleation, III) pseudo-classical nucleation, and IV) non-classical nucleation (Jones et al., 1999). At low levels of supersaturation, type IV is the main type of nucleation occurring. The homogeneous nucleation is not expected to take place during the membrane cleaning process, as it requires more than 100 atm of pressure difference between the pressure inside the module and the pressure from dissolved gas. Therefore, the main nucleation type will be heterogeneous, one in which bubbles are formed within pre-existing

gas pockets located at micro-cracks on the surface of the membrane (Scardina and Edwards, 2000; Liger-Belair et al., 2002; Mori and Baines, 2001), or what could be referred as ‘the pores’ within the membrane’s structure (Fig. 1).

Figure 1: Heterogeneous nucleation in porous membrane.

The rate of CO₂ bubbles’ nucleation is affected by several factors, including:

1. *Degree of super-saturation:* the higher the degree of CO₂ supersaturation in a solution, the higher the driving force for bubble formation. This degree of saturation can be controlled either by changing the pressure of the solution, its temperature or its salinity. Increasing the pressure or reducing the temperature of the CO₂ solution, using the ambient conditions as a reference, will increase the CO₂ saturation level and force more bubbles to dissolve in the solution (Fig. S3). The increase in salinity of the solution, to approximately seawater levels, reduces the degree of CO₂’s solubility, especially at higher pressures and lower temperatures, by approximately 20% (Fig. S3). The activity of the water will then be more saturated, with more salt content available for the same volume of water. As a consequence, the capacity of CO₂ gas’s capacity to dissolve in water will be reduced. Therefore, a water of lower salinity is preferred for obtaining a higher saturation of CO₂.

2. *Nucleation surface properties*: the presence of defects or roughness, at various locations on the surface of the membrane aids the formation of gas pockets (in these sites), which then become preferred nucleation sites for CO₂ bubbles (Fig. 1). The number of these preferred locations, which is expected to be very high in highly porous membranes, is leading to a higher nucleation rate of CO₂ bubbles.

The CO₂ nucleation cleaning method combines both hydraulic and chemical cleaning procedures. It is based on the formation of CO₂ bubbles that physically clean the surface of the membrane. As they nucleate and move away from the surface, these bubbles provide an extra physical cleaning process and chemical cleaning at the same time, via reduction of the pH of the solution that then acts as a new acid-cleaning medium. Only a few investigations on the CO₂ nucleation in membrane cleaning are reported in the literature; these include removing fouling deposits from membrane filtration surfaces and spacers experimentally (Ngene et al., 2010; Michałek et al., 2015) and numerically (Krzysztoforski and Henczka, 2018; Shahid et al., 2017; Lee and Tien, 2009), and reverse electrodialysis membranes (Moreno et al., 2017). These studies showed that the performance of this technique was superior to any other conventional technique. In these studies, a CO₂ solution was injected in the feed solution. To our knowledge, this is the first study proposing using this cleaning method as a backwash of hollow-fiber UF membranes which are widely used in practice.

This work is aimed at improving the overall operation of membrane filtration by developing an innovative cleaning method consisting of backwashing the UF membranes using a saturated CO₂ solution that nucleates bubbles when the pressure drops, not only on the surface of the membrane, but through its structure as well. During the backwash, bubbles will nucleate within the pores of the membrane, which are the preferred sites for CO₂ bubbles (gas pockets). The bubbles will then (physically) clean the pores of the membrane and its surface by sweeping away the foulants as they detach from the surface. We have evaluated

the effectiveness of this cleaning process using different types of foulants that are typically not cleaned with an acidic solution. We have also established an appropriate cleaning protocol.

2. Materials and methods

2.1. Experimental setup and membrane module

A fully automated experimental unit consisting of a membrane filtration cell and some cleaning components was custom-designed and built on-site, at King Abdullah University of Science and Technology (KAUST). A schematic diagram of the unit is presented in Fig. 2. All sensors to measure the flowrate, pressure, temperature, and weight were made of compatible materials with a high measurement accuracy ($\pm 0.25\%$, as given by the different manufacturers), which we manually verified prior to experiments. All sensors were calibrated and the whole setup was fully automated and controlled using Labview. The software used the feedback from the pressure or flow sensors to control the pump and operate at constant pressure or constant flux. Data were collected from all sensors, every 5 seconds, and the measurements were plotted and viewed directly on the monitor.

The membrane module was constructed using plexiglass material with a transparent surface in order to better visualize the accumulation of foulants during filtration, and to observe more easily the nucleation of bubbles and detachment of foulants during the membrane's cleaning operation.

In our study, we used a commercial-grade, widely available UF hollow-fiber polyvinylidene fluoride (PVDF) membrane with a mean pore size of $0.03\ \mu\text{m}$ operating in an outside-in operation mode, and commonly used as pretreatment in large scale commercial SWRO plants. 5-membrane fibers, with a length of 20 cm and a total surface area of $40.84\ \text{cm}^2$, were used for all our experiments.

Figure 2: Schematic diagram of a software- controlled experimental setup.

2.2. Preparation of the saturated CO₂ cleaning solution

A pressure vessel filled with Milli-Q water connected to a CO₂ gas cylinder and connecting this solution to the backwash side of the filtration module was added to the experimental setup (Fig. 2). This solution was prepared by, first, filling the pressure vessel with Milli-Q water, and then injecting CO₂ gas to the solution through gas diffusers, while keeping the pressure vessel open to strip all the other gases. After 10-15 minutes, the pressure vessel was closed and kept at a constant pressure for two days, to ensure that the solution was fully saturated with CO₂. The saturated CO₂ solution was then introduced into the membrane module as a backwash solution. We expected higher amounts of dissolved gas to produce higher amounts of gas nucleated as the pressure dropped. Tests were performed for different values of pressure, temperature and salinity of the CO₂-saturated water. We anticipated that the drop in pressure through the membrane would place the solution in a temporary supersaturated state, outside equilibrium, which would force the gas out until a

new equilibrium is reached, under the new pressure condition. This state of the solution, in addition to the pre-existing gas cavities (Bauget & Lenormand, 2002; Jones et al., 1999), would then generate the instant release of the CO₂ bubbles from the solution which is used to detach the foulants.

All experiments were repeated for each condition of the tested parameters. Errors were within the range of 5-7%.

2.3. Solutions and analysis

The main fouling observed in practice is due to organic and (bio)fouling. Our study focused on the cleaning of these foulants. Sodium alginate was used to represent the most common type of fouling (biofouling) in UF, either with or without the addition of colloidal silica (Arras et al., 2009). Solutions for different concentrations of foulants were prepared by dissolving it in Milli-Q water and testing it to ensure that an amount of 1-2 mg/L of total organic carbon (TOC) was present in the solution, in order to foul the membrane fibers within a reasonable time. Ultra-high purity colloidal silica with an average particle size of 23 nm was purchased from Sigma-Aldrich, and colloidal silica with an average particle size of 113 nm was obtained from Fuso Chemical Co. Ltd. (LUDOX® HS-40). Several concentrations of sea salts (Sigma-Aldrich) were used to increase the ionic strength of the solution and to increase the fouling effect on the membranes, in a way that mimics the actual marine salinity conditions. Several published research studies have shown that the use of divalent ions help to attach the fouling particles together, making the fouling more difficult (Costa et al., 2006; Katsoufidou et al., 2010; Kerdi et al., 2018).

Water and membrane characterization were performed to analyze the efficiency of the new cleaning method. The feed and permeate solutions were both characterized during each test. Turbidity was measured using a Hach 2100Q Portable Turbidimeter, and pH was measured

using a CyberScan pH 6000; conductivity was measured using an OAKTON CON 510 Benchtop Meter, and TOC was measured using a TOC-V CPH equipment from Shimadzu.

An analysis of the turbidity, pH, conductivity, and TOC was performed on selected samples collected from experiments run under operating conditions proving that the UF filtration process didn't show any anomalies. The turbidity of feed, initially ranging from 0.7 to 1.98 NTU, decreased to almost zero in the UF permeate, in all cases, regardless of any other operating parameter and condition. The removal rate of TOC fluctuated from 1.42 mg/L in the feed to 1.26 mg/L in the permeate mainly at higher pH values, to a lower rate from 2.84 mg/L in the feed to 0.81 mg/L in the permeate. These results were found to be within the typical range for UF membranes, depending on the feed water used and the membrane characteristics (Schurer et al., 2012; Li et al., 2016; Almasharawi et al., 2013).

2.4. TMP recovery

Experiments were conducted at a constant flux of 73 L/h.m² and the increase in trans-membrane pressure (TMP) was recorded. The recovery of TMP was measured after cleaning with the CO₂ saturated solution and compared to cleaning with Milli-Q water.

2.5. Cleaning frequency effect

Cleaning after each specific type of fouling could require longer cleaning times or more frequent cleaning cycles to recover the initial permeability of the membrane. This experiment is designed to compare the number of cleaning cycles required to recover the initial condition of the membrane by comparing the cleaning with CO₂ nucleation to cleaning with Milli-Q water. 10 cycles of cleaning with Milli-Q water is compared to 1 cycle of cleaning with CO₂ solution.

3. Results and discussion

3.1. Nucleation rate

Different parameters affect the solubility of CO₂ in water, and therefore can affect the efficiency of the cleaning process. To highlight this issue, we conducted several experiments using different operating parameters, mainly pressure, temperature and salinity. The values of saturated CO₂ were calculated under these different conditions using the prediction models described by (Duan et al., 2006). An example is given in Fig. S3. This figure clearly shows that the solubility of CO₂ increases as the pressure increases (Fig S3b). However, the solubility decreases when either the temperature or salinity increases (Figs S3a,c). These results are in line with reported data using different calculation methods (Carroll et al., 1991; Prini & Crovetto, 1989).

Each condition that we tested was video-recorded for visual analysis. Snapshots of specific times (15 s, 30 s, 45 s, and 60 s) were captured to show the differences between the various conditions (Fig. 3 showing the snapshot taken at 30 s from the start of backwash cleaning). We visually observed that more bubbles were present at higher pressure and lower salinity of the solution. The number of bubbles recorded, for each image (Fig. 3) reflects the nucleation rate for each of the tested conditions; a higher rate of nucleation means more CO₂ is being dissolved in the solution. We also observed the continuous creation, growth and detachment of bubbles from the entire surface of the membrane fibers, which explains the absence of stagnant bubbles, contrary to use of other gases, as discussed above. The optimum cleaning solution would be for a solution allowing the production of more bubbles generated from the nucleation process of the CO₂ solution that would be lifting the foulants away from the membrane pores and its surface, due to shear forces generated by the bubbles.

Increasing the pressure from 1 to 2 bar produced more bubbles with a higher rate of nucleation, as shown in Fig. 3-left. At 2 bar, a significant number of bubbles rapidly

nucleated uniformly across the pores of the membrane fibers, whereas, at 1 bar, a longer backwashing time was required to reach a more uniform nucleation of CO₂ on the membrane surface. In addition, we observed that more bubbles were formed on the membrane fibers, especially at the first 30 s of the backwash and then a steady state is reached, suggesting that 30 s could be an optimum or a sufficient backwash time to recover the membrane's permeability. This short time is a major advantage for practical applications. In addition, our experiments showed that the cleaning efficiency did not depend on the duration of the backwash process for most salt concentrations, except the very high ones (>50 g/L NaCl) that are typically above the range of UF seawater RO applications.

Figure 3: Screenshot obtained 30 s after initiating the backwash with a solution saturated in CO₂. Left top: 1 bar, left bottom: 2 bar, right top: 10 g/L NaCl, right bottom: 50 g/L NaCl.

3.2. TMP recovery

Preliminary results using 4 mg/L of sodium alginate and 4 g/L of sea salts in feed water showed that cleaning the membrane with Milli-Q water and UF permeate, through the backwash process had a similar performance, (Fig. S4). The slight difference was due to the presence of salt in the UF permeate, confirming the results presented in Fig. S3a. Therefore, in our subsequent experiments we used Milli-Q water to backwash the membranes, as we also do not have sufficient UF permeate (experiments using a small lab-scale filtration module).

Fig. 4 shows results of the experiments at constant flux (73 L/h.m^2) with 6 cycles of filtration, each cycle lasted for 60 minutes followed by 1 minute of backwash using Milli-Q water. At the end, one backwash using CO_2 solution was applied. In this figure, we clearly see that the CO_2 cleaning process significantly reduces the TMP to almost the value it had at the beginning of the testing experiments (before fouling). The same trend was observed for different concentrations.

Figure 4: TMP versus time using 8 mg/L sodium alginate at pH 6 and pH 9 running at constant flux (73 L/h.m^2). After 6 cycles using backwash with Milli-Q water, backwash using CO_2 was applied.

The addition of sea salts (10 g/L for this case) to sodium alginate (4 mg/L) led to a higher TMP, reaching 12 psi after the third cycle after which a stable irreversible fouling was reached (Fig. 5). In this case, TMP hardly recovered its initial value, when using a backwash with MilliQ water. This proved that the fouling was enhanced by the presence of calcium, a phenomenon widely known. However, a single backwash using a saturated CO_2 solution applied after the 6th cycle was sufficient to recover the TMP (Fig. 5).

Figure 5: TMP versus time using 4 mg/L sodium alginate + 10 g/L sea salts, at pH 6 and pH 9, running at constant flux (73 L/h.m^2). After 6 cycles using backwash with Milli-Q water, a backwash using CO_2 was applied.

Results from experiments run under similar conditions for a feed solution containing 4 mg/L sodium alginate and 20 g/L sea salts at pH 8 (Fig. 6), showed that a backwash with Milli-Q water could not restore the performance of the membrane from the severe irreversible fouling caused by the harsh conditions. TMP values as high as 25 psi were obtained, which was beyond our experimental set-up capacity and made it impossible for us to complete our investigations. However, a backwash using a CO_2 solution enabled us to operate under very stable conditions, from the first cycle. TMP values remained very acceptable (for a challenging feed water quality), between cycles, suggesting that the CO_2 bubbles that were nucleated effectively cleaned the pores of the membrane as well as the fouling deposits from its surface. This high efficiency of the cleaning process can be explained by the higher lift force from the nucleation process (spontaneous formation of

318 bubbles) of the CO₂ bubbles, not observed when using Milli-Q water. This result suggests
 319 that the proposed cleaning method could be used for saline UF filtration applications in
 320 which a UF permeate rich in salts is used for backwash.

321
 322 Figure 6: a comparison between backwashes using Milli-Q water and a CO₂ solution, for a
 323 feed solution with 4 mg/L of sodium alginate and 20 g/L of sea salts, at pH 8, running at a
 324 constant flux of 73 L/h.m².
 325

326 Fig. 7 presents a possible mechanism of CO₂ bubbles nucleated through the pores of the
 327 membrane and scrubbing its surface, offering a lift force created at beneath the deposited
 328 foulants, and generated by the nucleation of CO₂ bubbles on the surface of the membrane.
 329 We found that more bubbles were formed at those preferred sites, which led to a more
 330 effective physical cleaning process. The lift force was sufficient to detach the foulants from
 331 the surface, unlike conventional backwashes, including those using air bubbles and mostly
 332 based on flashing the membrane surface at relatively higher shear forces. We found that CO₂
 333 bubbles increased the shear force on the surface of the membrane, resulting in a better
 334 flashing and cleaning process.

The reaction between CO_2 and water is an example of an equilibrium reaction $[\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_2\text{CO}_3(\text{aq})]$. Aqueous CO_2 reacts with water forming carbonic acid, $\text{H}_2\text{CO}_3(\text{aq})$. Carbonic acid may lose protons to form bicarbonate, HCO_3^- and carbonate, CO_3^{2-} . In this case, the proton is liberated to the water, causing the pH to decrease. More details and figures can be found in the supplementary information (Figs. S5 and S6).

Figure 7: Illustration of nucleated CO_2 bubbles through the membrane pores and on its surface, during backwash (illustration prepared by Xavier Pita, Scientific illustrator at KAUST).

Fig. 8 summarizes the results of a set of tests carried out for the following operation parameters: 4 mg/L sodium alginate (SA4), 8 mg/L sodium alginate (SA8) w/wo sea salts concentration of 10 g/L (SS10) at different feed water pH values (represented by the graphs). These results clearly demonstrate the recovery of the initial TMP during the cleaning process with a CO_2 solution, with a significantly improved efficiency compared with a backwash using Milli-Q water. The CO_2 solution is much more effective at recovering the initial permeability of the membrane, for all tested operating parameters. In most cases, we found that the CO_2 cleaning process successfully recovered the initial permeability within 1 minute

of backwash cleaning. This is a major advantage for practical applications, especially when treating feeds with a high fouling potential. Values above 100% remained within the acceptable range of experimental errors (below 7%) and showed the complete recovery of the membrane's permeability.

As previously discussed, a cleaning process using Milli-Q water was always found less efficient at higher pH values. This was observed for SA4 feed solutions with 91% vs 73% TMP recovery, and SA8 feed solutions with 91% vs 81% TMP recovery. When sea salts were added to the feed solution, the backwash using Milli-Q water was very poor (37% TMP recovery). In order to prove that the physical (not chemical) cleaning (nucleation of CO₂ bubbles) was dominant, at low pH, a cleaning experiment was carried out using an acidic solution, at pH 4, which is the pH obtained when using a CO₂ solution (Fig. S1). Results showed a TMP recovery of only 48% (Fig. 8), due to the nature of foulants used in our experiments, which are not typically cleaned using acid solutions. The combination of physical and chemical cleanings makes our proposed cleaning method very efficient for various types of fouling.

As a comparison, even a chemical cleaning process using sodium hypochlorite did not, in some cases (Aschermann et al., 2016), fully recover the initial conditions of the membrane. Our study clearly shows the potential of the novel CO₂ cleaning method to be used as a more effective way to clean the membrane and recover its initial permeability, in most cases.

Figure 8: TMP recovery of backwash using Milli-Q water versus backwash using a saturated CO₂ solution, for different feed concentrations of sodium alginate SA and sea salts SS, at different pH values. Values above 100% remain within the acceptable range of experimental errors (below 7%). Right: an experiment run using an acidic solution for backwash shows that physical cleaning is dominant, not the chemical cleaning.

3.3. Effectiveness of the CO₂ cleaning method in the presence of mixed foulants

In order to test the efficiency of the novel cleaning method presented in this paper, we had set a series of experiments under challenging conditions, using feeds containing 4 mg/L sodium alginate, 50 mg/L of colloidal silica and 4 g/L of sea salts. As shown in Fig. 9, the TMP increased significantly throughout the filtration time, reaching 25 psi after 10 cycles. Backwashing the UF membrane fibers with Milli-Q water was not efficient, starting from the second cycle. However, applying a backwash with a saturated CO₂ solution, starting from the third cycle, could recover the membrane's permeability (Fig. 10) and stabilize the TMP. This suggests that the CO₂ backwash was very efficient in cleaning the severe membrane fouling observed in the first three cycles. The TMP recovery obtained when using Milli-Q water was

390 only 44%, whereas the recovery obtained with a saturated CO_2 solution was 80% (Fig. 10),
 391 under very challenging conditions that involved the use of a very high concentration of
 392 colloidal silica.

393
 394 Figure 9: TMP increase versus time (backwash with Milli-Q water) for a solution containing
 395 4 mg/L sodium alginate, 4 g/L sea salts, and 50 mg/L colloidal silica.

396
 397 Figure 10: TMP increase versus time (backwash with Milli-Q water and saturated CO_2
 398 solution after the third cycle with 15 minutes for each cycle) for a solution containing 4 mg/L
 399 sodium alginate, 4 g/L sea salts, and 50 mg/L colloidal silica.

400

401 A physical observation through 2 snapshots taken from a video, before and after cleaning,
402 using a saturated CO_2 solution (Fig. 11), shows the detachment of foulants, mainly colloidal
403 silica, from the membrane fibers, as a result of CO_2 nucleation. This explains the severe
404 fouling observed in the first 3 cycles, and the fact that a hydraulic cleaning cannot allow the
405 membrane to recover from an irreversible fouling.

406

407 Figure 11: Snapshot before (left) and after (right) cleaning with a saturated CO_2 backwash for
408 a feed solution containing 4 mg/L of sodium alginate and 50 mg/L of colloidal silica.

409

410 4. Conclusions

411 In this paper, we introduced a novel cleaning method for hollow-fiber UF membranes,
412 using a saturated CO_2 solution that we developed and successfully tested for different feed
413 water solutions containing sodium alginate, sea salts and colloidal silica. The optimum
414 operation conditions were selected to dissolve the highest amount of gas possible, so that
415 more nucleation occurs when the pressure drops during the cleaning process.

416 We found that cleaning with a saturated CO_2 solution was more effective than using
417 conventional cleaning methods with Milli-Q water and chemicals in order to recover the
418 membrane's permeability, after fouling, for all cases. During the backwash process, we

observed a continuous nucleation, growth and detachment of bubbles from the membrane's surface, especially at sites where foulants were deposited (considered as imperfections). The physical cleaning from the nucleated bubbles was dominant in an acidic solution, and enhanced by the presence of CO₂. A backwash with CO₂ quickly recovered 100% of the transmembrane pressure drop, in most cases. However, the backwash with CO₂ was much less effective at high sodium alginate's concentration or low pH. Under very harsh operating conditions, 80% of the membrane's permeability could be recovered using the proposed cleaning method versus 44% using Milli-Q water. These results make our novel cleaning method a promising alternative to current conventional chemical cleaning processes. It is also easy to implement, on an industrial scale, as well as being more environmentally friendly. A detailed theoretical aided by simulation investigation of the bubbles formation and detachment mechanism using advanced analytical equipment and imaging through high speed camera is under study and will be reported in future work.

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Highlights

- A novel membrane backwash cleaning technique using CO₂ solution is proposed.
- Physical cleaning created by the effect of CO₂ bubbles nucleation was dominant.
- Nucleation occurred inside the membrane pores and on its surface.
- Foulants considered as imperfection sites enhanced the bubbles nucleation.
- In most cases, the flux was fully recovered from irreversible fouling.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: